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Influence of the SO$_3$ Content of Cement on the Durability and Strength of Concrete Exposed to Sodium Sulfate Environment

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Influence of the SO_3 Content of Cement on the Durability and Strength

of Concrete Exposed to Sodium Sulfate Environment

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Civil Engineering
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LIST OF SYMBOLS AND ABBREVIATIONS

ASTM   American Society for Testing and Materials

SEM   Scanning Electron Microscope

XRD   X-Ray Diffraction

QXRD   Quantitative 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

$\hat{S}$ Sulfur Trioxide, SO_3

C3A   Tricalcium Aluminate, $3CaO.Al_2O_3$

C4AF   Tetracalcium Aluminoferrite, $4CaO.Al_2O_3.Fe_2O_3$

C2S   Dicalcium Silicate, $2CaO.SiO_2$

C3S   Tricalcium Silicate, $3CaO.SiO_2$

CH   Calcium Hydroxide, $Ca(OH)_2$

$C\hat{S}H_2$ Gypsum, $Ca_2SO_4.2H_2O$

$C\hat{S}H_{0.5}$ Bassanite, $Ca_2SO_4.0.5H_2O$

$C\hat{S}$ Anhydrite, Ca_2SO_4

C-S-H   Calcium Silicate Hydrate, $nCaO.SiO_2.mH_2O$

$C_6A\hat{S}H_{32}$ Ettringite, $3CaO.Al_2O_3.3CaSO_4.32H_2O$

$C_4A\hat{S}H_{12}$ Monosulfoaluminate, $3CaO.Al_2O_3.CaSO_4.12H_2O$

INFLUENCE OF THE SO$_3$ CONTENT OF CEMENT ON THE DURABILITY AND STRENGTH OF CONCRETE EXPOSED TO SODIUM SULFATE ENVIRONMENT

Amin A. Hanhan

ABSTRACT

The objective of this investigation was to assess the influence of the SO$_3$ content on the durability and strength of portland cement.

Four portland cements were used in this study. The cements had a variable tricalcium silicate, tricalcium aluminate, and alkali contents, as well as differences in the amount and form of calcium sulfates. The SO$_3$ content of the cements was increased by replacing part of the cement by gypsum according to ASTM C 452-95.

Mortar bars and cubes were prepared for the as-received as well as for the cements with an SO$_3$ content of 3.0% and 3.6%. The durability of the as-received and doped cements was determined by measuring the length change of the mortar bars that were exposed to sodium sulfate environment. The compressive strength of the mortar cubes prepared for the same mixes was measured at different ages for sets of cubes cured both in sodium sulfate solution and in saturated lime solution.

It was concluded at the end of this study that there is an optimum SO$_3$ content for the lowest expansion that is different from that determined for the highest compressive strength. Optimum values also differed from one cement to another and from one age to

another for the same cement. The results also indicate the dependence of SO_3 content on

tricalcium aluminate and alkali content of cements. In addition, for all cements examined

in this study with alkali content of less than 0.60%, increasing the SO_3 content above

3.0% had negative effects on durability assessed by strength or expansion measurements.

For the cement with highest alkali and tricalcium aluminate content, increasing the SO_3

content from 3.0% to 3.6% delayed the onset of strength drop; however, at 360 days the

strength drop experienced by both doping levels was the same.

CHAPTER 1.

INTRODUCTION

1.1 Objective

When portland cement clinker is ground without the addition of a retarder, the reactions with water are usually so rapid that quick set occurs. Consequently it is the common practice in the manufacturing process of portland cements, to add a retarder to control the rate of the initial reactions. At present, gypsum (calcium sulfate dihydrate) and hemihydrate are the retarders generally used. The addition of the correct amount of gypsum to the clinker is one of the most important steps in the manufacturing process. This added amount of gypsum, together with other sulfate sources determines the final sulfur trioxide (SO_3) content of the cement. Other sulfate sources in portland cement clinker include raw materials used for manufacturing the clinker and from products of fuel combustion.

Although gypsum was found to be beneficial in slowing down the early hydration reactions of tricalcium aluminate (C_3A), and thus controlling the setting time; nevertheless, and in order to provide sufficient protection against the abnormal expansion that could result from the use of excessive amounts of gypsum, placing a limit on the SO_3 content of portland cement in standard specifications has been the tradition. ASTM C 150 limits the SO_3 content for Types I and II cements to 3.0%, for Type III cement 3.5%,

and for Types IV and V cements to 2.3% (these limits apply for the case when the tricalcium aluminate C_3A is 8% or less). Alexander and co-workers [6] stated that "according to surveys published by CEMBUREAU and Cement and Lime Manufacture, the limit in various national standards ranges from 2.5 to 5.0% SO_3, depending on cement fineness or composition or both". During the last decades, the Blaine fineness of typical cements has increased dramatically, mainly in an attempt to increase concrete early strength. Since increasing cement fineness leads to higher early rate of hydration, and since gypsum is basically needed to control the early hydration reactions of tricalcium aluminate (C_3A), cement fineness would be an important consideration in determining the quantity of gypsum required for proper retardation. Also during the last decades, a large increase in the sulfate content of the five ASTM types of cement clinkers occurred. This increase was to some extent the result of environmental restrictions on sulfur and other emissions, which in turn resulted in the change of the burning and dust recycling practices. Since the total SO_3 content is limited in specifications, regardless of the origin of SO_3, this change had the effect of limiting the amounts of gypsum needed for proper retardation without exceeding the limits set in specifications.

The objective of this research was to assess the influence of increasing the SO_3 content of cement on the durability and strength.

1.2 Phases in Clinker and Portland Cement

The manufacturing of portland cement is in principle very simple and relies on the use of abundant raw materials. A mixture, usually of limestone and clay, is heated in a kiln to $1400 - 1600$ ° C (2550 to 2900° F), which is the temperature range in which the

two materials interact chemically to form the calcium silicates. The purity and uniformity of the raw materials determines the quality of the produced cement. A source of calcium oxide and a source of silica are the main sources needed. The most commonly used source of calcium oxide is limestone (calcium carbonate) although other sources such as chalk, shell deposits, and calcareous mud, are used. Iron-bearing aluminosilicates are the primary source of silica. Clays or silts are usually preferred because they exist in a finely divided state; but shales, schists, and other argillaceous rocks are also used. Although quartz is the major form of pure silica in nature, it is a relatively unreactive material and, moreover, pure lime-silica mixes have very high fusion temperatures. The aluminum and iron oxides coming from the siliceous raw materials, although they can lead to problems of durability and abnormal setting behavior, they act as fluxing agents, lowering the fusion temperature of the portion of the raw mix to a practical firing temperature [2].

The heat treatment of the raw feed is termed clinkering, to distinguish it from sintering (where no melting occurs) and fusion (where complete melting occurs) [2]. In the cement Kiln, partial melting takes place; only about one-fourth of the charge is in the liquid state at any time, but it is in this fraction that the necessary chemical reactions proceed. The kiln is a long steel cylinder lined with refractory brick and inclined a few degrees from the horizontal. It is rotated at about 60-200 rev/h about its axis. The raw feed enters the kiln at the high end, and is slowly moved down the length of the kiln by the actions of rotation and inclination. As the raw feed moves down, it moves gradually into zones of increasing temperature, where four distinct processes take place: evaporation, calcinations, clinkering, and cooling. Free water is lost by evaporation in the dehydration zone and consequently the charge quickly heats up to calcinations

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temperature. At 600 °C water is lost from the argillaceous material and at about 900 °C

limestone decomposes and carbon oxide is lost. In the calcinations zone, the charge

transforms into a reactive mixture of oxides that can enter into new chemical

combinations. At the later part of the calcinations zone and around 1200 °C, calcium

aluminates and ferrites form through solid-state reactions. These compounds act as

fluxes, melting around 1350 °C to begin the clinkering zone. This is the heart of the kiln

where final chemical combinations occur to form the calcium silicates. Finally, as the

charge moves past the flame in the final few meters, it rapidly drops off in temperature in

the cooling zone. As the liquid phase solidifies again, it produces hard, dark-gray porous

nodules (6 to 50 mm in diameter) known as clinker. The clinker is conveyed to ball mills,

where it is ground to a fine powder. A small amount of gypsum is inter-ground with the

clinker to control the early reactions of tricalcium aluminate that, without the addition of

gypsum, can cause flash setting of the clinker [2]. Portland cement is clinker inter-ground

with gypsum; without the gypsum, it is only ground clinker.

1.3 Composition of Portland Cement

1.3.1 Compound Composition

The typical chemical composition of portland cement consists of tricalcium silicate

($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$), tricalcium aluminate ($3CaO.Al_2O_3$),

tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$), and calcium sulfate dihydrate or

gypsum ($CaSO_4.2H_2O$). The oxide notation by which these compounds are traditionally

written and frequently used in ceramic chemistry, gave rise to a unique shorthand

notation that has universal use among cement scientists. Thus tricalcium silicate is

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usually written as C_3S, dicalcium silicate as C_2S, tricalcium aluminate as C_3A,

tetracalcium aluminoferrite as C_4AF, and calcium sulfate dihydrate as $C\hat{S}H_2$ where $\hat{S}$

represents SO_3.

The compound composition of portland cement is usually estimated by calculation

using the ideal compound stoichiometries and oxide analysis determined by standard

methods (usually X-ray fluorescence spectroscopy) and available from the cement

supplier (mill certificate). The calculation of the phases from the composition is known as

the Bogue calculations. The values obtained by Bogue calculations are only approximate

and do not necessarily represent the true values. This is mainly because Bogue

calculations are based on several assumptions that are not usually found in the cement

chemistry. Among these assumptions are chemical equilibrium and the consistency in the

composition of all the phases [22]. It is known that chemical equilibrium rarely occurs

inside the kiln during cooling, and it was found that a large number of substitutional ions

can be incorporated in most of the phases. Thus, the phases do not have the compositions

assumed for them. Nevertheless ASTM C 150 gives the Bogue calculations that are

suitable for most purposes, although more sophisticated procedures have been developed.

Knowing the compound composition of portland cement makes it possible to predict the

properties of the cement, but more important is the fact that manipulation of the

compound composition can be used to modify certain properties of the cement so that the

cement will perform more satisfactorily in particular applications. C_3A and C_3S are the

most reactive compounds, where as C_2S reacts much more slowly. The calcium silicates

provide most of the strength developed by portland cement; C_3S provides most of the

early strength (in the first three to four weeks); while C_2S provides most of the ultimate

strength. C_3A and C_4AF control the setting time and the presence of gypsum slows the early rate of hydration of C_3A. The reaction of C_4AF + gypsum + water is believed to be somewhat slower than C_3S, whereas the hydration of C_4AF without gypsum is faster. Gypsum also increases the rate of hydration of the calcium silicates, which also compete for sulfate during hydration.

1.3.2 Impurity Oxides

Since only approximate chemical equilibrium can be attained in the rotary kiln, it is to be expected that all cement compounds will contain small amounts of the other oxides present in the clinker. The calcium silicates probably contain about 3% by weight of impurity oxides, principally Al_2O_3, Fe_2O_3, and MgO [2]. Impure C_3S, as it exists in portland cement, is known as alite and impure C_2S as belite. Both alite and belite are more reactive than the pure silicates and hydrate more rapidly. C_3A contains considerable amounts (about 10% by weight) of SiO_2 and Fe_2O_3, while C_4AF contains considerable SiO_2 and much MgO [2].

1.3.3 Sources of Sulfates

The most important source of sulfates in portland cement is calcium sulfate. Various forms of calcium sulfate (anhydrite, hemihydrate, dihydrate) are added to clinker during cement grinding to control the cement setting characteristics as was stated previously. These sulfates may be added in the form of natural or industrial-grade calcium sulfate dihydrate (gypsum) or anhydrite. Additional sulfates originate from the clinker, in which they are formed during the manufacturing of the clinker from the raw materials, and from

the products of fuel combustion. Predominantly, they are present in the clinker in the form of alkali-and calcium-alkali sulfates (double salts), and occasionally, in the form of calcium sulfate anhydrite or other phases [3]. The most common sulfate phases present in clinkers are arcanite, K_2SO_4, calcium langbeinite, $KC_2\hat{S}_3$, and aphthitelite $K_3N\hat{S}_4$. As stated earlier, and as a result of environmental restrictions on sulfur and other emissions, a large increase in the sulfate content of currently produced cements occurred. Thus, the proportion of sulfate that is present in typical cements in the form of alkali-and alkali-calcium sulfates, originating from the clinker, could be in some cases higher than it was in the past [3].

Occasionally, additional sources of sulfate in concrete may be the sulfates (e.g. gypsum) or sulfides present in aggregate. Also, sulfates may be components of mineral and chemical admixtures. Thus, when using an unknown or new admixture in concrete applications potentially exposed to sulfate conditions, it is advisable to check the chemical or mineralogical nature of all concrete materials [3]. Finally, mixing water could be a possible source of sulfate, but this is considered to be an improbable source of serious damage.

Although the chemical requirements of portland cement given in ASTM C 150 allow wide variations in chemical composition, since it has been found that cements with quite different chemical compositions may have suitable physical behavior, the only limits placed on all cement types are the MgO and SO_3 levels and, optionally alkalis.

1.4 Hydration of Portland Cement

It is very important to understand the reactions that take place during the hydration of portland cement in order to assess the effect of the SO_3 content of the cement. Although the hydration of portland cement involves a complex of chemical reactions, three main reactions are the ones involving the calcium silicates and calcium aluminates. The hydration reactions of the two calcium silicates (Equations 1 and 2) are stoichiometrically very similar, differing only in the amount of calcium hydroxide formed:-

$$2C_3S \quad + \quad 11\,H \quad \rightarrow \quad C_3S_2H_8 \quad + \quad 3CH \qquad (1)$$

Tricalcium   water   C-S-H   calcium

silicate   hydroxide

$$2C_2S \quad + \quad 9H \quad \rightarrow \quad C_3S_2H_8 \quad + \quad CH \qquad (2)$$

Dicalcium   water   C-S-H   calcium

silicate   hydroxide
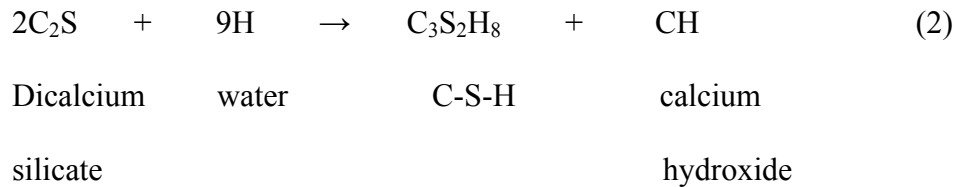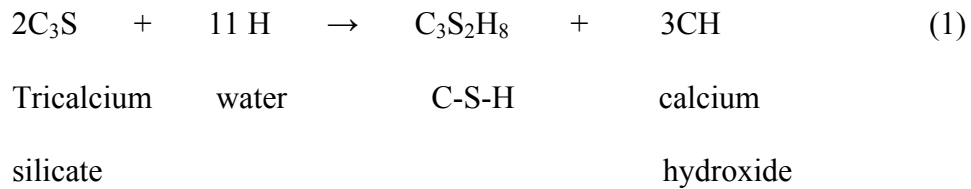
The principle hydration product is a calcium silicate hydrate. The formula $C_3S_2H_8$ is only approximate because the composition of this hydrate is actually variable over quite a wide range. $C_3S_2H_8$ is a poorly crystalline material that forms extremely small particles in the size range of colloidal matter (less than $1\mu m$) in any dimension [2]. Its name, C-S-H (or C-S-H gel) reflects these properties. In contrast, calcium hydroxide is a crystalline material with a fixed composition. Although C_2S hydrates in a similar manner to C_3S, it is much slower because it is a less reactive compound than C_3S.

The hydration of C_3A in portland cement involves reactions with sulfate ions that are mainly supplied by the dissolution of gypsum. The primary initial reaction of C_3A is

$$C_3A \quad + \quad 3C\hat{S}H_2 \quad + \quad 26H \quad \rightarrow \quad C_6A\hat{S}_3H_{32} \qquad (3)$$

Tricalcium   gypsum   water   ettringite
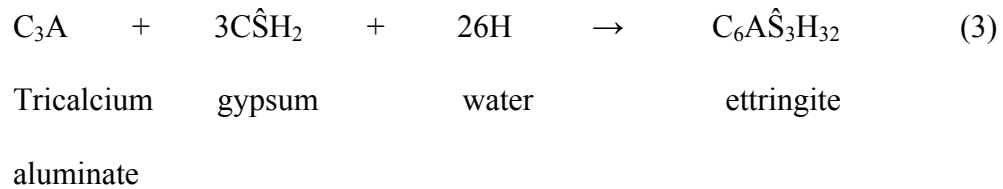
aluminate

The hydration product which is a calcium sulfoaluminate hydrate is called "ettringite". Ettringite is a stable hydration product only while there is an ample supply of sulfate available [2]. If the sulfate is all consumed before the C_3A has completely hydrated, then ettringite transforms to another calcium sulfoaluminate hydrate containing less sulfate:-

$$2C_3A \quad + \quad C_6A\hat{S}_3H_{32} \quad + \quad 4H \quad \rightarrow \quad 3C_4A\hat{S}H_{12} \qquad (4)$$

This second hydration product is simply called monosulfoaluminate. Monosulfoaluminate may sometimes form before ettringite if hydrating C_3A consumes the sulfate ions faster than they can be supplied by dissolution of the gypsum in the mix water. It was found that the formation of ettringite slows down the hydration of C_3A by creating a diffusion barrier around C_3A grains. This barrier is broken down during the conversion to monosulfoaluminate and allows C_3A to react rapidly again [2]. The more gypsum there is in the system, the longer the ettringite will remain stable. Conversion to monosulfoaluminate will occur in most cements within 12 to 36 h, after all the gypsum has been used to form ettringite. The formation of monosulfoaluminate occurs because in most cements there is not sufficient gypsum necessary to form ettringite from all the

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available aluminate ions. When monosulfoaluminate is brought into contact with a new source of sulfate ions, then ettringite can be formed once again:-

$$C_4A\hat{S}H_{12} \quad + \quad 2C\hat{S}H_2 \quad + \quad 16H \quad \rightarrow \quad C_6A\hat{S}_3H_{32} \qquad (5)$$
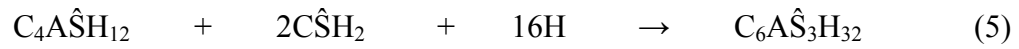
This potential for reforming ettringite is the basis for sulfate attack of portland cements when exposed to an external supply of sulfate ions.

If gypsum is not present, C_3A will react rapidly with water to form calcium aluminate hydrates:

$$C_3A \quad + \quad 21H \quad \rightarrow \quad C_4AH_{13} \quad + \quad C_2AH_8 \qquad (6)$$

These hydrates are not stable and later convert to C_3AH_6 (hydrogarnet):

$$C_4AH_{13} \quad + \quad C_2AH_8 \quad \rightarrow \quad 2C_3AH_6 \quad + \quad 9H \qquad (7)$$
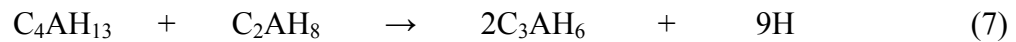
If C_3A is very reactive, even with the presence of gypsum, small amounts of hydrogarnet may be found in a hydrated cement. When small amounts of gypsum are present, there may still be unreacted C_3A present when all of the ettringite has been converted to monosulfoaluminate. In this case, a solid solution between $C_4A\hat{S}H_{12}$ and C_4AH_{13} is formed, the two hydrates having the same crystal structure. This solid solution is written as $C_3A(C\hat{S},CH)H_{12}$.

The hydration of the ferrite phase C_4AF forms similar hydration products to C_3A in both cases with or without gypsum, however the reactions are slower and involve less heat. Changes in the composition of the ferrite phase affect only the rate of hydration; as iron content is raised, hydration becomes slower. Practical experience has shown that cements low in C_3A, but high in C_4AF are much more resistant to sulfate attack [2]. This means that the formation of ettringite from monosulfoaluminate (Eq. 5), does not occur. It has not been established why this is so; it may be that an iron-substituted

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monosulfoaluminate cannot react to form ettringite. Alternatively, the presence of the amorphous product $(F,A)H_3$ may in someway prevent the reaction described in Eq. 5 from occurring.

1.5 Review of Previous Research

The phenomenon of optimum sulfate levels in portland cements has occupied researchers for decades. Beginning in 1870 Michaelis discovered the most remarkable effect of adding only 2% of raw gypsum to ground cement on regulating setting, that is to lower the setting time to 5-7 hours [4]. This discovery of Michaelis then became a very significant issue to the whole world especially when it was noticed that adding gypsum, not only regulates the rapid setting, but even improves the strength of cement mortars [4]. An early research work done on the setting time concluded that there would be no advantage in adding more than 2% $CaSO_4$ and that specifications should call for such a limit. In this work, one type of clinker was grounded with gypsum at 0.5% intervals from 0.5 to 7.0% and time of set was measured with a Vicat-Type apparatus. Maximum retardation was obtained with 1.5% $CaSO_4$ and additional gypsum did not further delay initial set for this clinker. ASTM adopted a limit of 2.0% SO_3 in 1920, but the recommended limits for SO_3 have increased consistently since then due to several factors, including higher sulfur fuels used in burning clinker and increased clinker fineness [4]. Several researchers observed an increase in strength with increasing gypsum content and the first publication indicating an optimum amount of gypsum for strength development was published in 1924. The researchers also observed that gypsum inter-ground with clinker produced higher strength mortars than cements made by blending ground clinker

plus gypsum. This suggests that gypsum fineness plays an important role in strength development, a significant finding which has been confirmed more precisely in recent years [4]. A study conducted by ASTM Committee C-1, Subcommittee B in 1931 concluded that more than 1.75% SO_3 was detrimental in cements with 8% C_3A but that higher C_3A cements (11-16%) could contain up to 2.5% SO_3 without detrimental effects. A close look at their data indicates that 2.5% SO_3 was optimum for strength development measured at one day, but that 3.0% SO_3 gave higher strengths at later ages. Other investigations also showed similar trends but indicated that for a certain optimum gypsum level, a set of conditions should be well defined including the fineness of the cement, the form and reactivity of the calcium sulfate, the curing conditions, the temperature during storage, and the age of the specimen at test. Kanare and Gartner [4] stated that "the sulfate addition level which gives optimum strength development may not give the best volume stability under all circumstances".

In 1941, Lerch [5], began a thorough study of the effects of gypsum and lime on cement hydration. Twelve commercial clinkers covering the range of chemical composition generally found in portland cements were selected for study. Each of these compositions was used with various SO_3 contents with fineness held constant at about 1900 sq. cm. per gram. In addition five of the clinkers were ground to varying degrees of fineness with SO_3 constant at about 1.8 percent. The results of the study showed that with some cement compositions, the gypsum retards the initial hydration and set, while with others it acts as an accelerator. It also showed that for many cements, the strengths can be increased and the drying shrinkage decreased by the use of larger additions of gypsum than were permitted by the specifications at that time. The results

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also showed that the fineness, the alkalis, and the C_3A content all influence the gypsum requirements. Lerch defined a "properly retarded" cement on the basis of the shape of the heat-liberation curve during the first 30 hr. of hydration. A "properly retarded" cement, according to Lerch, "is the one that contains the minimum quantity of gypsum required to give a heat-liberation curve that shows two cycles of ascending and descending rates and that shows no appreciable change with larger additions of gypsum". The results of the tests showed that when considering cements ground from a given clinker, those containing the proper amount of gypsum to give this type of curve will develop the highest strength and the lowest contraction.

As for the influence of the alkalis and C_3A content of the cement on the gypsum requirements for proper retardation, the results showed that with cements of low alkali content, those of high C_3A content require larger additions of gypsum than those of low C_3A. For cements of the same C_3A content, those high in alkalis react with gypsum more rapidly and require larger additions of gypsum than those low in alkalis. The author stated that "there is some evidence that cements containing Na_2O require larger amounts of gypsum than do similar cements containing an equivalent quantity of K_2O". The author adds that "it appears that at least part of the alkalis of the cement are present in the aluminate phases, and that aluminate phases containing alkalis react with water more rapidly than do similar phases which are alkali-free or of lower alkali content. Thus the cements of higher alkali content require larger additions of gypsum for proper retardation than do similar cements of lower alkali content".

The author also explained that increasing the specific surface of the cement increases the quantity of aluminate phases available for reaction with the water at early

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ages and thereby increases the quantity of gypsum required for proper retardation of cements of moderately high or high C_3A content.

It was stated that "cements of low C_3A and low alkali content without added gypsum can be mixed with water without the occurrence of a flash-set" [5]. The explanation of the author for this statement was that with cements of this type an amorphous hydrated calcium ferrite precipitates on the surface of the cement particles and seals the surface in a manner such as to retard subsequent hydration, while with added gypsum a crystalline hydrated calcium sulfoferrite is formed which does not seal the surface and the hydration is accelerated.

The results of the physical tests showed that for many cements the strengths can be increased and the contraction on drying or the expansion in water storage decreased by the use of larger additions of gypsum than were permitted by specifications. In some instances, the strengths were increased by as much as 20 to 50 percent and the contraction decreased by as much as 30 to 50 percent. For cements of low C_3A and low alkali content, the strengths were not increased nor were the contractions decreased by larger additions of gypsum. The cements high in C_3A regardless of their alkali content or cements high in alkalis regardless of C_3A content require larger additions of gypsum. Lerch concluded that gypsum could be added in larger amounts than was permitted by the specifications at that time without danger of delayed expansion.

Although some researchers found that Lerch's work could be faulted in some areas, other researchers reached essentially the same conclusions. Perhaps the most important conclusion which can be drawn from Lerch's study is that most cements show different

optimum gypsum requirements for different properties, such as strength or shrinkage, at different ages.

In 1956, the standard specification for portland cement C 150 was revised to reflect the thinking that SO_3 content should depend upon cement type and composition, and by 1961 up to 4.0% SO_3 was permitted in Type III cements with more than 8% C_3A [4].

Several researchers have attempted to find correlations between clinker composition, cement fineness, and the level of gypsum which produces optimum strength development, however none of the given equations proved to be sufficiently accurate or reliable for use as predictive tools. Kanare and Gartner [4] stated that, "it seems that the technology of optimizing the sulfate content in portland cements has remained virtually unchanged since the turn of the century when technologists first made cements with several levels of gypsum to see which got strongest. This is still the best and only method to use for the purpose of maximizing early strength in commercial cements".

Some research work was done on the effect of fineness of calcium sulfates in cements on the optimum sulfate content. Observations by several researchers suggest that gypsum interground with clinker might be "smeared" on the surfaces of clinker particles rather than simply ground into a fine powder which is intimately mixed with the clinker. Calcium sulfate particles several hundred micrometers in size are often observed in commercial cements [4]. These coarse gypsum particles could be effectively "inert" during early cement hydration, possibly as a result of encapsulation by hydrated cement phases. In such a case these large particles may influence the attempts to optimize sulfate content.

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Panigrahy et.al. [20], studied the differential comminution of gypsum in cements ground in different mills. Identical mixes containing fixed amounts of ordinary portland cement clinker and gypsum were ground in two types of industrial cement mills, ball mill (BM) and vertical roller mill (VRM), to identical Blaine fineness to examine the effect of any possible differential comminution of gypsum on cement setting times. The authors found that in every occasion, the VRM cement recorded much lower setting time than the BM cement. It was also found that although the SO_3 contents in all the cement samples are almost identical, their gypsum XRD pulse counts were quite different and they were always significantly less in the BM products than in the VRM products. Since the XRD spectra did not record any other crystalline Calcium sulfate phase, it is evident that the BM product contained a significant portion of Calcium sulfate in amorphous form. The effect of grinding on amorphism was also reported by other researchers and the authors stated that "it is only the differential amorphism of gypsum caused during grinding which is solely responsible for variation in setting times". It was concluded from the study that during comminution of cements, the degree of crystallinity of gypsum, as determined by X-ray diffraction (XRD), changes with used grinding mills and this causes changes in setting times of similar cements even when ground to identical Blaine fineness.

Goswami, Mohapatra, and Panda [1], studied gypsum dehydration during comminution and its effect on cement properties. The authors concluded that gypsum in cements, ground to the same fineness in different mills, may be subjected to different degrees of dehydration. During cement grinding in an industrial mill, gypsum is often dehydrated to hemihydrate. It was found that the presence of hemihydrate in the cement increases ettringite formation during early hydration, retards the setting times, and

reduces the strength of the cement by about 10%. The authors suggested that the fall in strength is particularly due to re-hydration of part of the hemihydrate present in the cement.

Among the earliest findings concerning the optimum gypsum content were those of Lerch [5] who found that the optimum gypsum for minimum shrinkage of mortars was slightly greater at 28 days than at 3 days. Another important finding was that of Alexander and co-workers [6] who studied the effects of variable SO_3 in concretes. In one study, using three commercial cements, each produced at four different levels of SO_3, creep under compressive loads was found to be very sensitive to the SO_3 content of the cement, and that the optimum SO_3 for minimum creep, generally 3-4% SO_3, was at least 0.6% higher than the optimum gypsum for minimum drying shrinkage. The SO_3 content of the cement was also shown to have no significant effect on concrete modulus of elasticity.

Some researchers investigated the effect of SO_3 on the hydration of the silicate phases. They concluded that calcium sulfate has an accelerating effect upon the hydration of C_3S [4]. One indication among the findings of these researchers is that any level of gypsum which keeps the hydration liquid saturated with sulfate ions at early ages will provide acceleration of the alite hydration. In addition to the fact that gypsum accelerates the hydration of the silicate phases, it is believed that it also influences the composition of the hydration products. It has been suggested that the silicate hydration products containing sulfate are intrinsically inferior to those without sulfate, but the opposite has also been claimed [4]. It appears that there is a trade-off between the increased amount of gel produced by the addition of gypsum and its inferior quality at later ages. It seems that

a certain combination of the amount and quality of gel was optimum for compressive strength. Sulfate ions are isostructural with silicate ions and might be expected to substitute for the silicate in CSH gels [4].

Bentur [9], studied the effect of gypsum on the hydration and strength of C_3S pastes. He studied pastes hydrated at 0.43 water-to-solid ratio of mixtures of C_3S with 0,2,4, and 9% analytical-grade gypsum. He found that the effect of gypsum content on compressive strength changes with time. At early ages (1 and 2 days) the compressive strengths of the pastes containing 2,4, and 9% gypsum were similar, whereas the pure C_3S was much weaker. At 3 and 7 days, the compressive strength was maximum at 2% gypsum content. At 28 and 90 days, the strengths of pure C_3S and the paste containing 2% gypsum were markedly greater than those of the pastes containing 4 and 9% gypsum. He also studied the C/S values of the pastes with different gypsum content. He found that in pure C_3S past, this value decreases as hydration advances; beyond 70% hydration, it tends to stabilize. In the pastes containing gypsum, the C/S ratio increases up to approximately 60% hydration and decreases thereafter. Bentur also found that in 70% hydrated pastes, the C/S ratio increases with the Ŝ/S ratio. This trend indicates that the reaction of the sulfate causes chemical changes in the structure of the CSH gel. He assumed that the variations in the strength of pastes having the same degree of hydration are related with changes in intrinsic strength. At 40 and 50% hydration, the C/S ratio is independent of gypsum content and so is the intrinsic strength. At higher degrees of hydration, the C/S ratio increases with gypsum content and the intrinsic strength decreases with it. He suggested that the difference in the gypsum effect at lower and higher degrees of hydration might be the result of a slow reaction between the sulfate and the CSH gel, so

that the influence of gypsum on the chemical constitution and mechanical quality of the CSH gel begins to be important only after a certain period of hydration. Thus the optimum gypsum content is the value at which the optimum combination of quantity and quality of the CSH gel occurs.

Me'ne'trier, et. al. [14], and in order to better understand both the effect of gypsum on cement hydration and the morphology of the hydration products, conducted studies on C_3S hydration in the presence of gypsum and then incorporated this into a mechanical study of cement hydration. The results of this study confirmed an increase in C_3S dissolution rate in the presence of gypsum. The study also revealed that a substantial amount of sulfur is incorporated in the C-S-H, this was evidenced by the disappearance of gypsum from the system. It is the belief of the authors that sulfate ions may replace the silicate ions in the amorphous structure of C-S-H. The authors also concluded that the morphology of the C-S-H formed in the first minutes of hydration is similar to that of C-S-H formed in a saturated lime solution rather than in pure H_2O. However, the morphology developed in later stages resembles that of usually-observed C-S-H.

Observations of other researchers suggest that sulfate may affect the strength by modifying the morphology of the hydration products, or by modifying the pore structure which surrounds and permeates the solids. Other investigators found that although gypsum produced a higher hydration rate and, therefore, a more rapid strength increase, the resulting gel was less condensed (had more pores) and had higher lime-silica ratio, at the same degree of hydration, in the pastes containing gypsum. The lime-silica ratio is one of the most intensively studied aspects of cement chemistry. At a given degree of

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hydration, compressive strength was related to the inverse of the C/S ratio as determined by QXRD, with best strength at C/S = 1.9 (molar basis). C/S decreased with increasing degree of hydration and increased with increasing sulfate-to-silica ($\hat{S}$/S) ratio [4]. Some researchers estimated the maximum amount of sulfate which could be accommodated in the gel to be equivalent to a S/$\hat{S}$ molar ratio of 5.85, which is approximately equal to 4.5% SO_3 by weight in ordinary portland cement. Since most commercial cements contain far less than 4.5% SO_3, all of the gypsum could, in principle, be accommodated in the CSH. The sulfate substitution for silicon in hydrated C_3S paste appears to have a small contribution to the increase in strength since optimizing the SO_3 content of a cement typically can produce a 25% increase in compressive strength of mortar cubes [4]. The most important effect of gypsum is to accelerate C_3S hydration in addition to the important role of retarding C_3A and C_4AF hydration.

According to Kanare and Gartener [4], "it could be concluded that the uptake of SO_3 by CSH is potentially an important factor in determining the kinetics of SO_3 depletion in cement hydration at early ages. Although by the end of the induction period (which usually takes few hours) only very little C_3S is consumed and very little CSH is formed, the steady hydration of C_3S that occurs after that results in a rapid uptake of $CaSO_4$ by CSH, well before the onset of the renewed rapid aluminate-phase hydration".

Ish-Shalom and Bentur [8], studied the effects of aluminate and sulfate contents on the hydration and strength of portland cement pastes and mortars. They used three cement samples varying in C_3A content and one varying in SO_3 content. In the interpretation of their results, bound water was used as a measure of quantity of binding material, and free lime to bound water ratio (FLWR) as a measure of chemical constitution and quality. In

their work they stated that aluminate and gypsum can influence the hydration in two different ways: directly, by the presence of sulfoaluminate hydrate, or, indirectly, by affecting the rate of hydration of the silicate phases or the quality of the hydrosilicate gel that is formed or both. They assumed that the extent of hydration represents the quantity of binding material while FLWR represents some measure of its quality. Their results showed that when comparing different cements hydrated under the same conditions (period and temperature of hydration) high compressive strength is associated with the higher FLWR but not with bound water. They suggested that in these cases high FLWR indicates the existence of a high quality gel. According to their explanation, high FLWR implies low Bound Lime to Bound Water Ratio (BLWR) and since bound water is approximately proportional to the amount of hydrated silicates, then low (BLWR) means low CaO/SiO_2 ratio in the hydrated gel. Thus, a high FLWR indicates the existence of a low CaO/SiO_2 hydrated gel and this gel indicates according to other researchers a large proportion of double tobermorite layered structure in it, which is also connected with higher specific surface, which in turn leads to higher strength.

They concluded from their work that the highest compressive strength is achieved with medium aluminate content cement for all the temperatures and ages investigated. A good correlation was observed between strength and free lime water ratio (FLWR), which is a parameter of the chemical constitution of the cement gel. They also concluded that the increase in sulfate content of the medium aluminate cement caused an increase in extent of hydration (bound water) and a reduction in the quality of the gel (FLWR). An optimum combination of both parameters (expressing quality and quantity of gel) was achieved at the medium sulfate cement which exhibited the highest compressive strength.

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They also found that the medium aluminate cement exhibited an optimum response to the effect of high initial temperature: The beneficial effect at early age (high strength and degree of hydration) was highest while the deleterious effect at later age was lowest.

The effect of added gypsum on the compressive strength of portland cement clinker was also studied by Soroka and Relis [15]. The authors state that there is an optimum gypsum content which imparts the cement maximum strength and minimum shrinkage without excessive expansion. This optimum, generally speaking, depends on, and increases, with C_3A and alkali oxide contents of the cement and with its fineness. The observed optimum content in the strength curve, and according to the authors, implies that the addition of gypsum involves two opposing effects. The first, which pre-dominates the lower range of SO_3 content, has a beneficial effect on strength, and brings about the ascending part of the curve. The second, which pre-dominates the range of SO_3 content greater than the optimum, has an adverse effect and brings about retro-gradation in strength and the associated descending part of the curve. This adverse effect may be attributed to internal cracking which takes place when an excessive amount of gypsum (i.e., more than the optimum) is added to the cement. It should be noted, however, that sulfate expansion is probably not the only mechanism involved because such retro-gradation in strength was observed also in C_3S and alite pastes, i.e., under conditions where no ettringite is formed. It was, accordingly, suggested by researchers that the hydration of C_3S and alite in the presence of gypsum resulted in a C-S-H gel of inferior quality (a gel of a lower intrinsic strength), and it was shown that such a gel was characterized by lattice-substituted $\hat{S}$ and a higher C/S ratio [9].

The test data of this study also indicated that the addition of gypsum to portland cement clinker resulted in higher strength, in particular at the early ages of one and three days. This higher strength was associated with a lower degree of hydration and a greater porosity. Under test conditions, this observation, implied that the beneficial effect of the gypsum on the strength of the cement was attributable to the improved quality of the gel which was produced in the presence of gypsum. The study showed that the addition of the gypsum resulted in hydration products of greater average density and it was suggested that this greater density brought about the higher strength. The authors also suggested that the greater density of the hydration products was due to the pressure generated on formation of ettringite due to the increase in the volume of the solids involved in the reaction.

Alexander and Ivanusec [16], studied the long-term effects of cement SO_3 content on the strength of concrete. Six brands of cements were each manufactured at four SO_3 contents, in full scale plants. The strengths were determined, at up to one year, in concretes of high and low w/c ratios. The study showed that strength was usually independent of, or linearly related to, the SO_3 content observed. Only rarely was a well defined optimum SO_3 content observed. The study also showed that there is an appreciable increase in strength between 28 days and one year at all SO_3 levels. The greatest strength increase with time occurred with low-C_3A cement. Almost invariably, with each cement, the strength v. SO_3 content relationships at 28 days and one year are similar, and the strength increase between these ages is therefore largely insensitive to the SO_3 content of cement. The authors concluded that the association between the 28-day strength of concrete and the C_3S content of cement does not vary greatly with the SO_3

content of cement. However, the correlation coefficient for C_3A and strengths shows considerable sensitivity to SO_3 content. The one-year strengths of concrete made from under-sulfated cements showed a strong negative association with the C_3A content of cement. Under these conditions, differences in the C_3A contents could account for up to 10 MPa difference in strength. It was also concluded that the strength of the association between one-year concrete strength and the C_3A content of cement varies with the SO_3 content of cement. At this age, the degree of sensitivity of the C_3A coefficient to SO_3 content depends, in turn, on w/c ratio.

Since only few explanations have been suggested in order to explain the effect of gypsum on the mechanical properties of the cement and since these explanations are not always complete and even sometimes contradictory, Soroka and Abayneh [17], conducted a study aimed to establish the effect of gypsum, if any, on the structure of the cement paste, and to try and relate, if possible, this effect to the mechanical properties of the paste. It was clearly evident from the study, that an optimum SO_3 content existed in most cases, but not always, with respect to the strength and drying shrinkage of the pastes. Strength-wise, the optimum was 2 to 3%, increasing to 4% in the finer cement. It was pointed out that the increase in the optimum content with the fineness of the cement was generally observed. The authors explained the higher value of 4% which was observed in the finer cement by the higher rate of hydration of such cements in comparison with their coarser counterparts. Sulfate expansion is generally attributed to the continued formation of ettringite in the set cement as a result of topochemical reaction between the gypsum and the C_3A of the cement. As more gypsum is consumed at an earlier stage with a higher rate of hydration, and because only the gypsum which is left to

react at the later stages causes expansion, a greater gypsum content can be tolerated in the finer cements. The study also showed that for SO_3 contents exceeding the optimum of 3%, and particularly at the later ages of 28 and 90 days, the presence of the gypsum significantly retarded the hydration of the cements. It was concluded from the study that the strength of a cement at a given SO_3 content in the range studied (i.e., to 5%), is significantly related to the degree of hydration, and that at a given degree of hydration or porosity, strength is increased with the increase in the SO_3 content of the cement. The authors found that the improved strength with the increased SO_3 content could not be related to the quality of the gel, as it is reflected in the density of the hydration products, nor to differences in pore-size distribution. The authors concluded that there are apparently some other factors involved and this warrents further study.

The increase in strength with increasing SO_3 content, can be explained by the fact that the presence of calcium sulfate accelerates the hydration of alite, but this does not explain the existence of a maximum. Kanare and Gartner [4], suggests one possible explanation as follows:- "When the optimum amount of calcium sulfate is present, the aluminate phases are retarded and the liquid phase remains saturated with respect to gypsum until after the alite has experienced its maximum rate of hydration and the cement has achieved final set. This permits the maximum rate of alite hydration and therefore maximizes early strength development. However, if too much sulfate is present, then the remaining aluminate hydration will be retarded and so will continue to produce ettringite after the paste has hardened, causing localized expansion of the paste structure and consequent reduction in strength development due to micro-cracking". This explanation is supported by the fact that the 1-day strength-versus-SO_3 curves for low

C$_3$A cements are virtually flat in the region beyond the SO$_3$ level that gives maximum strength, whereas the curves for cements containing more than 5% C$_3$A show significant decreases in strength at higher SO$_3$ levels. When gypsum continues to be present beyond the time of final set, this need not be necessarily detrimental to the early paste structure because the growth of expansive ettringite can be accommodated and micro-cracks which may develop can be autogenously filled by newly formed CSH [4]. Another important fact is that it is reasonable to assume that the strength increases as the total volume of hydrates increases and this includes the calcium aluminate hydrates, thus early gypsum depletion could be advantageous in that it will result in a high degree of C$_3$A hydration within the first day. Accordingly, a relatively small excess level of SO$_3$ could retard this process and therefore lowers 1-day strengths, although it need not necessarily produce any obvious expansion. SO$_3$ levels well beyond the optimum are usually necessary to produce deleterious expansions [4].

Tang and Gartner [19], studied the influence of sulfate source on portland cement hydration. Cements were synthesized by blending a Type I low alkali portland cement clinker with sulfate salts. The authors developed a quantitative X-ray diffraction method to measure the rate at which C$_3$A and C$_4$AF phases in these cements were consumed in pastes hydrated at 23 $^\circ$ C. It was found that the initial high rate of aluminate phase consumption was influenced significantly by the rate of solubility of the sulfate source and especially the rate at which it released CaSO$_4$ into solution. Interground gypsum was far more effective than interblended gypsum in controlling aluminate hydration. It was also found that a better control of the initial aluminate hydration generally led to higher 28-day paste strengths. For all sulfated cements, ettringite was the only aluminate hydrate

detected by XRDA over the first 30 min. However, by 24 hr. it was in most cases accompanied by detectable amounts of an AFm phase which usually appeared to be monosulfoaluminate. The authors stated that although it has been suggested that high alkali cements require more SO_3 for optimization because the alkali accelerates aluminate hydration, their data did not support this as a general rule. They added that other factors, such as the solubility or "reactivity" of the sulfate source, seem to be just as important. Thus, much less aluminate reacts initially in the low alkali cements containing hemihydrate than in the comparable cement made only with gypsum, because hemihydrate is more soluble than gypsum. After 30 min. however, the difference is lost, but this initial control of the aluminate phase hydration could lead to higher 28 day strength. More remarkably, the cement made by inter-grinding clinker and gypsum showed significantly lower aluminate consumption than the interblend at all ages, and even after 24 hr. its aluminate was severely retarded. This indicates that distribution of sulfates is just as important as their chemical form, and that results obtained with interblends can never completely represent what would occur in commercially produced cements made from clinkers containing alkali sulfates. The study showed that there is an approximate inverse correlation between initial aluminate consumption and initial mini-slump of the pastes. The data for the paste compressive strength show the positive effect of soluble alkali on 1-day strengths, but at 7 and 28 days, there was little significant difference between the high and low alkali cement groups. The practical consequence of this work lies in the observation that a reduced initial rate of aluminate phase consumption tends to improve both the workability of the fresh cement paste and the ultimate strength of the hardened product [19].

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1.5.1 C$_3$A and C$_4$AF Hydration

Considerable controversy still exists regarding whether the formation of ettringite is the primary mechanism for early retardation of C$_3$A. According to Kanare and Gartner [4], some researchers suggest that retardation of C$_3$A in mixtures with CaSO$_4$ is due to ettringite formation, but in cements it is due to amorphous hydration products. They also suggest that monosulfoaluminate can form even when gypsum particles are present, and thus local dissolution and transport rates are an essential part of the retardation mechanism. Other researchers demonstrated that the hydration of C$_3$A and C$_4$AF is retarded in solutions saturated with both lime and gypsum and that the ferroaluminate phase is the one being more strongly affected. They suggest that ettringite forms first on the C$_4$AF surface, and when the sulfate concentration becomes low, monosulfoaluminate is produced, the ettringite layer is broken up, and C$_4$AF hydration accelerates. Other researchers stated that evidence was found that a retarding coating of ettringite and hydrous alumina exists which disappears at later stages as the sulfate is used up, permitting renewed acceleration. The findings reported by several researchers indicate that gypsum retards C$_3$A only when calcium hydroxide is also present. In this case, ettringite forms protective films on the surface of the C$_3$A as long as the solute concentration exceeds 14.5 mg CaSO$_4$/liter.

When all the gypsum is used to form ettringite, further reaction of C$_3$A converts ettringite to a solid solution of monosulfoalumiante and hydrated tetracalcium sulfoaluminate [4]. Other researchers hydrated cements in the presence of isotopically labeled gypsum and then treated the products with lime water to remove residual gypsum. They concluded that a calcium sulfoaluminate coating formed initially on the grains as a

slightly permeable film, and that the minimum amount of sulfate required to give a complete film coating to the grains was the amount which would properly retard the cement.

Skalny and Tadros [11], investigated the mechanism of retardation of the C_3A dissolution rate by $CaSO_4$ and concluded that the retardation of the C_3A-H interaction in the presence of $CaSO_4$ is not primarily the result of the formation of an ettringite film on its surface. Upon contact with water, C_3A dissolves incongruently, leaving an aluminum-rich layer on the surface. Calcium ions adsorb on this surface, producing positively charged particles even though the medium is highly alkaline. The formation of such a structure appears to minimize the active dissolution sites, and the dissolution rate of C_3A decreases. In the presence of small amounts of $CaSO_4$, sulfate ions adsorb on the positively charged particles, resulting in further reduction of the dissolution sites which would otherwise be available for hydroxyl ions to catalyze the dissolution.

Collepardi et.al. [13], studied the hydration of tricalcium aluminate in the presence of lime, gypsum, or sodium sulfate. The results of his work confirmed that the mechanism of C_3A hydration by gypsum is based on ettringite coating C_3A grains. The authors concluded that ettringite crystals are formed by a through-solution mechanism but that they are assumed preferentially to form on the surface of C_3A because of the catalytic action of the C_3A surface on the nucleation of ettringite. The retardation due to gypsum is more effective in the presence of CH as ettringite crystals are smaller and can fit to the irregular shape of C_3A grains better than larger ettringite crystals obtained in the absence of CH. The same hypothesis was proposed to explain why CH retards C_3A hydration. The authors also found that after some hours, the ettringite coating C_3A grains

is converted to monosulfate because of the consumption of gypsum, and C_3A hydration is renewed. The results of this work did not confirm two other proposed mechanisms for the retardation of C_3A hydration in the presence of CH and gypsum. The first mechanism was the one based on the formation of C_4AH_x impervious layer coating the C_3A grains, this was due to the fact that ettringite was observed instead of C_4AH_x during the initial period of C_3A hydration. Also expansion caused by the formation of monosulfate from C_4AH_x was not observed. The second mechanism was the one based on the adsorption of sulfate ions on C_3A grains, this is because the results of this work showed that Na_2SO_4 does not retard C_3A hydration as gypsum does. Also the renewal of C_3A hydration which was observed after some hours when C_3A hydrates in the presence of gypsum or gypsum and CH, can not be explained by this mechanism.

The Rilem Committee 68-MMH, in their report about the hydration of tricalcium aluminate and tetracalcium aluminoferrite in the presence of calcium sulfate [18], summarized the state of knowledge regarding the hydration of C_3A and C_4AF in the presence of calcium sulfate at ordinary temperatures. The report states that there does not appear to be general agreement as to the mechanism by which C_3A hydration is retarded in the presence of calcium sulfate. Most of the experimental evidence favors the view that retardation is associated with AFt formation. However, recent electron optical studies have shown the formation of a hydration product layer of uncertain composition that may control the rate of early C_3A hydration. A number of investigations have analyzed the kinetics of ettringite formation and have suggested a diffusionally controlled mechanism. However, reported activation energies are not consistent with a diffusionally controlled process. Some researchers proposed a mechanism in which a thin layer of ettringite

rapidly forms around the surface of a C_3A particle by a topochemichal mechanism. As this layer thickens, pressure resulting from the volume increase as C_3A is converted to ettringite, develops and causes fissures in the layer. As the fissures form, calcium and sulfate ions and water gain access to the C_3A surface and the fissures are filled by the formation of additional ettringite. Finally, when sulfate ion is exhausted, ettringite begins to convert to AFm in the presence of unreacted C_3A.

Other researchers disagree with the fissure mechanism. They stated that they observed the development of hollow, tubular, amorphous calcium sulfoaluminate hydrate filaments early in the hydration process, which they reported to form as a result of osmotic swelling of amorphous calcium sulfoaluminate layers initially surrounding the C_3A particles. These observations support other proposed mechanisms in which semi-permeable membranes form around the C_3A grains. Water, diffusing through these membranes, eventually results in their rupture. This results in the mixing of an aluminate-rich solution with calcium and sulfate ions and the precipitation of ettringite. Another proposed mechanism suggests that the retardation of C_3A hydration results from the formation of alumina gel in the interfacial region between the C_3A surface and an outer hydrate layer. Observations have shown that CH and gypsum, when mutually present, are more effective in retarding C_3A hydration than is gypsum alone. Other studies indicated that the size of the ettringite crystals was reported to increase with increasing temperature and, as a consequence, become less effective as a diffusion barrier. Studies have also indicated that while ettringite forms during initial hydration of portland cement, it is slowly converted to an AFt solid solution in which hydroxyl ion partially replaces sulfate ion. Fe^{+3} may substitute for Al^{+3} in the ettringite structure and a solid solution between

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the aluminum and iron AFt phases exists. Other researchers concluded that at a pH of about 12.8, the AFt phase is unstable with respect to the AFm phase and gypsum.

As for the ferrite phase, in general, the hydration of the ferrite phase in the presence of calcium sulfate follows the same mechanistic path as that of C_3A: early formation of AFt phase, followed by its conversion to AFm on exhaustion of gypsum.

Kanare and Gartner [4], stated that "No researcher has presented unequivocal evidence for the formation of a crystalline ettringite coating which can seal the surfaces of C_3A grains and thereby retard hydration. While the formation of crystalline ettringite is coincident with retardation, the experimental evidence suggests that a slightly permeable, gel-like layer is formed on the surface of C_3A grains surmounted by several layers of varying composition ranging from amorphous to crystalline. Sulfate and other ions are to be found in this coating and its composition will determine its permeability and propensity toward further re-crystallization".

The effect of temperature is another important factor reported by researchers who showed that the hydration of C_3A is very sensitive to temperature, and can be greatly accelerated by heating. They also showed that at much higher temperatures than 20° C, gypsum is far less effective in controlling the rate of C_3A hydration.

1.5.2 Effect of Alkalis

It is known that sulfate solubility increases and calcium solubility decreases with increasing alkali ion concentration [4]. Some researchers have pointed out that the fineness, distribution, and mineral form of the interground calcium sulfate affects the rate at which calcium and sulfate can go into solution and interact with the other phases already present. The presence of alkalis will cause a change in the rate of gypsum

consumption and thus affects the levels of calcium and sulfate in solution. The alkalis in portland cement clinker are found partly as soluble sulfates and partly as constituents of the clinker minerals. The effects of alkalis on the strength development properties of hydrating cement can be attributed to changes in the composition of the liquid phase mainly caused by the alkali sulfates, or to changes in the hydraulic properties of the clinker minerals caused by the presence of alkalis in their lattice structure [4].

Osbaeck and Jons [7], and in order to evaluate the importance of the distribution of the alkalis, prepared a series of laboratory-burned clinker, differing only in content and distribution of alkalis, and have been ground to cement fineness at various gypsum addition levels. Their investigation indicated that it is the soluble alkalis that affect strength. They concluded that the influence of the content of alkalis in clinker on cement strength is dependent on the content of SO_3 in clinker as well as the content of gypsum in the cement. Increased SO_3 levels in clinker of the same alkali content imply that a greater fraction of the alkalis will be in an easily soluble form. The effect of this transfer of alkalis will generally be an increase of early strength and a decrease in late strengths. However, the effects are modified by the content of gypsum in the cement. Thus the effect on early strength seems to be absent when gypsum content is higher than the optimum content. By analogy high gypsum contents tends to diminish the negative effect of alkalis on late strengths. The authors explained the above by assuming that the presence of soluble alkalis causes entrainment of air in mortar during mixing by promoting premature structure formation in the paste (precipitation of gypsum, syngenite or ettringite). Such an indirect effect of alkalis will introduce a general reduction of strength at all ages, but most pronounced at late ages. The authors also explained the

favorable influence of high gypsum contents on late strength of cements rich in soluble

alkalis to the fact that more gypsum is necessary to counteract the faster removal of

gypsum from the system caused by the alkalis. Thus the presence of gypsum to control

the composition of the liquid phase is believed to be favorable for the hydration of C_3S.

However, too much gypsum will be detrimental to strength development even after 28

days. This could be due to a prolonged retardation of the C_3A and C_4AF phases and thus

a reduced contribution from these phases to the total hydrate formation.

The research work done by Lerch [5] showed similar trend and this led Lerch to

state that: " For cements of the same C_3A content, those high in alkalis react with gypsum

more rapidly and require larger additions of gypsum than those low in alkalis".

Various studies have shown that the presence of alkali metal sulfates, and of anions

other than sulfate, also have a marked effect on the reaction kinetics of C_3A hydration. It

is of particular interest that, as the ratio of alkali sulfate to calcium sulfate is increased,

the effect is first to retard C_3A hydration, and then, at higher alkali levels, to accelerate it

very severely [4]. The results of these investigations, although they were done on pure

C_3A, they indicate that the optimum level of SO_3 in a cement is likely to be strongly

influenced by the presence of soluble alkalis. The mechanisms and kinetics of SO_3

reactions in cements are not fully understood and the data that exists leads to conflicting

conclusions. As stated previously, the availability of calcium hydroxide and sulfate ions

in solution at very early ages is an important factor in determining the amount of C_3A

which reacts in the first few minutes. This amount of reacted C_3A and of sulfate uptake

during the first few minutes is very important to the overall reaction kinetics and may

affect the whole course of the reactions at later ages, because it determines how much

gypsum is remaining to keep the liquid phase saturated during the initial hydration of alite.

Jelenic, et. al. [10], studied the influence of gypsum content on the hydration and compressive strengths of two commercial portland cements having the same amount of alite, a similar amount of C_3A, but different amounts of readily soluble alkalis and sulfates. This work was intended to find out how much the effects observed on pure systems may be significant for the determination of the optimum gypsum content in the case of portland cements, especially in the presence of alkali sulfates which cause a higher concentration of SO_4^{2-} ions in the liquid phase of portland cement pastes. The effects observed on the strength of their samples were in accordance with those observed by Lerch [5], mainly for a clinker rich in alite and C_3A, and low in alkalis; the maximum strength shifts to the lower values of SO_3 as the hydration proceeds. On the other hand for a clinker high in alite and moderately high in C_3A but containing a considerable amount of readily soluble alkalis and sulfates, the shift of the maximum to the higher values of SO_3 was noticeable. They found that gypsum had a remarkable effect in accelerating alite hydration at all ages for the clinker rich in soluble alkalis and sulfates. For the clinker that is low in alkalis, the accelerating effect was noticed up to the age of 28 days but not at 90 days. They concluded that the difference in the optimum addition of SO_3 is influenced not only by the difference in C_3A content, but also by the difference in alkalis, as well as in the amount of the primary present water soluble sulfates. They also found that only a part of the SO_3 content (1.14%) is used in forming ettringite at the age of 1 day, and this is much lower than 2.58% which is the total SO_3 value determined by chemical analysis, and since the calcium aluminate monosulfate hydrate has not been detected at 2% of SO_3

added, they concluded that the rest of the total SO_3 amount (i.e. ~ 1.4%) has been

incorporated into the C-(S,Ŝ)-H. They also concluded that the amount of SO_3

incorporated in the C-(S,Ŝ)-H increases with the increase of total SO_3, thus giving a bad-

quality gel, and consequently lower compressive strengths. The two examined clinker

samples behaved differently with respect to ettringite formation and the authors

suggested that this was caused by the difference in the composition of the liquid phase,

i.e. by the presence of a higher amount of readily soluble alkalis and higher amount of

glassy phase in the clinker sample rich in alkalis. The authors also noticed differences in

the morphological characteristics of the ettringite formed by the two different clinker

samples. There were also indications that the nature of ettringite coatings on C_3A grains

has been influenced by the amount of the gypsum added; at higher SO_3/C_3A ratios the

retardation of C_3A hydration is more effective, most probably because a faster reaction

forms a much denser coating.

Jawed and Skalny [12], in their review about alkalis in cement, states that there is a

worldwide trend towards higher alkali content in cements. This is due to various factors

including changes in clinkers pyprocessing technology, call for energy conservation, the

limited availability of low-alkali raw materials, and tightened environmental restrictions,

and the use of coal as the primary fuel source. The authors stated that the presence of

sulfur leads to reduction of alkali volatility during clinker formation and that alkali

compounds in clinker can be divided into three main groups:

a)Alkali sulfates; b)Alkali aluminates and aluminoferrites; c)Alkali silicates. Also in

some cases, alkalis may occur in the form of carbonates. The authors added that the

clinker's SO_3 makes prior demand on the alkalis, the resulting quantity of alkali sulfate is

determined by the ratio of total clinker sulfate to total alkali. The remaining sulfate forms calcium sulfate. After allocating alkalis to sulfate, the remainder appears to be distributed between the silicates, aluminates, and aluminoferrites. The rules governing the quantitative division of alkalis between silicates, aluminates and ferrites are not yet clear but, it is known that aluminates and ferrites accommodate about half or more of the available alkalis. The introduction of alkalis into clinker minerals modifies their crystal structure which in turn, can change their hydraulic reactivity. Some researchers have shown that introduction of alkalis into C_3A modifies its normal cubic form to orthorhombic. This orthorhombic form of C_3A is formed with a minimum alkali content of 2.8% equivalent Na_2O or 1.8% equivalent K_2O [12]. The authors also pointed out the effect of SO_3 on clinker in the presence of alkalis. A positive effect of gypsum addition to alkali containing raw materials on the formation of clinker minerals has been reported by some researchers. The clinkering temperature decreased, the amount of C_3S increased and a positive effect on the binding of CaO was noticed. The presence of alkali sulfates resulted in well developed alite and belite crystals. Different alkali containing raw materials required different amounts of gypsum. It is claimed that the use of proper amount of gypsum resulted in higher kiln output and reduction of fuel consumption [12].

Some other research work showed that almost 17% of the total C_3A in cement reacts during the first 20 minutes of hydration while other results from another research work in which gypsum was substituted by hemihydrate (which has a high initial solubility) at the same total SO_3 level in cements showed that at the first 20 minutes of hydration a decrease in the amount of formed ettringite and of consumed gypsum happened. Also a small but significant increase in the time to the second C_3A heat peak happened. These

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results contradict the previous ones because they imply that the amount of C_3A consumed in the initial period is reduced by the increased sulfate availability resulting from using the hemihydrat [4].

Also previous research work has shown that C_3A hydration rates in cement pastes differ considerably from those observed in the $C_3A\text{-}CaSO_4\text{-}Ca(OH)_2$ system, mainly with respect to the time of occurrence of the second heat peak which is usually associated with depletion of gypsum [4]. In pure $C_3A\text{-}CaSO_4\text{-}Ca(OH)_2$ system, and at a $\hat{S}/A = 0.7$, the retardation of the second peak is expected to be about 50-70 hours at 20-25° C. Since most optimized Type I portland cements ($\hat{S}/C_3A = 0.7\text{-}1.5$) does not show any heat peak after 18 hrs, regardless of alkali content, this implies that sulfate uptake in cements is more rapid than what is expected in pure C_3A/C_4AF systems. One explanation is that it is most likely a result of its uptake by the CSH [4]. The importance of CSH in gypsum depletion is a subject worthy of further examination. It was found that CSH can contain as much as 20% SO_3 relative to SiO_2 in cement pastes after 1-day hydration at typical w/c ratios. Although these same pastes show a decreasing level of SO_3 substitution in CSH reducing to about 10% relative to SiO_2 at 28 days, the fact that there is typically twice CSH present at 28 days compared to 1 day, this shows that the same total amount of SO_3 is contained at both ages and the concentration is reduced by dilution [4]. Another interesting observation was that the concentration of Al_2O_3 and Fe_2O_3 in the CSH in the same pastes were increasing from 1 to 28 days. This implies that initially and while sulfate is still available to form ettringite, there is little initial dissolution of Al^{3+} or Fe^{3+} in CSH. Once all the sulfate has been consumed, and AFm phases begin to form in large amounts, Al^{3+} and Fe^{3+} become more soluble and can apparently diffuse into the

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CSH more readily. The results of a research work showed that the reaction of C_3A with sulfate-rich CSH, or the reaction of gypsum with Al^{3+}-rich CSH, tends to result in the formation of ettringite, in preference to monosulfoaluminate. Some researchers concluded from these results that CSH has a stronger tendency to dissolve Al^{3+} than it does to dissolve SO_4^{2-}. This implies that a mixture of monosulfoaluminate plus excess CSH will tend to disproportionate towards ettringite plus substituted CSH [4].

1.5.3 Effects of Temperature

The temperature during mixing and curing is expected to have a significant effect on the optimum level of gypsum. This is due to the rapid increase in C_3A hydration rate with increasing temperature. It is worthwhile to note that the time to the second heat peak at a molar $\hat{S}/C_3A$ ratio of 0.5 decreases from 60 hours at $15°$ C to 15 hours at $30°$ C, to 5 hours at $40°$ C, and to less than 1 hour at $70°$ C [4].

It was found that cements can accommodate more SO_3 at higher curing temperatures with no detrimental effects, possibly because ettringite becomes increasingly less stable with respect to monosulfoaluminate, and the formation of the latter phase is apparently not destructive to the matrix. Also, more Al_2O_3 and SO_3 may enter the CSH during high temperature curing [4].

CHAPTER 2.

EXPERIMENTAL PROCEDURE

2.1 Materials

The materials used in this study consisted of cements, gypsum, sand, distilled water, sodium sulfate, and fly ash.

2.1.1 Cements

Four types of cements were used in this study. They were randomly labeled as C, D2, E, and P cement.

2.1.1.1 Oxide Chemical Composition of the Cements

The cements were analyzed for their oxide chemical composition in an external laboratory. The laboratory report of chemical analysis stated that the samples were fused at 1000 $^{\circ}$ C with $Li_2B_4O_7$ and the oxide analysis was done by X-ray fluorescence spectrometry. This analysis meets the precision and accuracy requirements for rapid methods per ASTM C 114-00 "Test Methods for Chemical Analysis of Hydraulic Cement".

2.1.1.2 Bogue Calculations

Bogue formulas as stated in ASTM C 150-00 "Standard Specification for Portland Cement" were used to calculate the theoretical mineralogical composition of the cements.

2.1.2 Gypsum

The gypsum used in this study was Terra Alba No.1 gypsum as it meets the requirements specified in ASTM C 452-95 "Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate". The SO_3 content of the gypsum was determined by an external laboratory and was found to be 46.5%. This value was used in calculating the percentage of cement and gypsum required to provide a mixture containing 3.0 and 3.6 mass % SO_3 according to the formula given in ASTM C 452-95.

2.1.3 Sand

The sand used in this study was ASTM Graded Sand furnished by U.S. Silica Company. The sand conforms to ASTM Designation C 778-00 "Standard Specification for Standard Sand". The sand was delivered in bags of 50 lbs each and was oven dried before use.

2.1.4 Water

All the water used in mixing of mortar and in preparing of sodium sulfate solution for this study was pure distilled water conforming to Type IV of Specification D 1193.

2.1.5 Sodium Sulfate

All the sodium sulfate used in this study was a certified ACS sodium sulfate anhydrous obtained from Fisher Scientific.

2.1.6 Fly Ash

The fly ash used in this study was a Class F fly ash with a LOI of 4.8%. It was sieved and the amount used was reconstituted from the fly ash that was retaining on different sieves.

2.2 Strength and Durability Tests

In order to assess the effect of the SO_3 content of the cement on the durability and strength, mortar cubes and bars were prepared for the as-received cements as well as for the cements with an SO_3 content of 3.0% and 3.6%. The mortar cubes were tested for their compressive strength both in saturated lime solution and in sodium sulfate solution. The mortar bars were stored in sodium sulfate solution and their length was measured at certain ages in order to assess the expansion that was happening to the bars.

2.2.1 Mortar Cubes

Mortar cubes were prepared for each type of the four as-received cements. The cubes were mixed in accordance to ASTM C 305-99 "Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency". The mix proportions are listed in Table 1. All the mixes had 1 part cement to 2.75 parts of sand by mass. The water/cement ratio by mass was 0.485 .

Table 1. Mix Proportions for the Mortar Cubes Prepared from the As-Received Cements

	9 cubes mix
Cement , g	740
Sand , g	2035
Water , ml	359

The cubes were molded according to the ASTM C 109-99 "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. Cube Specimens)".

For each type of cement, 39 cubes were prepared for the first mix. Three cubes were tested immediately after de-molding at the age of 1 day and 18 of the remaining 36 cubes were stored in saturated lime solution while the other 18 were stored in sodium sulfate solution.

Three cubes from each set were tested at the ages of 3, 7, 28, 90, 180, and 360 days respectively. The cubes were tested according to the ASTM C 109-99 also and the testing machine was an MTS 809 Axial/Torsional Test System. The sodium sulfate solution was a 5 weight percent solution and was prepared according to the ASTM C 1012. The sodium sulfate solution was changed for the remaining cubes of each set after the testing was done at any age. Before placing the cubes in the new solution, the pH of the solution was measured with a pH meter to ensure that the pH was within the range of $6.0 - 8.0$ as per ASTM C 1012.

The same procedure was repeated for a second mix where another 39 cubes were prepared for each type of cement. The cubes were stored and tested exactly as the first mix and the average strength of the first and second mix at any age (i.e. the average strength of 6 cubes, 3 from each mix) was taken to represent the compressive strength at that age.

Mortar cubes were also prepared for the cements with an SO_3 content of 3.0% and 3.6%. As was the case for the as-received cements, the first mix for each type of cement with an SO_3 content of 3.0% consisted of 39 cubes. The SO_3 content of the cement was increased by replacing part of the cement with Terra Alba gypsum. The percentage of cement and gypsum required to provide the mixture for each type of cement was calculated according to the formula given in ASTM C 452-95. The mix proportions for

the cements with SO_3 content of 3.0% are listed in Table 2 while those for the SO_3

content of 3.6% are listed in Table 3.

Table 2. Mix Proportions for the Mortar Cubes Prepared from the Cements with

        3.0% SO_3 Content

	Cement C	Cement D2	Cement E	Cement P
Cement , g	736.78	732.26	732.92	737.96
Gypsum , g	3.22	7.74	7.08	2.04
Sand , g	2035	2035	2035	2035
Water , ml	359	359	359	359

Table 3. Mix Proportions for the Mortar Cubes Prepared from the Cements with

        3.6% SO_3 Content

	Cement C	Cement D2	Cement E	Cement P
Cement , g	726.62	722.16	722.81	727.79
Gypsum , g	13.38	17.8435	17.19	12.21
Sand , g	2035	2035	2035	2035
Water , ml	359	359	359	359

In both cases, the mortar was mixed according to the procedure for mixing mortars of

Practice C 305, with the exception that after placing the mixing water in the bowl, the

gypsum was added and mixed at the slow speed for 15 seconds, then the mixer was stopped and the cement was added and the mixing continued as prescribed in Practice C 305. This was done according to the procedure as per ASTM C 452-95.

Three cubes from each set of cement were tested at the age of 1 day and the remaining 36 cubes were stored half in saturated lime solution and the other half in sodium sulfate solution. As was the case for the as-received cements, the cubes were tested at the ages of 3, 7, 28, 90, 180, and 360 days. The sodium sulfate solution was also replaced every time testing was done.

On a different date, a second mix was prepared for each type of cement (i.e. 39 cubes per each type of cement with an SO_3 content of 3.0%). The second mix was also cured and tested under the same conditions as the first mix and the average value of the compressive strength for the two mixes was taken to represent the compressive strength at any age.

The same procedure that was done for the as-received cements and for the cements with an SO_3 content of 3.0% was repeated for the case of the 3.6% and again the average value of the compressive strength for the first and second mixes for each type of cement was taken to represent the compressive strength of the 3.6% SO_3 content mortar at any age.

In all the cases, the 5 weight percent sodium sulfate solution was changed at the ages of 3, 7, 28, 90, and 180 days for the remaining cubes of each set on the same day when testing was done. Again the pH of the solution was measured every time before placing the cubes to ensure that the pH is between 6.0 and 8.0 .

2.2.2 Mortar Bars

For each type of cement, mortar bars were prepared for the three cases of the as-received cement, 3.0% SO_3 content cement, and 3.6% SO_3 content cement. The bars were prepared according to ASTM C 1012-95a "Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution". The mix proportions for the mortar used to prepare the bars were the same as those used for preparing the cubes and are listed in Tables 1, 2, and 3. In all the cases the mortar bars were cured in saturated lime solution until they attained a compressive strength of 20.0 ± 1.0 MPa (3000 ± 150 psi), as measured using cubes made of the same mortar, before the bars were immersed in the sodium sulfate solution. The apparatus used for the determination of the length change was according to the ASTM C 490-00 "Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste, Mortar, and Concrete". The initial reading for the length of the bars was taken immediately before they were immersed in the sodium sulfate solution. A digital comparator manufactured by Humboldt Co. (model H 3250) was used for measuring the length change of the bars. After the initial reading, the bars were measured at 7, 14, 21, 28, 56, 91, 105, 120, 150, 180 days, and then every 15 days after that. The sodium sulfate solution was changed every time the bars were measured and the pH of the new solution was measured before immersing the bars to ensure that it is in the range of 6.0-8.0 .

All the sets of bars were repeated another time on different dates to verify the trend of the expansion found in the first sets. The second sets were prepared, cured, and measured in the same way and on the same ages as the first sets.

In addition to all the above sets of bars, an additional set of bars was prepared for each type of cement by replacing 20% of the cement by fly ash. The fly ash used was a Class F fly ash with LOI of 4.8%. The SO_3 content of the remaining 80% of the cement was increased to 3.6% by replacing part of the cement by Terra Alba gypsum. The mix proportions for the fly ash bars are listed in Table 4.

Table 4. Mix Proportions for the Mortar Bars Prepared from the Cements With 20% Fly Ash Replacement and 3.6 % SO3 Content of the Remaining Cement

	Cement C	Cement D2	Cement E	Cement P
Cement, g	581.30	577.73	578.25	582.23
Gypsum, g	10.70	14.27	13.75	9.77
Fly Ash, g	148	148	148	148
Sand, g	2035	2035	2035	2035
Water, ml	359	359	359	359

The fly ash was sieved before use and the 148 grams required for each mix were reconstituted from the fly ash retained on different sieves according to Table 5.

Table 5. Proportions of Class F Fly Ash, LOI 4.8%, for 20% Replacement of

Cement

Sieve No.	Weight (grams)
40	0.91
50	1.12
70	1.60
100	3.31
200	26.61
325	107.84
Pan	6.61
Total	148.00

After weighing the fly ash, it was added to the dry cement and mixed together in a

glass beaker with a spatula for several minutes until a homogeneous mixture was

obtained. After placing the water in the mixing bowl, the gypsum was added and mixed

with the water at the slow speed for 15 seconds. Then the mixer was stopped and the

cement-fly ash mixture was added and the mixing continued as prescribed in Practice C

305. As was the case with the other sets of bars, the fly ash bars were also prepared

according to the ASTM C 1012-95a, and after de-molding, the bars were cured in a

saturated lime solution until they attained a strength of 20 ± 1.0 MPa (3000 ± 150 psi), as

measured using cubes made of the same mortar, before the bars were immersed in the

sodium sulfate solution. The Fly Ash bars were measured at the same ages as the other bars, and the solution was changed every time a set of bars was measured.

2.3 X-Ray Powder Diffraction Analysis of Mortar Cubes and Bars

X-Ray powder diffraction analysis was done for the mortar cubes that were tested at the age of 360 days. Pieces of the crushed cube, after testing, were ground in a mortar for several minutes and then sieved using sieve number 325. The amount passing the sieve was collected in a vial and 0.45 grams of it were weighed and placed in another vial. An amount of 0.05 grams of TiO_2 were weighed and added to the vial containing the 0.45 g sample. The sample was mixed inside the vial with a spatula for approximately 5 minutes until a homogeneous mixture was achieved. The sample was then placed in a diffractometer. The diffractometer used for analyzing the sample was a Phillips X'Pert PW3040 Pro diffractometer.

In a similar manner, XRD analysis was also done for the mortar bars at the age of 480 days. For each type of bars, a piece of approximately two inches was taken out from the middle of the bar. The bars were broken using a hammer and a screwdriver. The outside perimeter of the 2 inch piece was sawed off at a thickness of 2-3 mm, and the sawed pieces were soaked in acetone for an hour, then ground in a mortar and the same procedure as described above was done for sieving, mixing with TiO_2 and placing in the diffractometer.

CHAPTER 3.

RESULTS AND DISCUSSION

3.1 Characteristics of the As-Received Cements

3.1.1. Cements Fineness

As was stated earlier in Chapter 1, the limit on the SO_3 content of cement in various

national standards ranges from 2.5 to 5.0% depending on cement fineness or composition

or both. Since increasing the cement fineness will lead to a higher rate of hydration due to

an increase in the surface area of the cement that would be in contact with water, the

cement fineness plays an important role in determining the quantity of gypsum required

to obtain proper retardation and the proper optimum SO_3 content. Based on this

consideration, it was decided to eliminate cement fineness as a variable in this work. All

of the four types of cements used in this study, have very similar fineness, but vary in

their C_3S, C_3A, and alkali contents.

Table 6 lists the Blaine Fineness values of the as-received cements.

Table 6. Blaine Fineness

Cement	C	D2	E	P
Blaine Fineness (cm^2/g)	3840	3880	3800	3820

The values range between 3800 – 3880 cm^2/g with cement E having the lowest value and cement D2 having the highest although the difference is not significant. Based on this, the four types of cements are expected to have similar reactivity.

3.1.2 Oxide Chemical Composition

Table 7 lists the oxide chemical composition of the as-received cements as determined by X-ray fluorescence spectroscopy.

Table 7. Oxide Chemical Composition of the As-Received Cements

	Cement Type			
	C	D2	E	P
Analyte	Weight %	Weight %	Weight %	Weight %
SiO_2	20.52	20.55	21.15	20.78
Al_2O_3	4.92	4.4	4.78	5.47
Fe_2O_3	3.7	3.61	3.76	4.15
CaO	64.31	64.6	64.41	63.14
MgO	1.71	2.47	0.95	0.85
SO_3	2.81	2.54	2.58	2.88
Na_2O	0.01	0.03	0.18	0.26
K_2O	0.41	0.54	0.34	0.6
TiO_2	0.27	0.22	0.33	0.32
P_2O_5	0.03	0.05	0.07	0.18
Mn_2O_3	0.04	0.05	0.03	0.03
SrO	0.04	0.02	0.12	0.05
Cr_2O_3	< 0.01	0.02	< 0.01	0.02
ZnO	< 0.01	0.03	0.02	0.02
L.O.I. (950° C)	1.08	0.99	1.15	1.3
Total	99.83	100.12	99.84	100.04
Alkalies as Na_2O	0.27	0.39	0.4	0.65
Free CaO	0.92	2.31	1.05	0.44

P cement has the highest SO_3 content followed by C cement, while cements E and D2 have lower SO_3 content. P cement also has the highest Na_2O and K_2O content and consequently the highest Na_2O equivalent. Cement C has the lowest Na_2O content and Na_2O equivalent. Cements E and D2 have similar Na_2O equivalent values although E has much higher Na_2O content while D2 has a higher K_2O content. Among the four cements, only the equivalent alkali content of cement P marginally exceeds the limit established by the ASTM C 150. Cement D2 has the highest MgO content followed by cement C although the values are well below the limit established in the ASTM C 150 (6%). Cement D2 also has the highest level of free CaO.

3.2. Compound Composition

3.2.1. Mineralogical Composition According to Bogue Calculations

Table 8 lists the mineralogical composition of all the cements according to Bogue calculations.

Table 8. Mineralogical Composition According to Bogue Calculations

Compound	Cement Type			
	C	D2	E	P
C_3S	60	65	57	48
C_2S	14	10	18	23
C_3A	7	6	6	7
C_4AF	11	11	11	13
C_3S/C_2S	4.3	6.5	3.2	2.1

The C_3S content of the cements varies between 48% for cement P and 65% for cement D2. Cements P and C have a C_3A content of 7% while cements D2 and E has a slightly

lower value (6%). Cements C, D2, and E have a C_4AF content of 11% while cement P

has a slightly higher value of 13%. It is worth noting that as the C_3S content of the

cements increases, so does the C_3S/C_2S ratio. Cement D2 has the highest C_3S/C_2S ratio

(6.5) while cement P has the lowest ratio of 2.1 .

According to the Bogue calculations for the compound composition, the four types of

cements can be considered as ASTM Type I portland cements.

3.2.2. Mineralogical Composition According to Internal Standard Method and Rietveld Refinement Method

In order to determine a more accurate mineralogical composition of the four cements

used in this study, both the Internal Standard Method and the Rietveld Refinement

Method were used.

Table 9 shows the amounts of C_3S, C_3A, C_4AF, and MgO in the as-received cements

based on the Internal Standard Method [21].

Table 9. Mineralogical Composition Based on the Internal Standard Method

	Cement Type			
Compound	C	D2	E	P
C_3S	70	63	58	55
Cubic C_3A	3	3	4	6
C_4AF	14	11	10	15
MgO	1	2	0	0

The results for the C_3S content of the cements according to the internal standard method differed from those according to Bogue calculations. Although cement P still has the lowest C_3S content, the new value is 55% compared to 48% according to Bogue calculations. The new value for cement E is very close to the previous one, but for cements D2 and C, the internal standard method showed that cement C has the highest C_3S content of 70% (60% according to Bogue) followed by cement D2 63% (65% according to Bogue).

For the C_3A content, only cement P had a value close to that determined through Bogue calculations, while all the other three cements had a much lower C_3A content than that determined by Bogue calculations. The internal standard method showed that cement P has the highest C_3A content, followed by cement E, while cements C and D2 have the lowest C_3A content.

The C_4AF content of the cements according to the internal standard method is similar to that according to Bogue calculations. Cements P and C had a higher value and both were higher than those for D2 and E cements.

Table 10 shows the results obtained by the Rietveld Refinement Method [21]. The results of the Rietveld refinement method are similar to those of the internal standard method. Cement P has the lowest C_3S content and the highest C_3A content. Cement C has the highest C_3S content and the lowest C_3A content.

It is worth noting that the Rietveld refinement method showed that cement E has the highest total calcium sulfates (3.6%) followed by cement C (2.8%). Gypsum was not found in cements C and D2, while insoluble anhydrite was only found in cement C (1.3%). Since the solubility of this form of anhydrite is extremely low, it is expected that

it will not participate in the hydration process and thus the actual total $CaSO_4$ content for cement C can be considered to be 1.5%.

This is similar to the values obtained for cements D2 and P. Although cements C and D2 have no gypsum, calcium sulfate is present in them in the form of Bassanite which is more soluble than gypsum.

Table 10. Rietveld Refinement Results for the As-Received Cements

	Cement Type			
Compound	C	D2	E	P
C_3S	67	61	54	53
β-C_2S	15	19	25	23
Cubic C_3A	2	3	4	8
C_4AF	14	12	13	11
Gypsum ($Ca_2SO_4.2H_2O$)	--	--	2.0	1.1
Bassanite ($Ca_2SO_4. 0.5 H_2O$)	1.5	1.6	1.6	0.7
Insoluble Anhydrite (Ca_2SO_4)	1.3	--	--	--
Magnesite ($MgCO_3$)	--	--	--	1.8
Periclase (MgO)	0.6	1.8	--	--
Dolomite ($CaMg(CO_3)_2$)	--	--	--	0.8
Portlandite ($Ca(OH)_2$)	--	1.2	--	--
C_3S/C_2S	4.5	3.2	2.2	2.3
Total Ca_2SO_4	2.8	1.6	3.6	1.8

3.3 Strength and Durability

The effect of the SO_3 content of the cements on their strength and durability was determined in this study by measuring the compressive strength of mortar cubes prepared for the As-Received cements as well as for the cements with an SO_3 content of 3.0% and 3.6%, and also by measuring the length change of mortar bars prepared for the same mixes and stored in sodium sulfate solution.

3.3.1 Compressive Strength of Mortar Cubes

Sets of cubes for all the mixes and for the four types of cements were prepared and stored in both saturated lime solution and sodium sulfate solution. The cubes were tested for their compressive strength at several ages. Figure 1 shows the compressive strength verses the SO_3 content for C cement cubes stored in saturated lime solution while Figure 2 shows the same relationship but for the cubes stored in sodium sulfate solution. In saturated lime solution C-3.0 cubes had the highest compressive strength for all the ages up to 28 days, although the C-3.6 had a very close strength at the age of 7 days. In sodium sulfate solution, the C-3.0 had the highest strength only at the age of 3 days, while the C-3.6 had the highest strength at 7 days and the as-received at 28 days, although the differences between the strengths for the as-received and 3.0 and 3.6 at the same age were not that significant.

Figures 3 and 4 shows the compressive strength verses age for the as-received C cement as well as the cement with SO_3 content of 3.0% and 3.6% in both lime and sodium sulfate solutions. The strength of C cement in lime was not affected by increasing the SO_3 content with the 3.0 having a slightly higher strength.
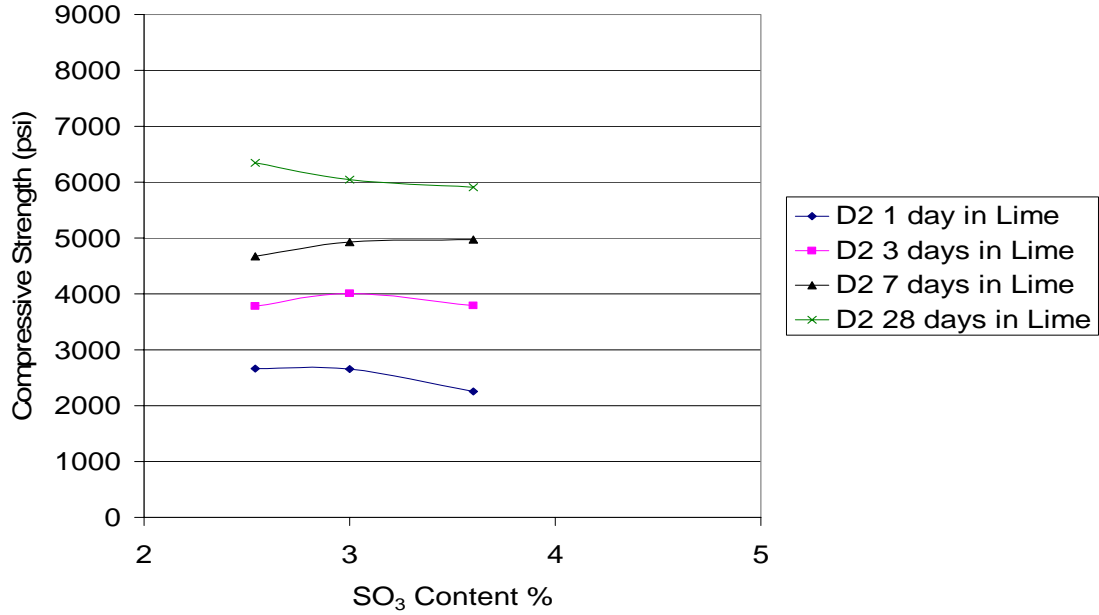
56
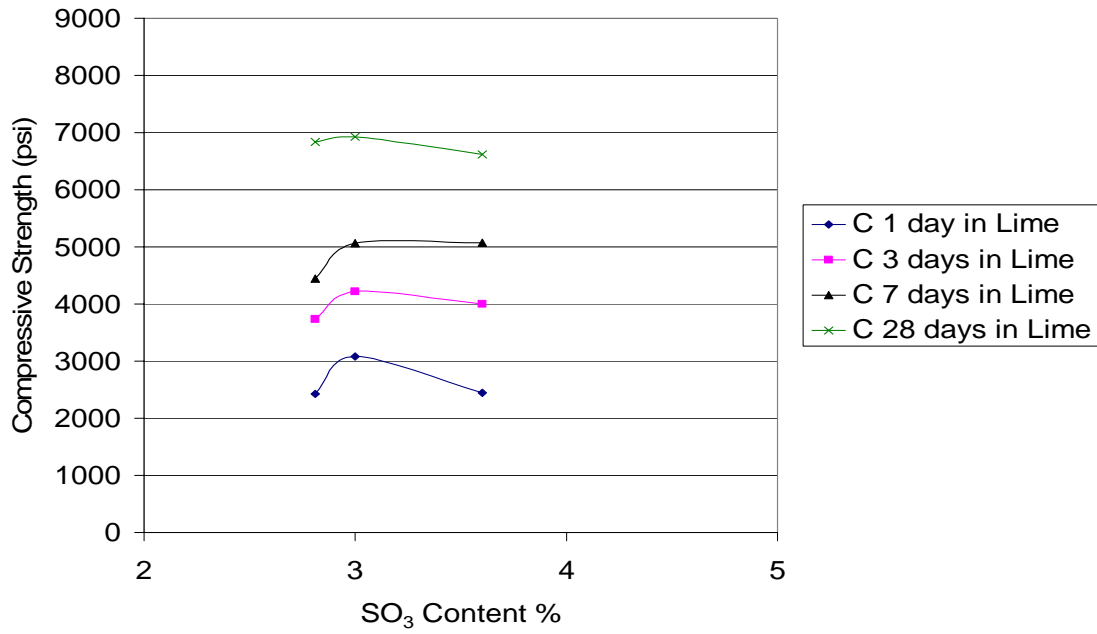
Figure 1. Compressive Strength verses SO$_3$ Content for C Cement in Lime
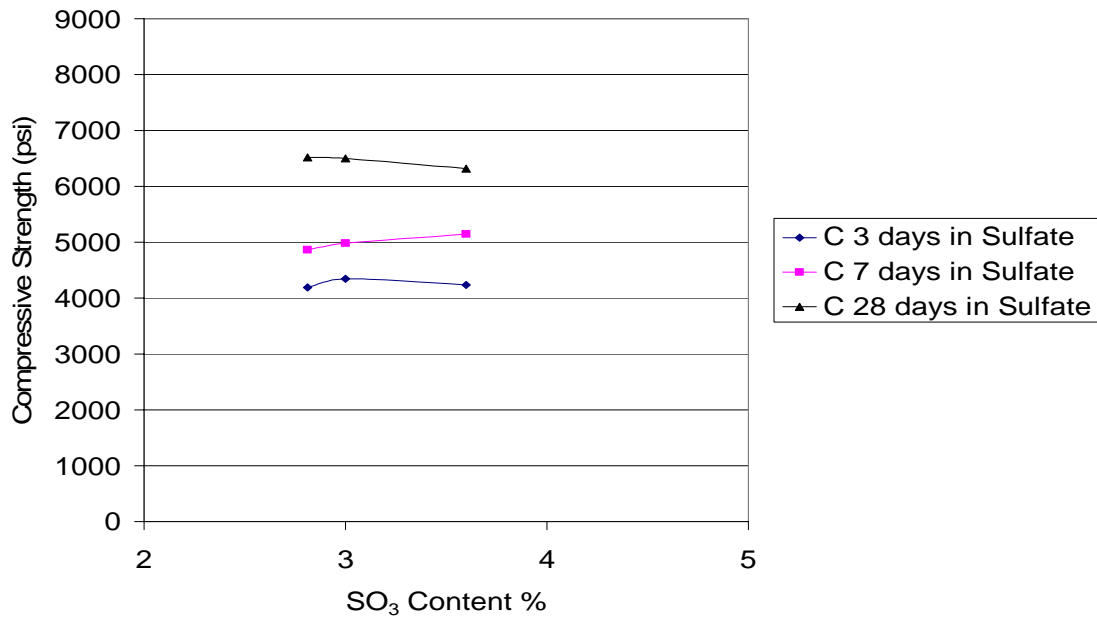
Figure 2. Compressive Strength verses SO$_3$ Content for C Cement in Sulfate
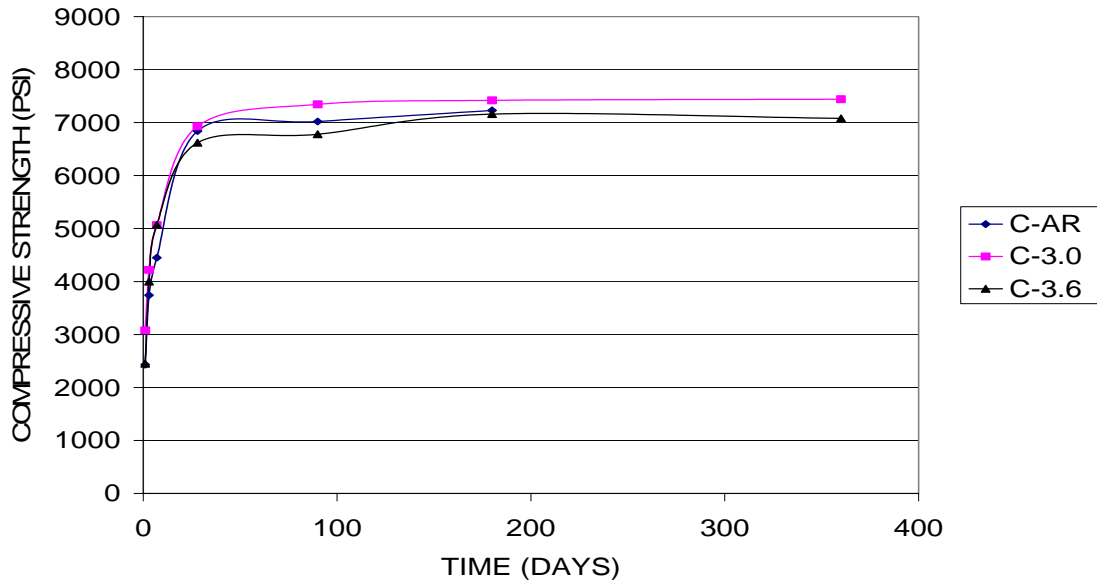
Figure 3. Compressive Strength verses Age for C, C-3.0, and C-3.6 in Lime
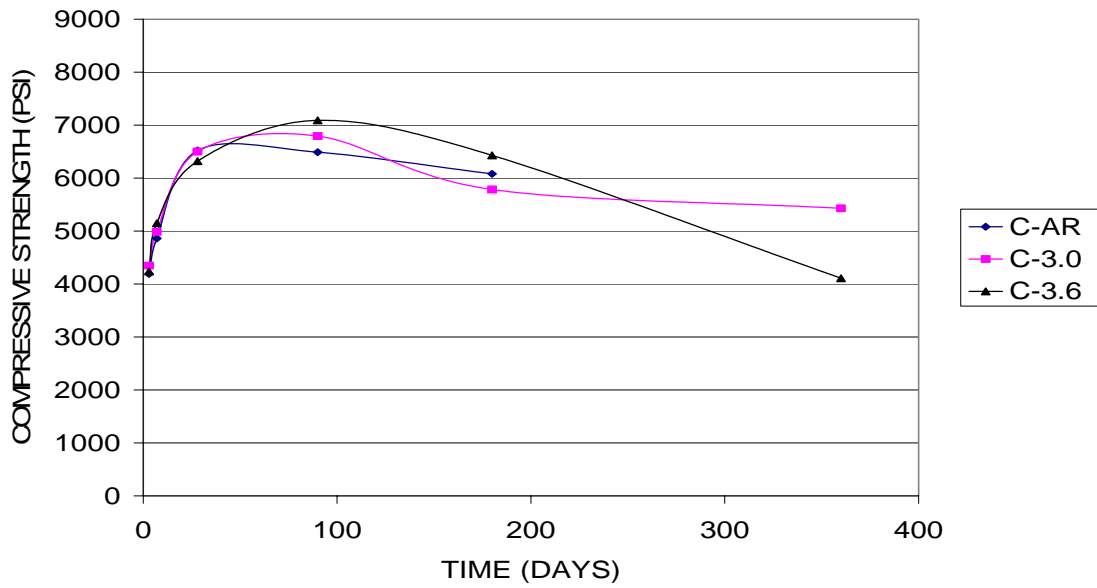
Figure 4. Compressive Strength verses Age for C, C-3.0, and C-3.6 in Sulfate

In all the three cases for C cement, the strength keeps on increasing up to the age of 180 days with the value of the increase in the strength between the ages of 180 days and 28 days being 390 psi for the as-received, 490 psi for the 3.0 and 540 psi for the 3.6. Only a slight increase in strength happens after the age of 28 days and this can be explained by the fact that C cement has a very high C_3S content, which is responsible for the high early strength, and a low C_2S content, which governs later-age strength development. In sodium sulfate solution, and for all the three cases, the strength increases only up to the age of 90 days and then starts dropping. The value of this drop between the ages of 180 days and 28 days was 440 psi for the as-received and 720 psi for the C-3.0. For the C-3.6 and although a drop happened after 90 days, the strength at 180 days was slightly more than that at 28 days by 110 psi. The strength of the C as-received in lime at the age of 180 days was higher than that in sulfate at the same age by 1150 psi while the same difference for the case of the C-3.0 was 1640 psi and for the C-3.6 was 730 psi. A big drop in strength of 2320 psi happened to the C-3.6 cubes in sodium sulfate exposure between the ages of 180 days and 360 days while the drop that happened for the C-3.0 between the same two ages was 360 psi only. Thus a big difference in the strength was observed between the CS-3.0 and CS-3.6 at 180 and 360 days in sulfate. Also the difference in the strength between the C-3.0 in lime and sulfate at the age of 360 days was 2010 psi while the same difference for the C-3.6 was 2970 psi. Thus it is clear that increasing the SO_3 content of C cement has a very detrimental effect on the strength in sodium sulfate exposure but this effect only becomes obvious at late ages. It is worth noting that C cement has the highest C_3S content according to both the Internal Standard Method and the Rietveld Refinement Method, and also has the lowest alkali content.

The compressive strength verses the SO_3 content for cement D2 in both lime and sodium sulfate solutions are shown in figures 5 and 6.

Figure 5. Compressive Strength verses SO_3 Content for Cement D2 in Lime
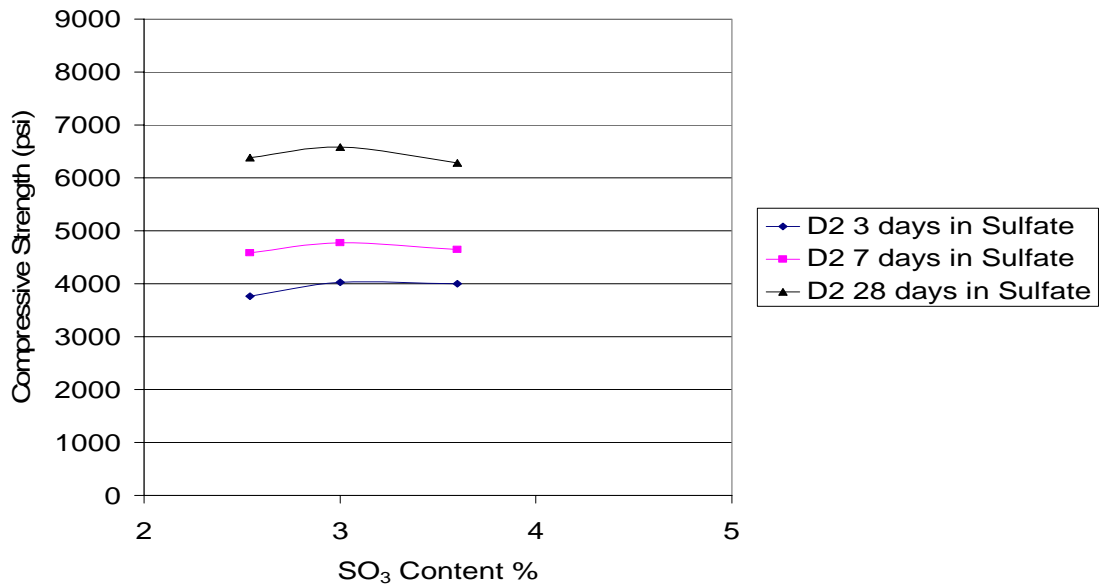
Figure 6. Compressive Strength verses SO_3 Content for Cement D2 in Sulfate

In the saturated lime solution, the As-Received D2 had the highest strength at 1 day and at 28 days while the D2-3.0 had the highest strength at 3 days. The D2-3.6 had the highest strength at 7 days. In the sodium sulfate solution, the D2-3.0 had the highest strength at the ages of 3, 7, and 28 days. Figures 7 and 8 shows the compressive strength verses age for the D2 As-Received, D2-3.0, and D2-3.6 in both lime and sulfate solutions. In lime solution and for the three cases, the strength keeps on increasing up to the age of 180 days. The value of the increase in strength for the as-received case between the ages of 180 days and 28 days was 650 psi while the increase for the D2-3.0 between the same ages was 1350 psi and for the D2-3.6 880 psi. In the sodium sulfate solution, and as it was the case of the C cement, for all the three cases of the D2 cement the strength keeps on increasing up to the age of 90 days and then starts dropping.
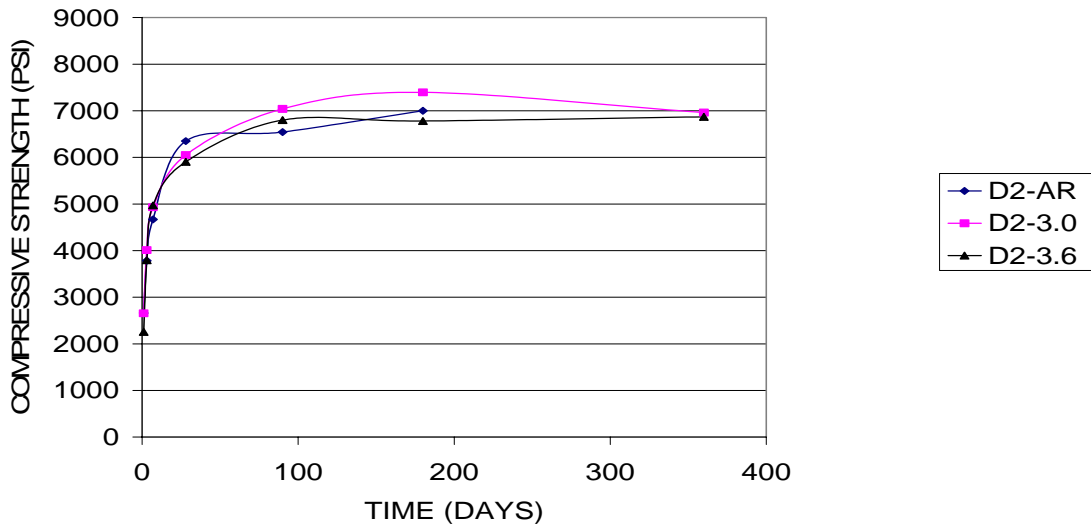
Figure 7. Compressive Strength verses Age for Cement D2, D2-3.0, and D2-3.6 in

    Lime
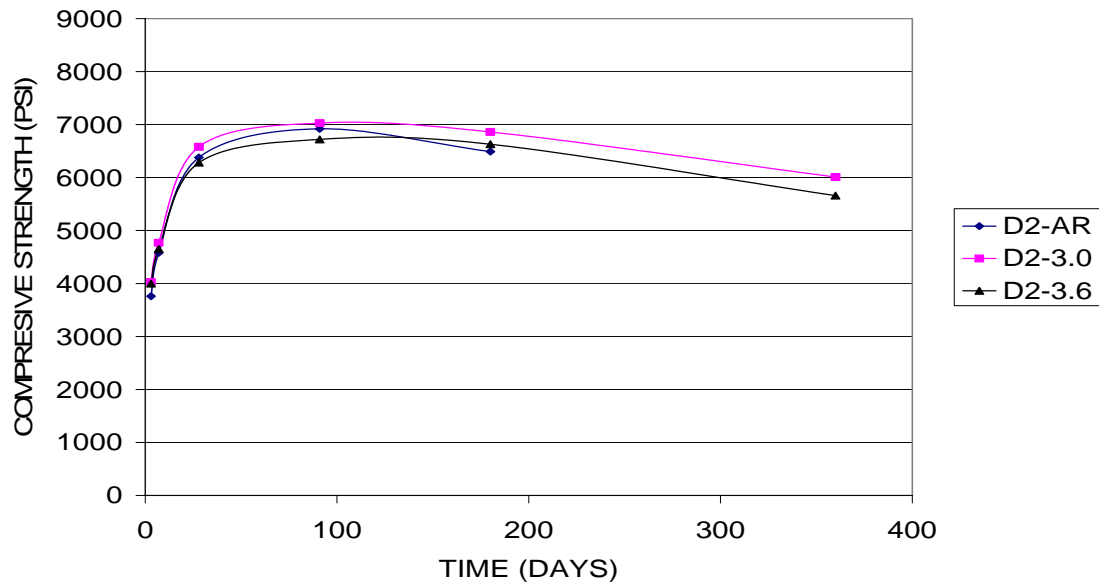
Figure 8. Compressive Strength verses Age for Cement D2, D2-3.0, and D2-3.6 in Sulfate

Despite this drop, the value of the strength of the as-received was higher at 180 days than that at 28 days by 110 psi and for the case of the D2-3.0 was higher by 280 psi while for the D2-3.6, it was higher by 350 psi. At the age of 180 days, the difference in the strength between the lime and sulfate conditions was 510 psi while that for the D2-3.0 was 540 psi and for the D2-3.6 was 150 psi only. On the other hand, the D2-3.6 in sulfate that had the lowest difference in the strength between the lime and sulfate exposures at the age of 180 days, had a large drop of 970 psi at the age of 360 days with the D2-3.0 having a higher strength. D2 cement has the second highest C_3S content (61% according to the Rietveld Refinement Method) and the second highest K_2O content (0.54%), but has the lowest SO_3 content (2.54%). The D2 cement handled the increase in its SO_3 content in a better way than the C Cement, but again the detrimental effect was only obvious at late ages.

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The relationship between the compressive strength and the SO_3 content for cement E in lime and sodium sulfate solutions is shown in Figures 9 and 10. In the lime solution, the E As-Received had the highest strength at all the ages of 1, 3, 7, and 28 days. In the sodium sulfate solution, the E As-Received only had the highest strength at the ages of 3 and 7 days, while the E-3.0 had the highest strength at 28 days. In the saturated lime solution the strength of the three cases of E cement also keeps on increasing up to the age of 180 days as was the case with the C and D2 cements. The increase in the strength between the ages of 180 days and 28 days was higher in both the cases of E-3.0 and E-3.6 than it was for the as-received case. The value of the increase was 1950 psi for E-3.0 and 1220 psi for the E-3.6 while it was only 900 psi for the as-received cement. In the sodium sulfate exposure and unlike both the C and D2 cements the E cement, and for its three cases, kept on increasing in its strength up to 180 days without any drop at 90 days. This is shown in figures 11 and 12 which show the relationship between the compressive strength and age for the E cement As-Received, E-3.0, and E-3.6 cubes cured in both saturated lime and sodium sulfate solutions. The increase in the strength between the ages of 180 days and 28 days for the E as-received in sulfate was 1610 psi while that for the E-3.0 was 1680 psi and for the E-3.6 was 1250 psi only. At the age of 180 days, the difference in the strength between the lime and sodium sulfate exposures was only 70 psi for the E-3.0 and 660 psi for the E-3.6. On the other hand, for the as-received case, the strength in sulfate exposure was slightly higher by 80 psi than that in lime exposure. At the age of 180 days, the strength of the E-3.6 in sulfate was much lower than the E-3.0.

After that age, both the E-3.0 and E-3.6 in sulfate had a drop in strength, and although the drop for the E-3.0 was greater than that that of the E-3.6, it still had the higher strength.
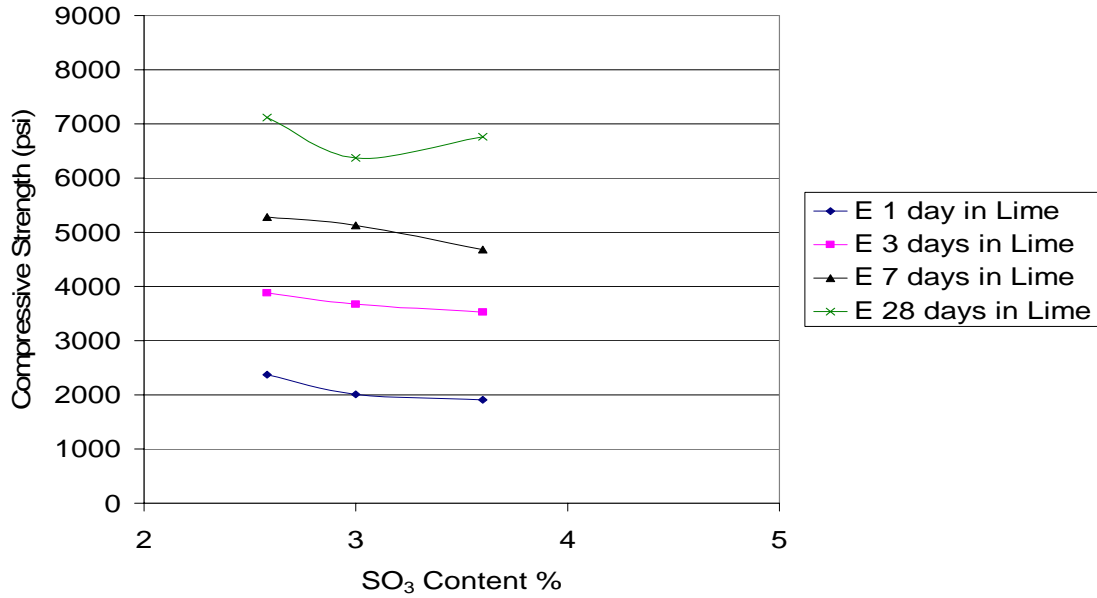
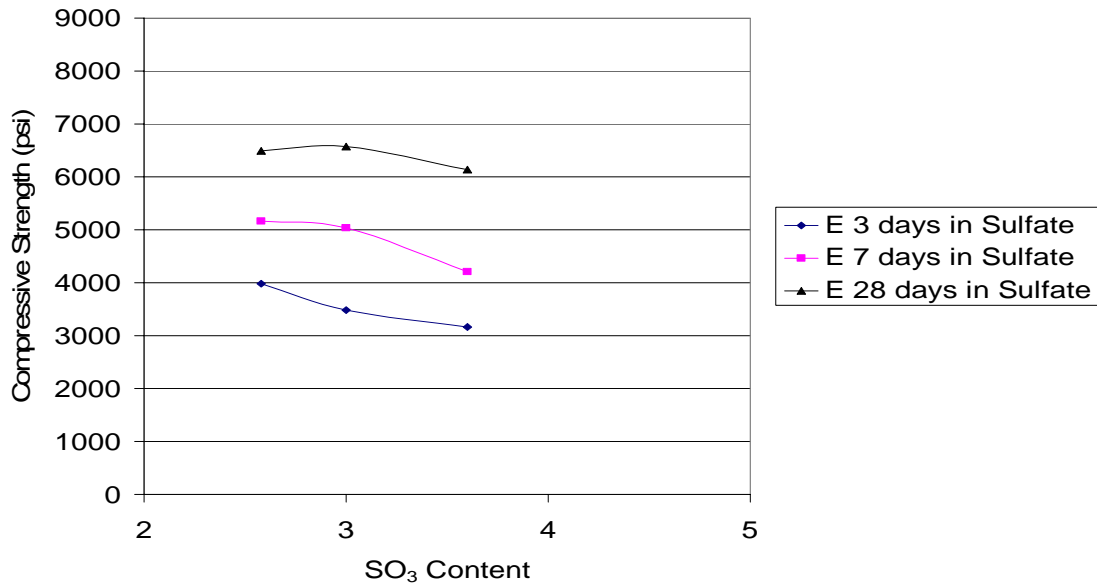**Figure 9. Compressive Strength verses SO₃ Content for Cement E in Lime**

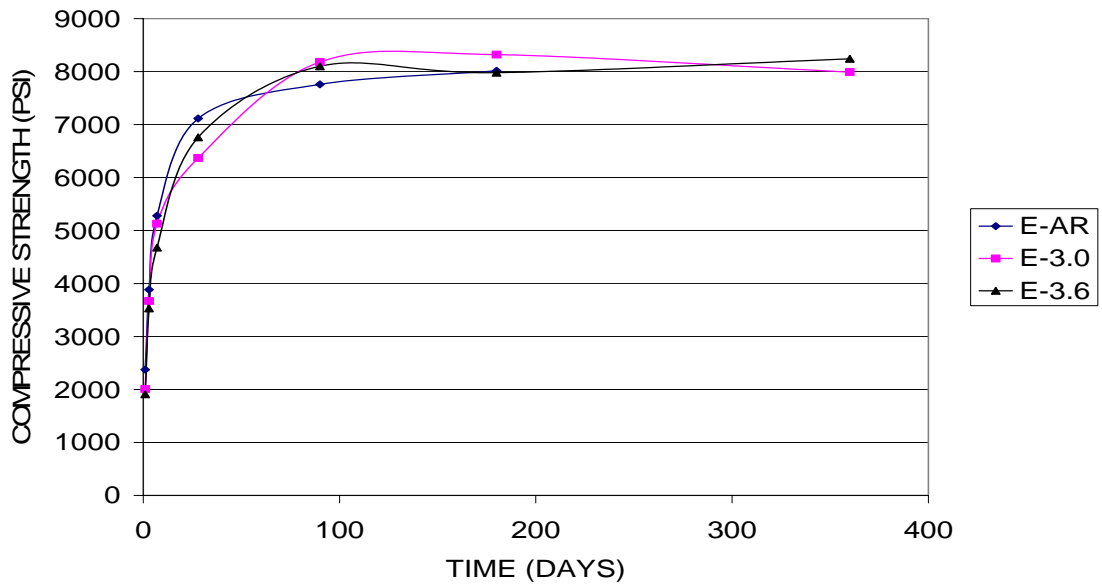**Figure 10. Compressive Strength verses SO₃ Content for Cement E in Sulfate**

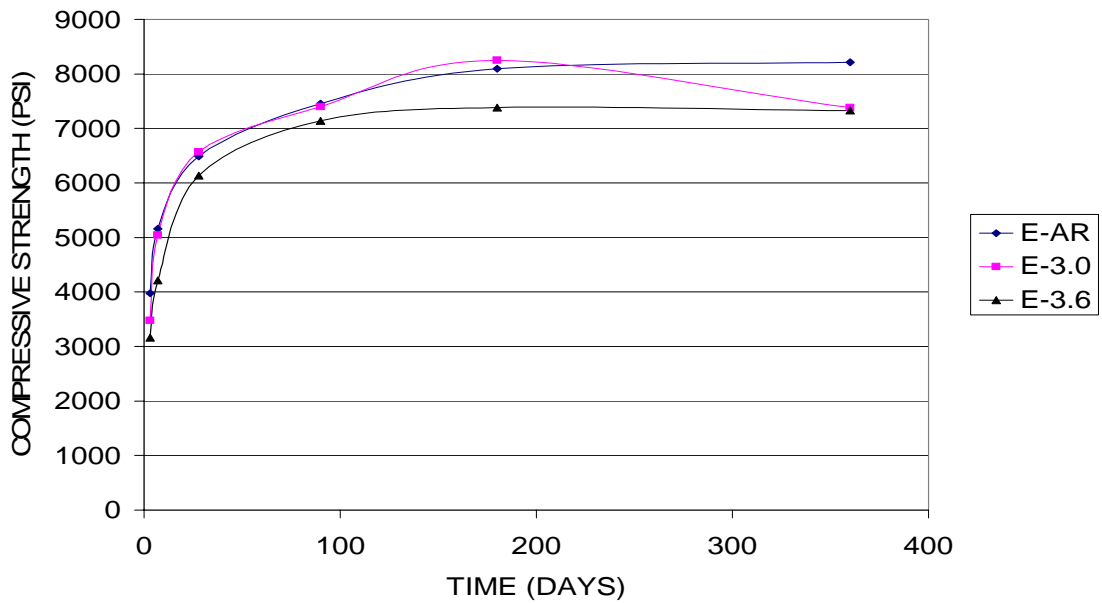**Figure 11. Compressive Strength verses Age for Cement E, E-3.0, and E-3.6 in Lime**

Figure 12. Compressive Strength verses Age for Cement E, E-3.0, and E-3.6 in

Sulfate

It is worth noting that cement E has the second lowest C_3S content and the highest C_2S content (according to the Rietveld Refinement Method). This explains its low early strength and high late strength. Cement E also has the second highest Na_2O content and accordingly the second highest Na_2O equivalent.

The relationship between the compressive strength and the SO_3 content for cement P is illustrated in Figures 13 and 14. In the saturated lime solution, the P-3.0 had the highest strength from the age of 1 day up to the age of 28 days. The P As-Received and P-3.6 had very similar strengths during that period with the 3.6 having a slightly higher strength. In the sodium sulfate solution, the P-3.0 also had the highest strength up to the age of 28 days. Figures 15 and 16 illustrate the relationship between the compressive strength and age for cement P, P-3.0, and P-3.6 cured in both lime and sodium sulfate solution. Again in lime solution, the strengths of both the P cement and P-3.6 keep on increasing up to the age of 180 days, while the P-3.0 had a slight drop in strength after 90 days. The increase in the strength between the ages of 180 days and 28 days in lime was 1060 psi for the as-received, and was 810 psi for the P-3.6 case. For the P-3.0 the value of the strength at 180 days was equivalent to that at 28 days. The increase in the strength of the P-3.6 in lime between the ages of 180 days and 360 days was also greater than that of the P-3.0 but the final strength of the P-3.0 was slightly higher than that of the P-3.6. In the sodium sulfate solution the strengths of the P as-received and P-3.0 keep on increasing up to the age of 90 days and then begins to drop, while that of the P-3.6 keeps on increasing up to the age
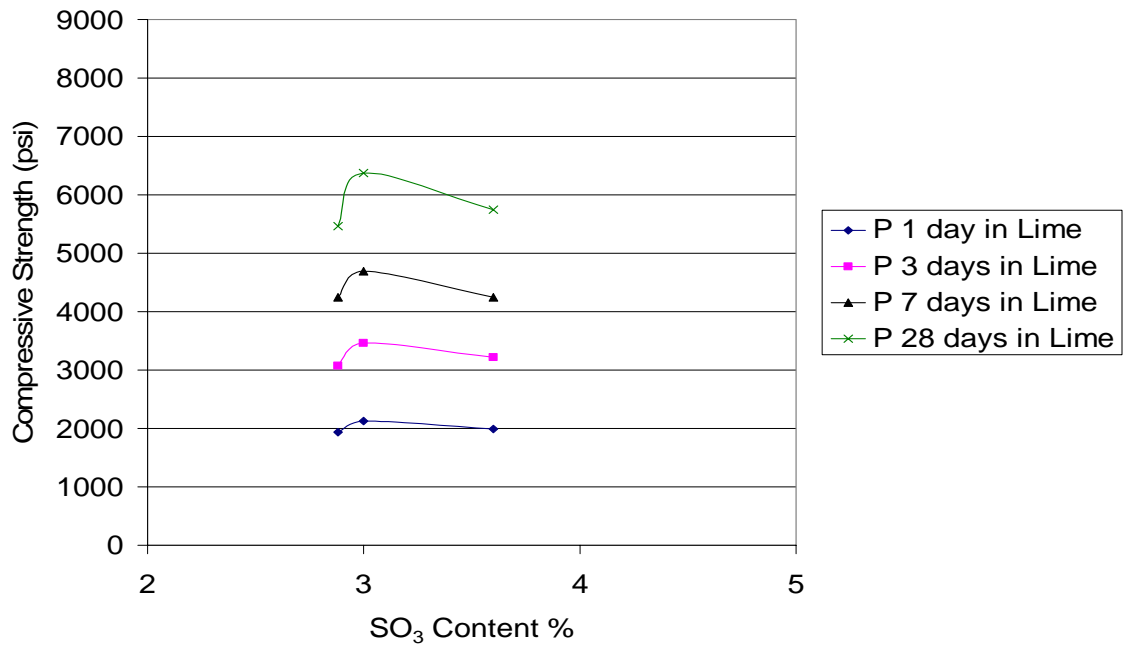
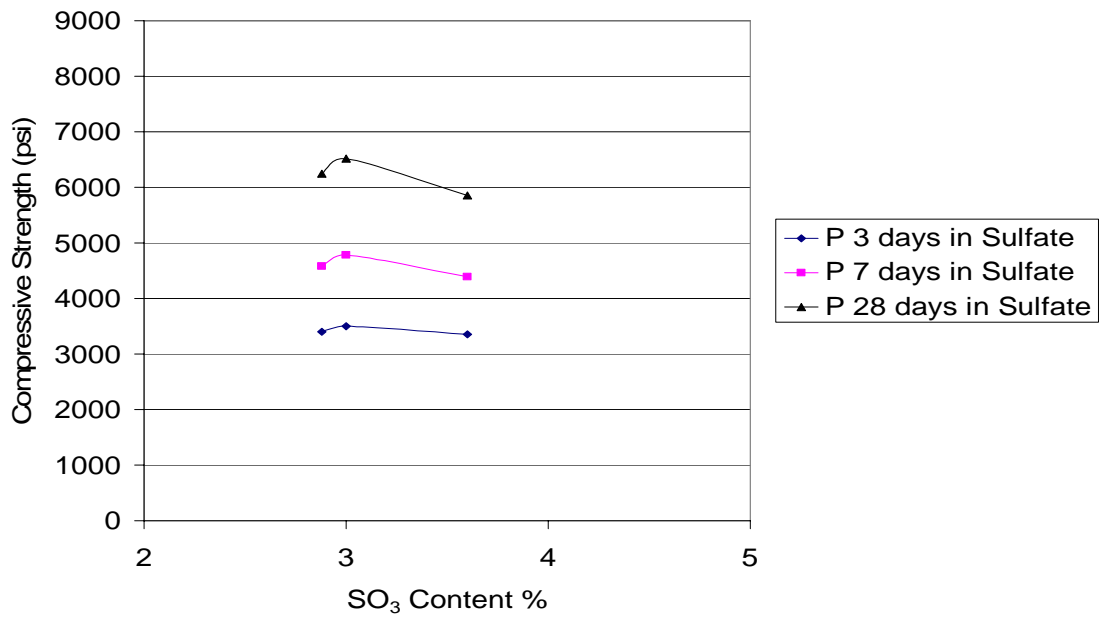**Figure 13. Compressive Strength verses SO₃ Content for Cement P in Lime**

Figure 14. Compressive Strength verses SO₃ Content for Cement P in Sulfate

of 180 days without any drop. The strength of the P as-received in sulfate at 180 days was less than that at 28 days by 280 psi and for the P-3.0 was less by 570 psi. On the other hand an increase in strength of 670 psi happened for the P-3.6 in sulfate between the same ages.

Also the difference in the strength at 180 days between the lime and sodium sulfate exposures were much less for both the P-3.0 and P-3.6 than it was for the P as-received. The difference for the P as-received was 550 psi while the difference for the P-3.0 was 420 psi and for the P-3.6 was only 40 psi. Also the difference in the strength between lime and sulfate at 360 days was approximately similar at 1000 psi for both the P-3.0 (1240 psi) and P-3.6 (1030 psi).

P cement has the lowest C_3S content and the second highest C_2S content. This explains the low early strength of 1 and 3 days and the large increase in strength that happened after 28 days. On the other hand, P cement has the highest Na_2O, the highest K_2O, and consequently the highest Na_2O equivalent. This could explain the continuous increase in the strength of the P-3.6 without any drop up to the age of 180 days where it got a much higher strength than both the as-received and the P-3.0 in sulfate.
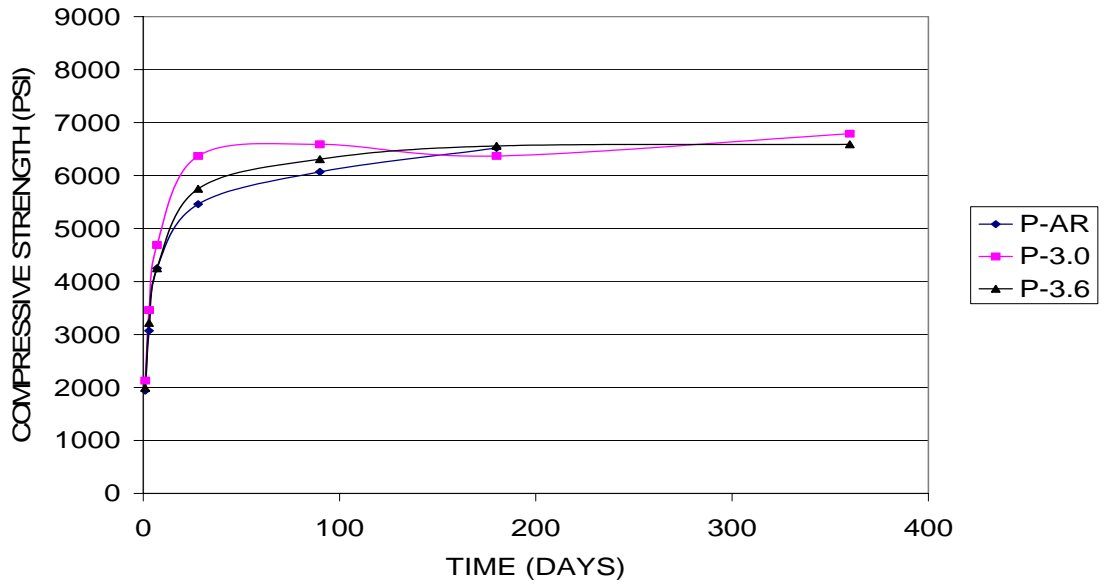
Figure 15. Compressive Strength verses Age for Cement P, P-3.0, and P-3.6 in Lime
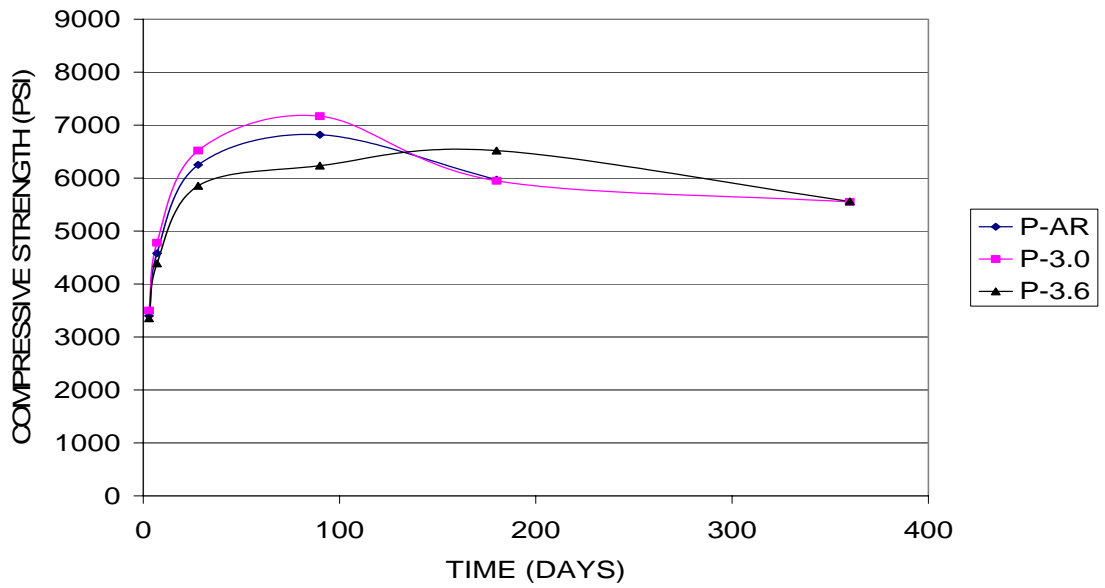

Figure 16. Compressive Strength verses Age for Cement P, P-3.0, and P-3.6 in

Sulfate

Figure 17 illustrates the relationship between the compressive strength of the as-received cements cured in saturated lime solution verses age, while figures 18 and 19 shows the same relationship for the cements with an SO_3 content of 3.0 and 3.6% respectively. In all the three cases, E cement had the highest strength with the E-3.0 having a slightly higher value. C cement got the second highest with the C-3.0 having a slightly higher strength, followed by cement D2 with the D2-3.0 also having a slightly higher value. P cement had the lowest strength with the P-3.6 having a slightly higher value. It was found that a big difference in the compressive strength of the cubes in lime exists between cements E and P although they have very similar C_3S and C_2S contents.
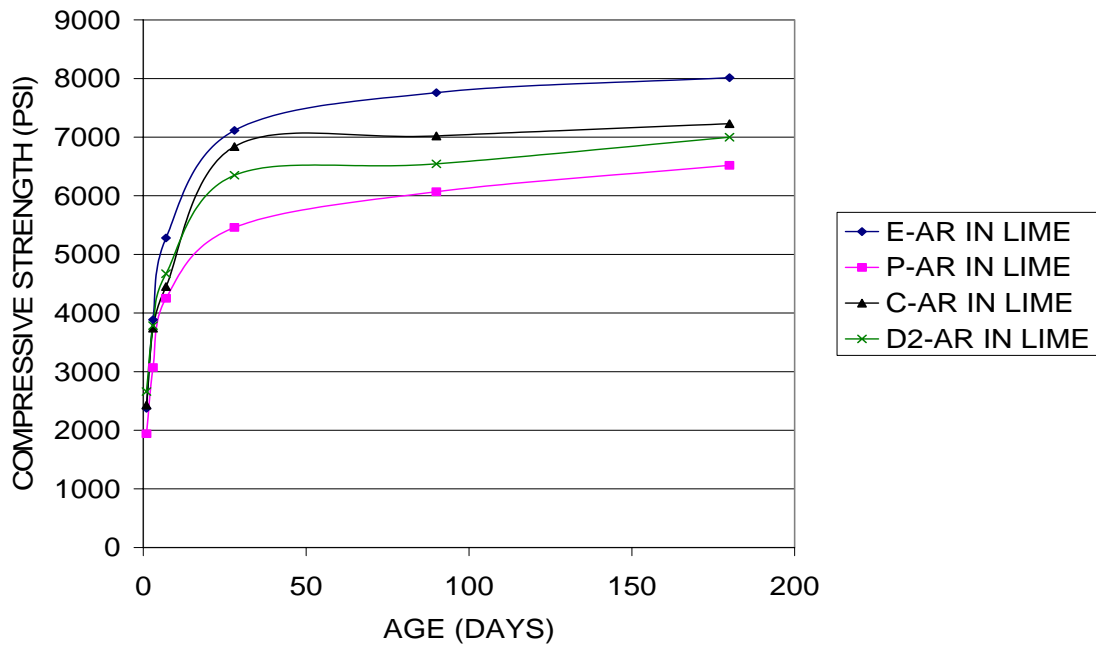
Figure 17. Compressive Strength verses Age for the As-Received Cements in Lime
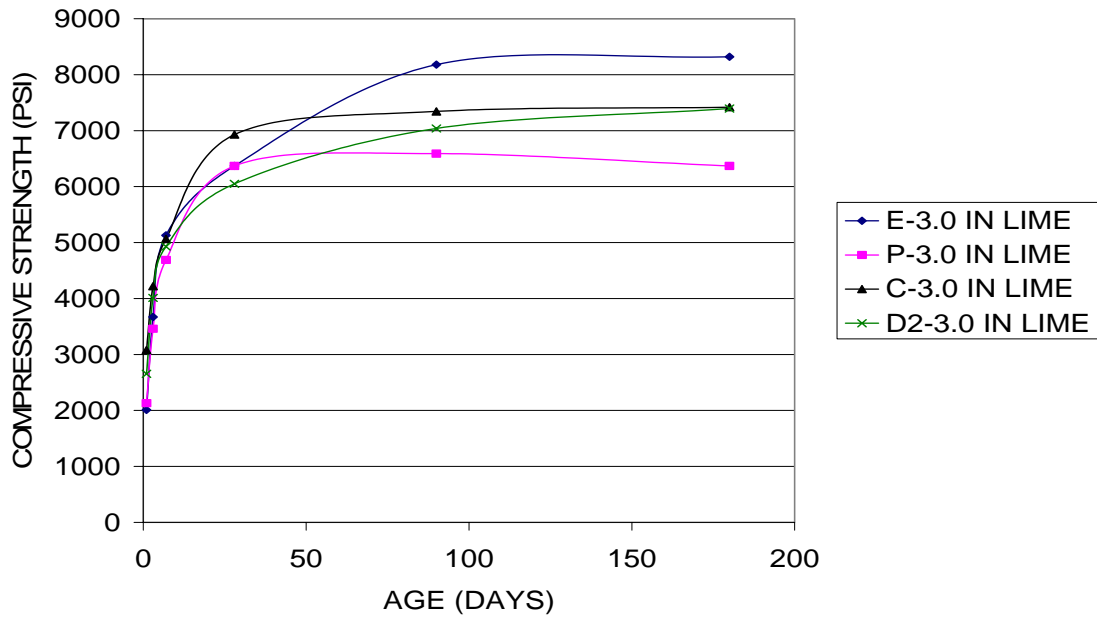
Figure 18. Compressive Strength verses Age for the Cements with 3.0% SO₃
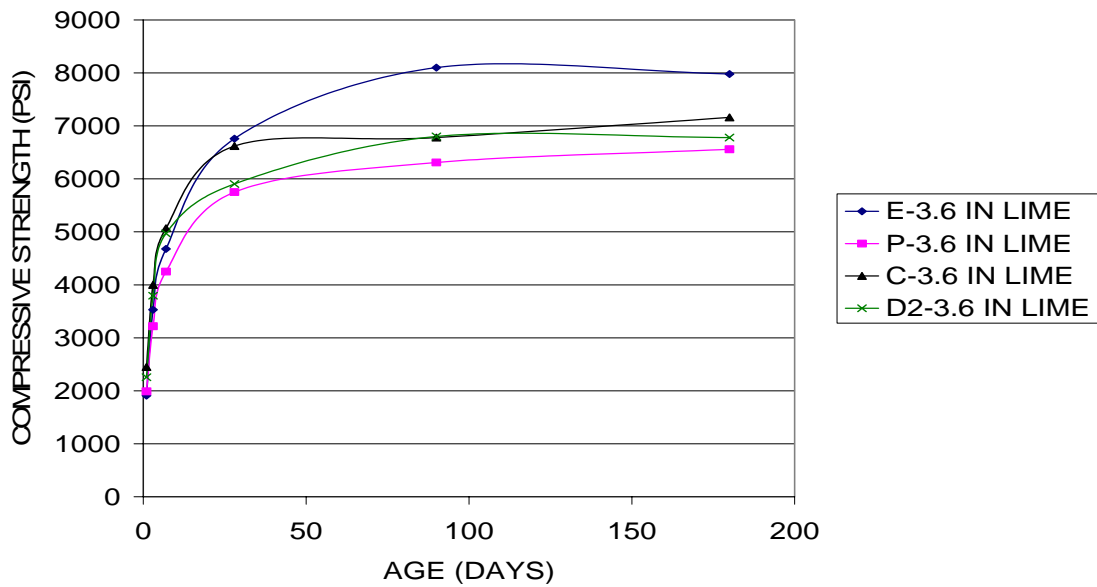
Content in Lime

Figure 19. Compressive Strength verses Age for the Cements with 3.6% SO₃

Content in Lime

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Most of the cements exposed to the sodium sulfate environment had lower strengths than their equivalents that were cured in saturated lime solution especially at the late ages. Figures 20, 21, and 22 illustrates the relationship between the compressive strength and age for the as-received cements, 3.0% , and 3.6% SO_3 content cements respectively, all cured in sodium sulfate solution. As was the case in lime solution, E cement had the highest strength in all the cases with the E-3.0 and the as-received having slightly higher late strengths than the E-3.6 cement. D2 cement had the second highest strength with the D2-3.0 and D2-3.6 having a better late strength also. Although C and D2 cements had relatively close strengths in the as-received condition, this was not the case in the doped cements as the C-3.0 and C-3.6 had a large drop in their late strengths. It was found that the largest drop in strength between the lime and sulfate exposures occurred for the C cement and especially for the C-3.6 case were the drop was ~ 3000 psi at 360 days.
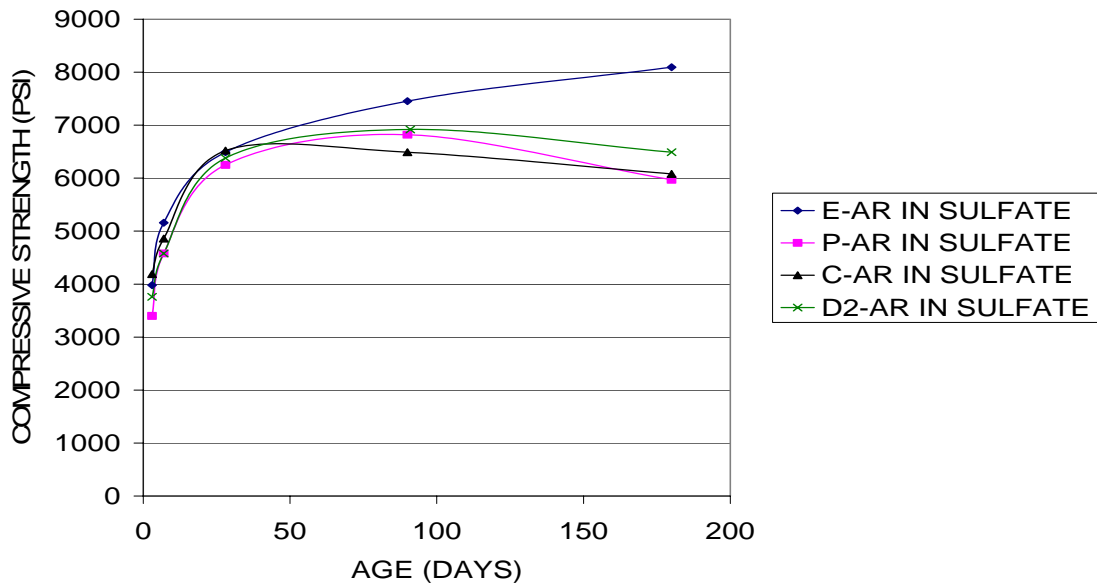

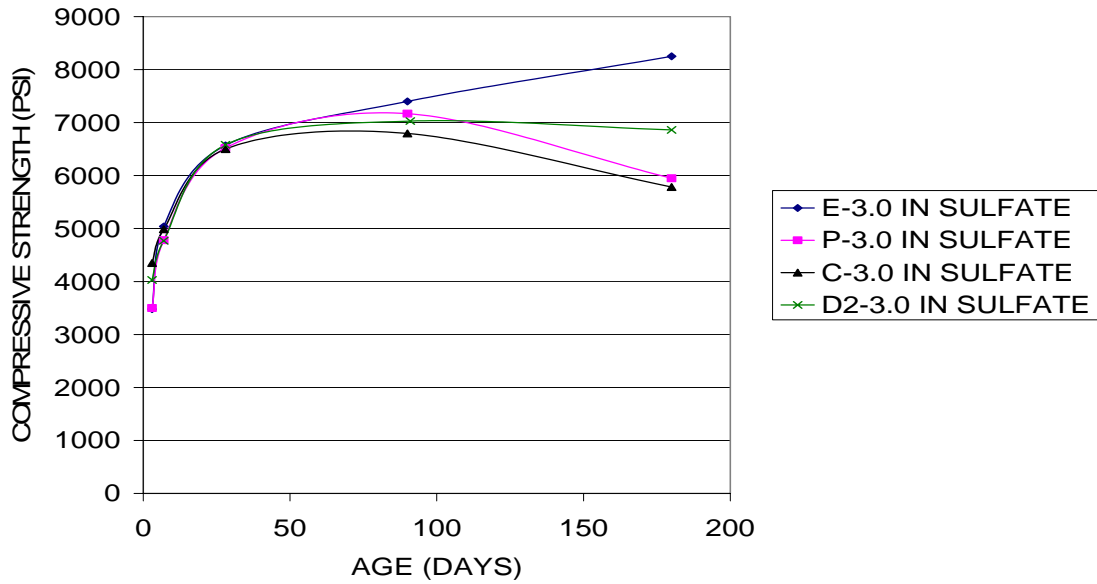**Figure 20. Compressive Strength verses Age for the As-Received Cements in Sulfate**

Figure 21. Compressive Strength verses Age for the Cements with 3.0% SO$_3$
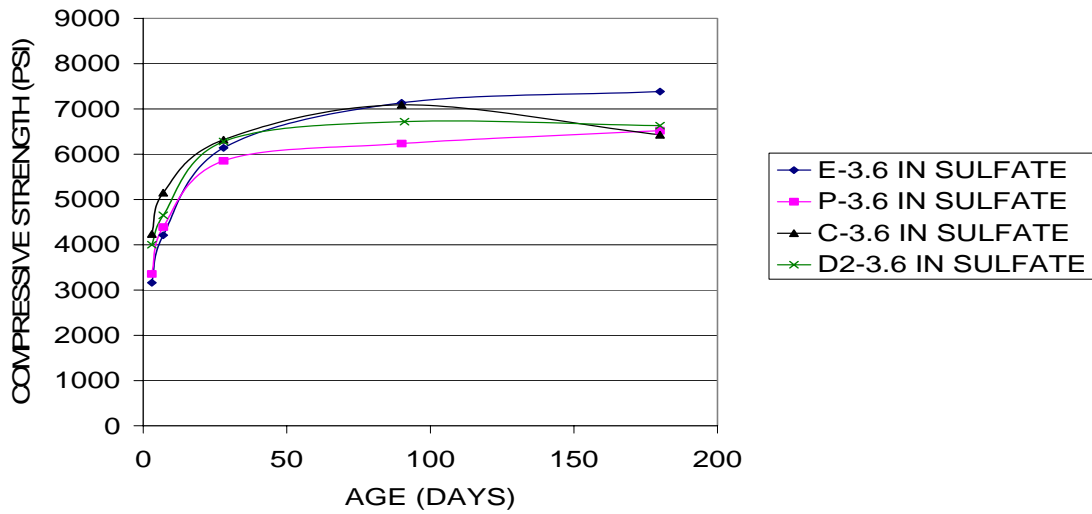
      Content in Sulfate

Figure 22. Compressive Strength verses Age for the Cements with 3.6% SO$_3$

      Content in Sulfate

Although P cement had the lowest strength in sulfate for the as-received case, increasing the SO_3 content to 3.6% seems to increase the durability of the cement against sulfate attack. This can be seen by the fact that a drop in strength between the ages of 90 and 180 days did not happen for the P-3.6 as was the case for both the as-received and P-3.0. Also, the drop in strength at 360 days for the P-3.6 cement was less than that for D2-3.6 cement, thus bringing both P-3.6 and D2-3.6 to a very close strength at 360 days of exposure to sodium sulfate solution.

Figures 23 and 24 illustrates the difference in the strength between the 3.0 % cements and 3.6 % cements at the age of 360 days in both saturated lime solution and sodium sulfate solution respectively.
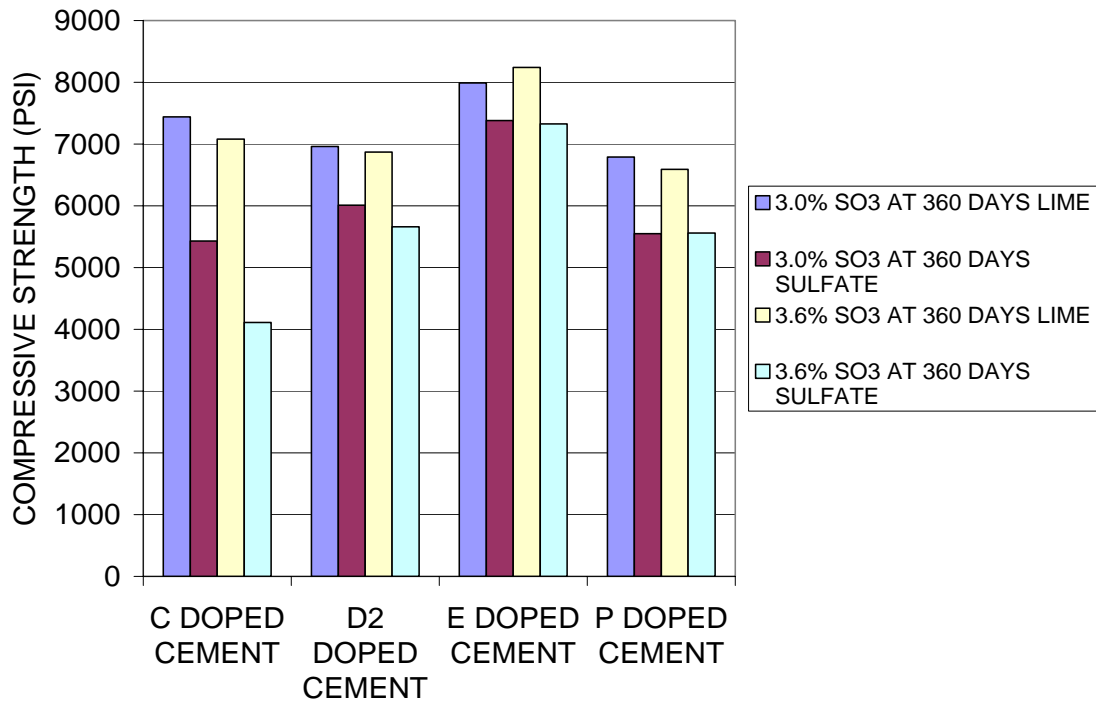

Figure 23. Compressive Strength of Doped Cements at 360 Days in Lime
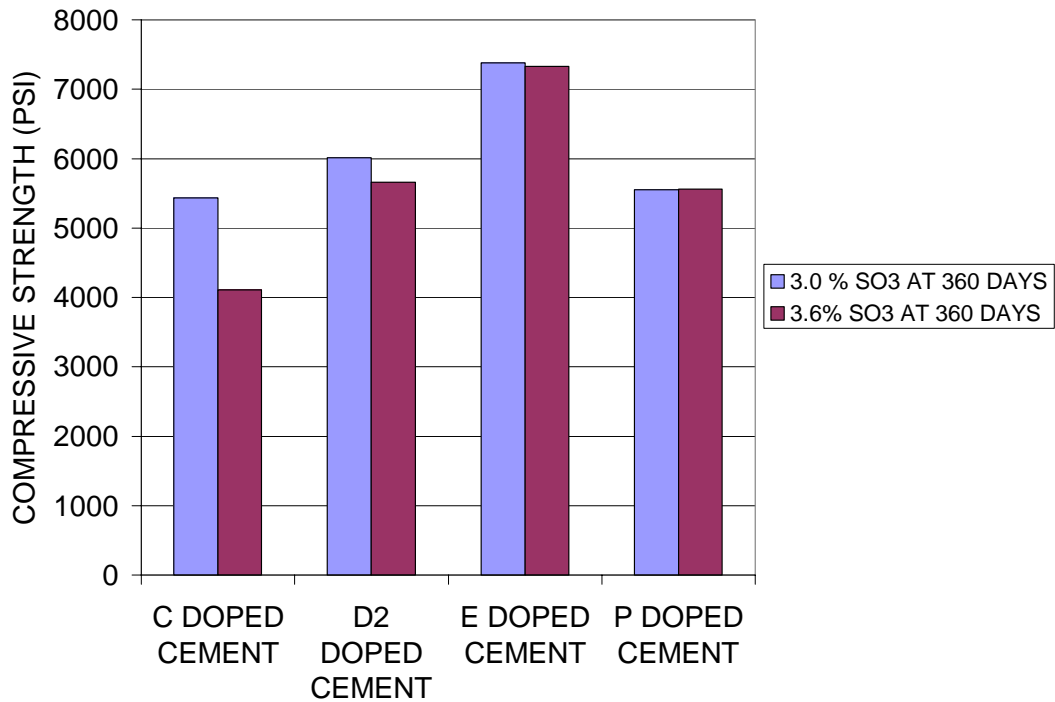
       and Sulfate

Figure 24. Compressive Strength of Doped Cements at 360 Days in Sulfate

It can be seen from the figures that increasing the SO_3 content of the cements did not greatly affect the compressive strength in lime exposure, but this was not the case in sodium sulfate exposure. C cement which had the highest C_3S content and the lowest alkali content was greatly affected by increasing its SO_3 content. On the other hand, the cements high in its C_3A content and alkali content like cement P got a beneficial effect from this increase. Cements D2 and E and due to their higher alkali content relative to cement C were able to handle the increase in a better way. Cement E also had a lower C_3S content and a higher C_2S content.

3.3.2 Expansion of Mortar Bars in Sodium Sulfate Solution

The length change of mortar bars prepared for the as-received cements as well as for the cements with an SO_3 content of 3.0% and 3.6% was measured in order to assess the expansion of the bars that were cured in sodium sulfate solution. Figure 25 illustrates the expansion of the bars prepared from the as-received cements.
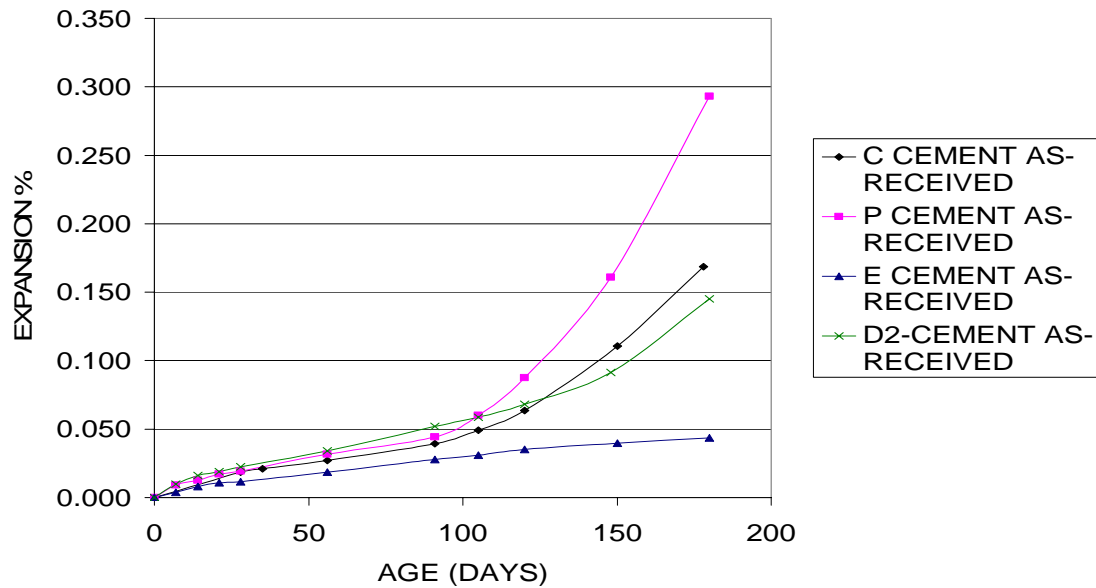

Figure 25. Expansion of Bars Prepared with the As-Received Cements

It can be seen from the figure that the expansion of the mortar bars can be divided into two stages. The first stage is characterized by a relatively minor expansion and can be referred to as the induction period, while the second stage is characterized by a rapid increase in expansion which continues at the same rate until failure. P cement had the shortest induction period of 105 days with an expansion of 0.06% at that age. After that the expansion started to increase dramatically and at 180 days of exposure to sodium sulfate solution, the P bars expanded by 0.293%. P bars had the largest expansion at 180 days. It should be noted that P cement had the highest C_3A content and the highest alkali

content. C and D2 bars had the same induction period of 120 days with an expansion of 0.063% for C and 0.068% for D2. C bars had the second highest expansion followed by D2 bars. At 180 days, the expansion of C bars was 0.169%, while that for D2 bars was 0.145%. Although C and D2 cements had approximately the same low C_3A content, both had a high C_3S content with the C having the highest C_3S content. The induction period of the E cement lasted much more longer than the other three cements and can be estimated to be 210 days with an expansion of 0.06%. The final expansion of the E bars at 180 days (0.044%) was way less than the other three cements and this made it difficult to exactly locate the end of the induction period. The expansion was much lower although E cement had a slightly higher C_3A content than both C and D2 cements according to Rietveld Refinement Method. It is worth noting that E cement had the second lowest C_3S content, the highest C_2S content, and the highest total $CaSO_4$ content of 3.6% with 2.0% of it in the form of gypsum.

The expansion trend of the four cements suggests dividing them into three categories. The first one is that of high expansion and includes P cement, followed by medium expansion (C and D2 cements), and finally low expansion which includes E cement.

Figure 26 illustrates the expansion of the C, C-3.0, C-3.6, and C-FA bars cured in sodium sulfate solution.
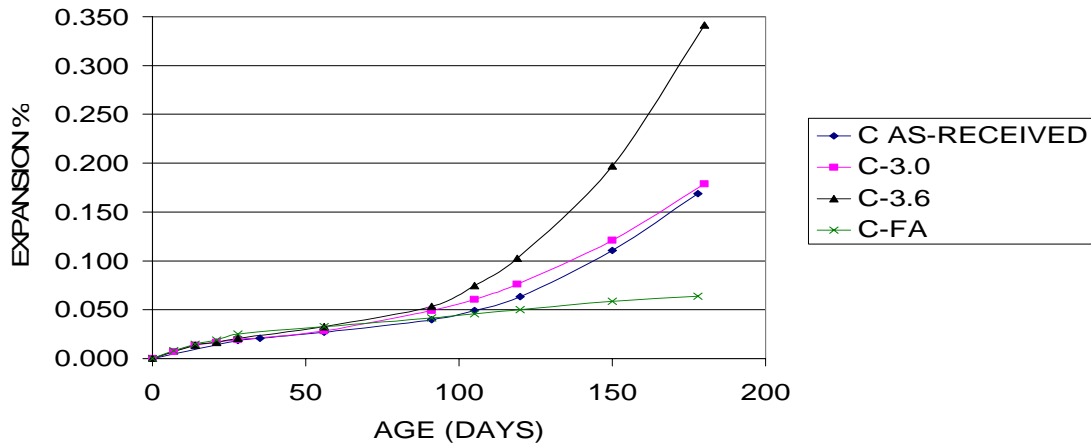

Figure 26. Expansion verses Age for the C, C-3.0, C-3.6, and C-FA Bars in Sulfate

Increasing the SO_3 content of cement C led to an increase in the expansion of the bars exposed to sodium sulfate environment. While the expansion of C bars at 180 days was 0.169%, the expansion of the C-3.0 bars was 0.179% and that of the C-3.6 bars was 0.342%.

Although the increase in expansion was not significant at early ages up to 105 days, a 102% increase in expansion happened for the bars at the age of 180 days due to increasing the SO_3 content of the cement from 2.81% to 3.6%. This increase in the expansion explains the results obtained for the strength of the cubes cured in sodium sulfate solution where the strength was not significantly affected in the early ages, but a significant drop happened at later ages. Also, the big difference in the strength observed

between the CS-3.0 and CS-3.6 at 180 and 360 days, can be explained by the big

difference in the expansion of the C-3.0 and C-3.6 bars at these ages.

It can also be seen from the figure that by replacing 20% of the C cement by fly ash,

the expansion of the bars was lowered dramatically to 0.064% at 180 days. This huge

drop in the expansion happened although the SO_3 content of the remaining 80% of the

cement was increased to 3.6%. Thus, incorporating Fly Ash in the mix greatly increased

the durability of the cement against sulfate attack despite the increase in the SO_3 content.

The expansion of D2, D2-3.0, D2-3.6, D2-4.0, and D2-FA bars in sodium sulfate

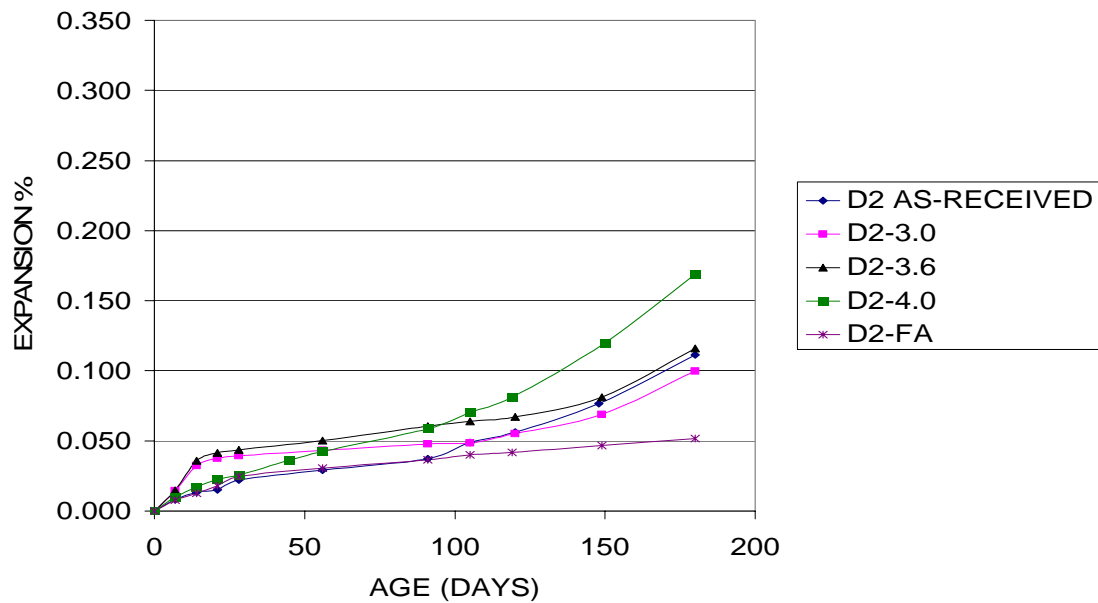solution is illustrated in Figure 27.

Figure 27. Expansion verses Age for the D2, D2-3.0, D2-3.6, D2-4.0,

and D2-FA Bars in Sulfate

In the case of the D2 cement which has a low C_3A content (3%) but the second

highest C_3S content and the second highest K_2O content (0.54%), increasing the SO_3

content to 3.0% led to a decrease in the expansion of the bars. On the other hand, increasing it further to 3.6% and 4.0%, led to an increase in the expansion with a final expansion greater than the as-received cement. Thus it seems that the optimum SO_3 content for minimum expansion in sodium sulfate solution for the D2 cement is around 3.0%. The results of the cubes compressive strength showed that the D2-3.6 cubes had a higher strength than the as-received at the ages of 3, and 7 days. At the ages of 28 and 90 days the strength of the as-received was higher, but at the age of 180 days the D2-3.0 had a higher strength which is in compliance with the expansion results. This indicates that the optimum SO_3 content for maximum compressive strength is not the same for all ages of the D2 cement and also indicates that this optimum can be different than that for minimum expansion of bars. Similar results were found by other researchers, among them was Lerch [5] who concluded that most cements show different optimum gypsum requirements for different properties, such as strength or shrinkage, at different ages.

As was the case with the C cement, replacing 20% of the D2 cement with Fly Ash led to a significant decrease in the expansion of the bars even to a much lower value than that of the D2-3.6 bars. While the D2 as-received bars had a final expansion of 0.145% at the age of 180 days, the D2-FA bars had an expansion of 0.052% at the same age. The SO_3 content of the remaining 80% of the cement was increased to 3.6%, and still we had this big difference in the expansion of the bars. This indicates the effectiveness of the pozzolanic materials in improving the durability of mortar and concrete against sulfate attack.

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Figure 28 illustrates the expansion of E, E-3.0, E-3.6, E-4.2, and E-FA bars in sodium sulfate solution.
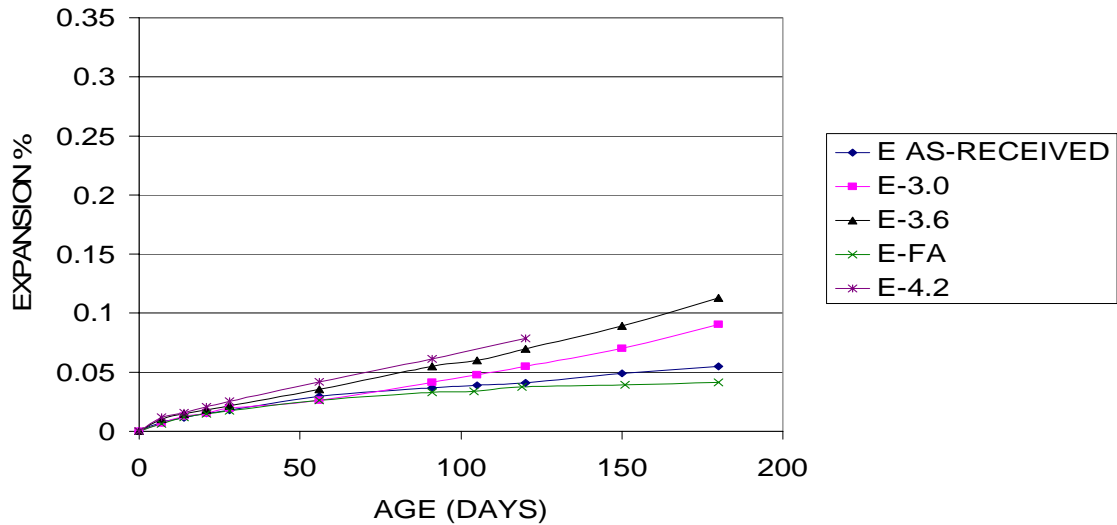

Figure 28. Expansion verses Age for the E, E-3.0, E-3.6, E-4.2, and E-FA Bars in

   Sulfate

The expansion of the E cement bars was generally very low compared to the other cements and increasing the SO_3 content led to an increase in the expansion, although this increase was not much significant. Although the E as-received had the lowest expansion, it did not have the highest compressive strength at all the ages. The E-3.0 had the highest strength at 28, and 180 days while the strengths at 90 days were very similar with the as-received having a slightly higher value.

As was the case with the D2 cement, it was found that also for the E cement, the optimum SO_3 content for minimum expansion of bars is different than the optimum for maximum compressive strength, and that the optimum for maximum strength differs with age. In general, for both cements, increasing the SO_3 content to 3.0% led to an increase in

the strength especially at the late ages. It is worth noting that E cement had the second lowest C_3S content and the highest C_2S content. It also had the second highest Na_2O content and accordingly the second highest Na_2O equivalent.

The increase in strength with increasing the SO_3 content of other cements was also reported by other researchers [15]. These researchers stated that the beneficial effect of gypsum on the strength of the cement was attributable to the improved quality of the gel which was produced in the presence of gypsum. Their study showed that the addition of gypsum resulted in hydration products of greater average density and it was suggested that this greater density brought about the higher strength.

The expansion of the E-FA bars was very similar to that of the as-received cement, thus incorporating 20% Fly Ash in the mix did not cause a significant decrease in the expansion, most probably because the expansion of the E cement is generally very low.

The expansion of the P, P-3.0, P-3.6, and P-FA bars in sodium sulfate solution is illustrated in Figure 29. Increasing the SO_3 content of cement P to 3.0% caused a significant decrease in the expansion of the bars, and increasing it further to 3.6% caused an additional significant decrease in the expansion. Thus P cement requires a higher amount of SO_3 content to reach the optimum for lowest expansion. The P-3.6 with an SO_3 content of 3.6%, which is higher than the specified limit of 3.0% had the lowest expansion under sodium sulfate exposure. P cement had the highest C_3A content and the lowest C_3S content. It also had the highest Na_2O, the highest K_2O, and accordingly the highest Na_2O equivalent.
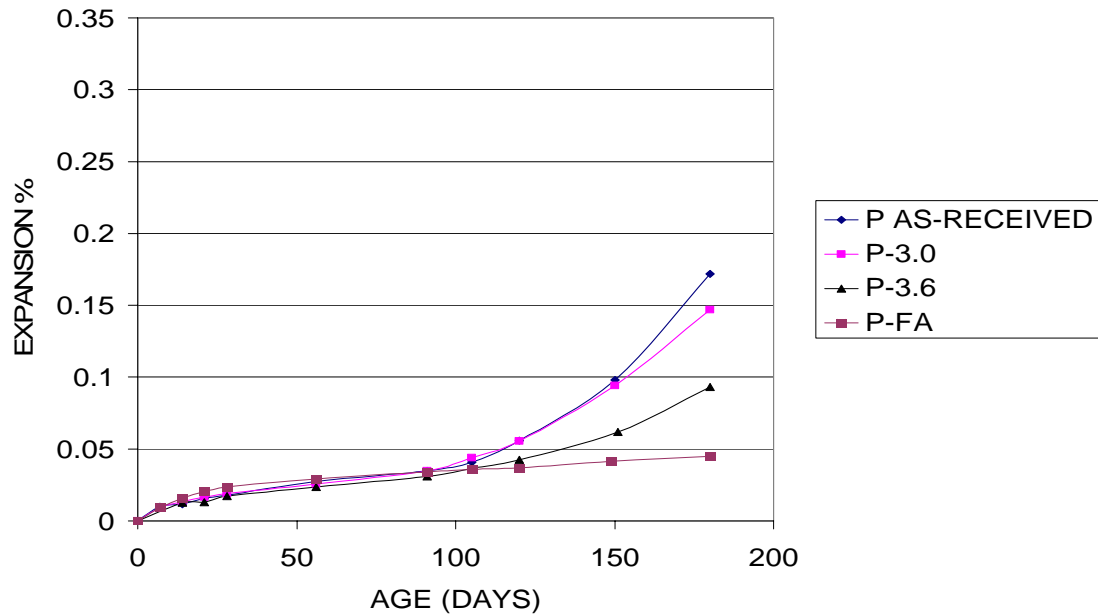
82

Figure 29. Expansion verses Age for P, P-3.0, P-3.6, and P-FA Bars in

Sulfate

The result that cements with high C_3A content and high alkali content requires larger

additions of gypsum to reach the optimum was also reported by other researchers.

The results for the compressive strength of the P cubes in sulfate showed that the P-3.0

had the highest strength up to the age of 90 days, and it can be seen from Figure 29 that

the expansion of all the sets of P bars does not vary significantly up to that age. The

strength results also showed that a large drop in strength happened to both the as-received

and P-3.0 at the age of 180 days while an increase happened in the strength of the P-3.6.

The expansion results matches the strength results as it is clear from Figure 29 that a

significant difference in expansion exists between the 3 sets at the age of 180 days with

the P-3.6 having the lowest expansion. The reason why the P-3.6 had a higher drop in

strength between the ages of 180 and 360 days than the P-3.0 can not be explained from

the expansion results as the P-3.0 continued to have a much higher expansion than the P-3.6 at that age.

Figures 30, 31, and 32, compares the expansion of the different types of cements used in this study in the three cases of 3.0% SO_3 content, 3.6% SO_3 content, and replacement of 20% of the cement with Fly Ash respectively.
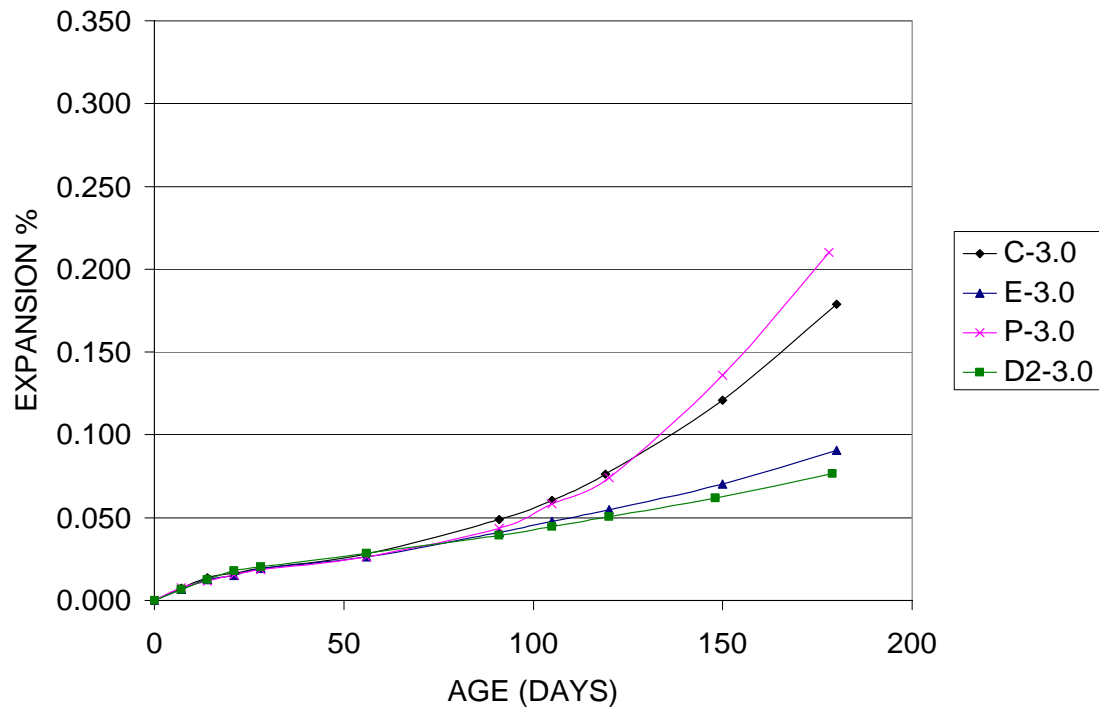

Figure 30. Expansion verses Age for the Cements with 3.0% SO_3 Content in Sulfate
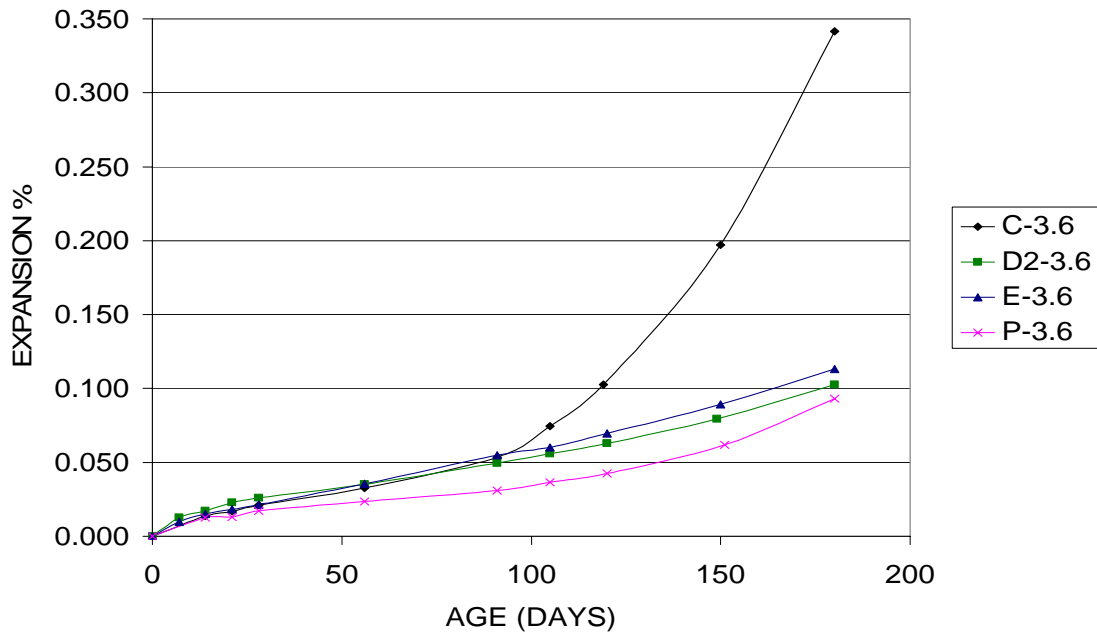
Figure 31. Expansion verses Age for the Cements with 3.6% SO$_3$ Content in Sulfate
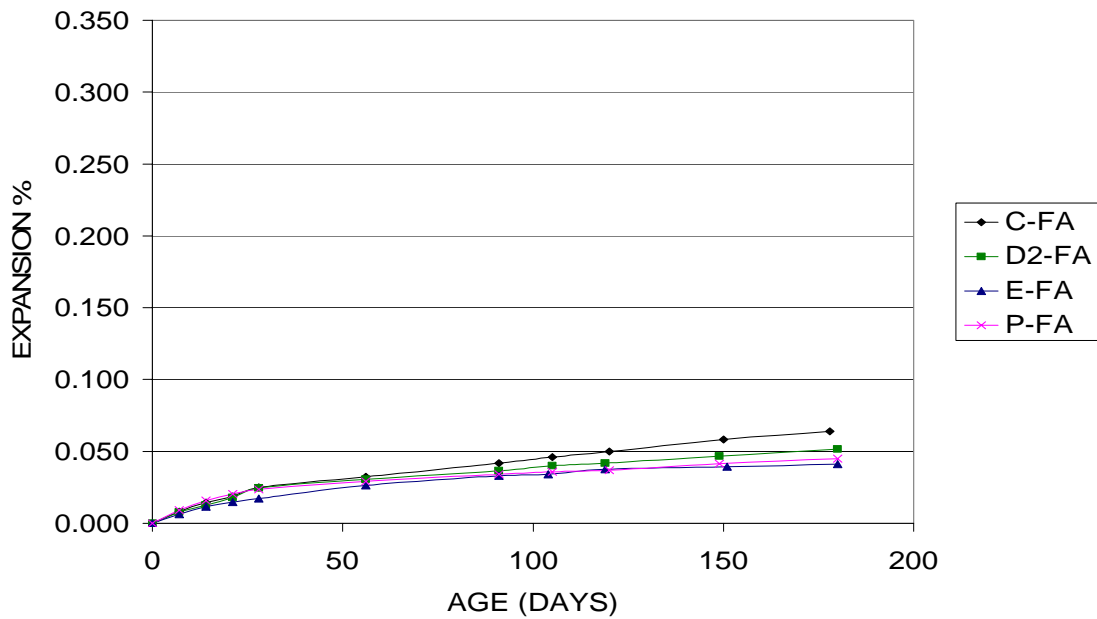

Figure 32. Expansion verses Age for the Cements with 20% Replacement by Fly Ash

The figures show the beneficial effect of increasing the SO_3 content of cement D2 to 3.0% and cement P to 3.6% on decreasing their expansion in sodium sulfate environment. The D2-3.0 had the lowest expansion of the 3.0% sets, while a significant decrease in the expansion of the P bars happened in the case of P-3.6 as compared to the as-received case.

Figure 32 shows that incorporating 20% Fly Ash in the mix, had a significant effect in reducing the expansion of all the cements, bringing them to very close low values regardless of the differences that exist in their chemical and mineralogical composition. This result also happened despite the fact that the SO_3 content of the remaining 80% of the cement was increased to 3.6%.

3.4 X-Ray Diffraction Analysis of Mortar Cubes

Tables 11 and 12 illustrates the Relative Intensity Ratios for ettringite and gypsum as measured by the X-Ray diffraction analysis done on pieces of the crushed cubes at the age of 360 days for both the 3.0% sets and 3.6% sets respectively.

Table 11. Relative Intensity Ratios of Ettringite and Gypsum for the 3.0% SO_3 Content Mortar Cubes at the Age of 360 Days in Sulfate

	Mortar cubes at 360 days in Sulfate Solution			
	C-3.0	D2-3.0	E-3.0	P-3.0
Ettringite Intensity Ratio	0.166	0.245	0.206	0.288
Gypsum Intensity Ratio	0.196	0.220	0.215	0.271

Table 12. Relative Intensity Ratios of Ettringite and Gypsum for the 3.6% SO₃

Content Mortar Cubes at the Age of 360 Days in Sulfate

	Mortar Cubes at 360 days in Sulfate Solution			
	C-3.6	D2-3.6	E-3.6	P-3.6
Ettringite Intensity Ratio	0.169	0.262	0.199	0.313
Gypsum Intensity Ratio	0.206	0.279	0.300	0.276

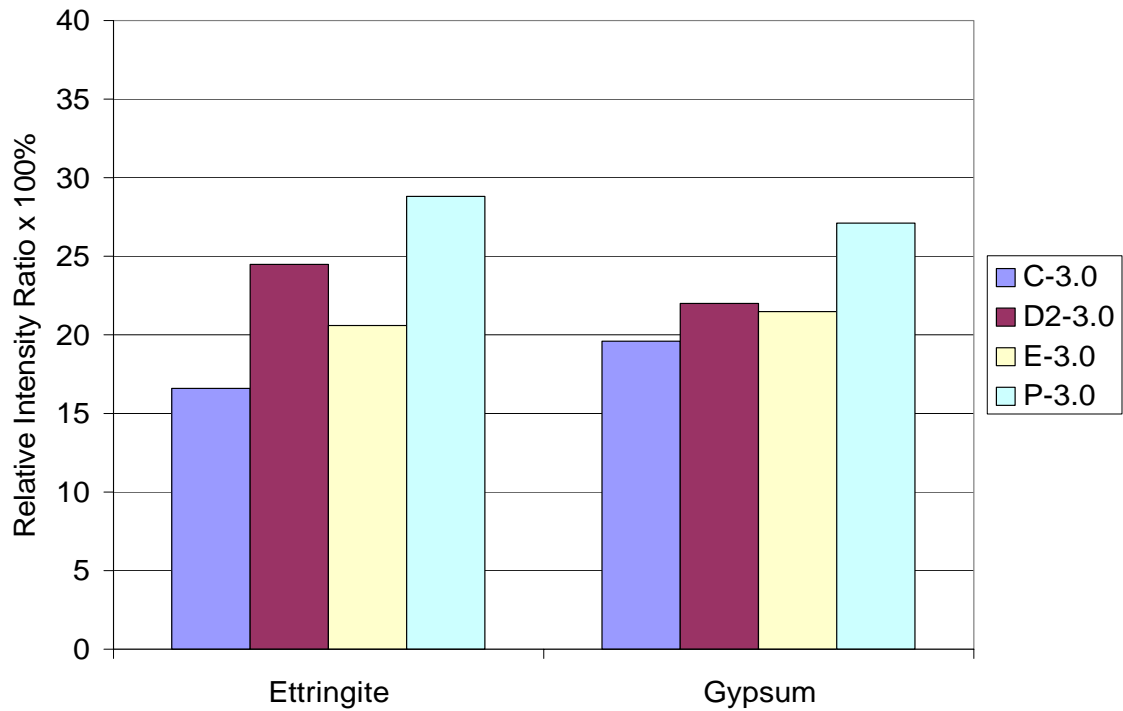The relative intensity ratios are also illustrated in Figures 33 and 34.

Figure 33. Relative Intensity Ratios of Ettringite and Gypsum for the 3.0% SO₃

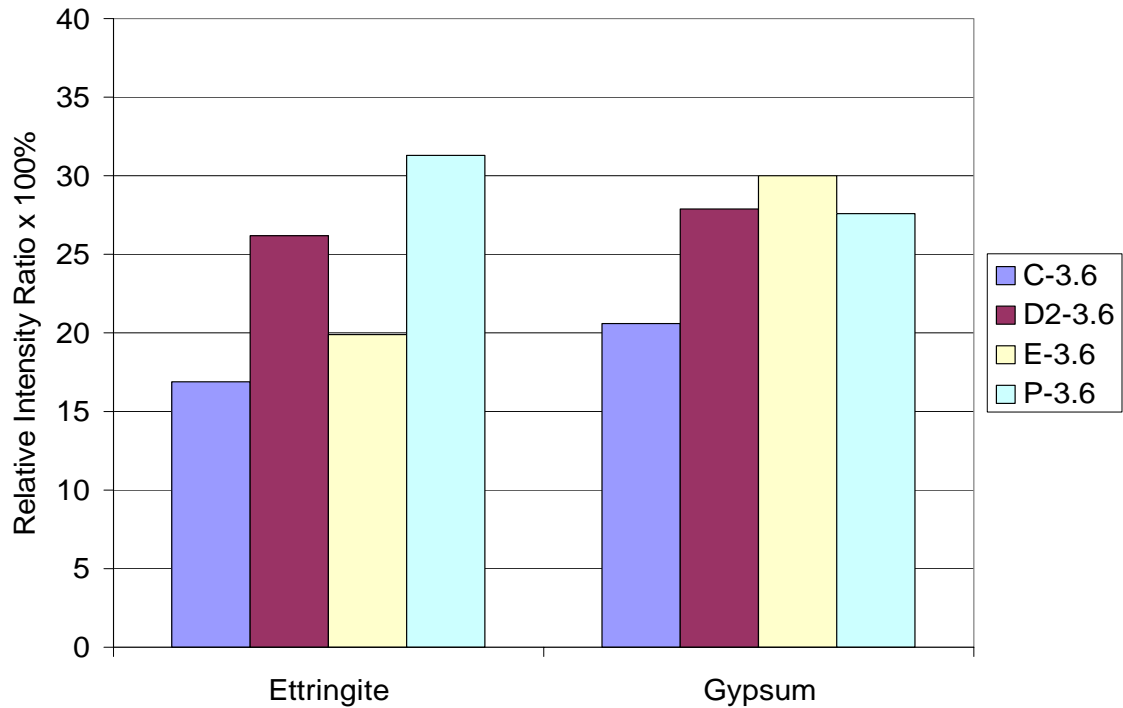**Content Mortar Cubes at the Age of 360 Days in Sulfate**

Figure 34. Relative Intensity Ratios of Ettringite and Gypsum for the 3.6% SO$_3$ Content Mortar Cubes at the Age of 360 Days in Sulfate

From the above figures, it can be seen that for both the 3.0% sets and the 3.6% sets, P cubes contained the highest amounts of ettringite as expected, since P cement has a much higher C$_3$A content than the other three cements. P cubes also contained the highest gypsum content for the 3.0% set. For the C, D2, and E cements, which have a relatively similar C$_3$A content, D2 cubes contained the highest ettringite content in both 3.0% and 3.6% sets. It is worth noting that cement D2 has the highest K$_2$O content of the three cements (0.54%) and the lowest SO$_3$ content (2.54%).

As for the gypsum content, P-3.0 cubes had the highest gypsum content for the 3.0% set, while E-3.6 cubes had the highest gypsum content for the 3.6% set. It is worth noting that increasing the SO_3 content of E cement from 3.0% to 3.6% caused a significant increase in the gypsum content while the ettringite content only increased slightly.

3.5 X-Ray Diffraction Analysis of Mortar Bars

Tables 13 and 14 illustrates the Relative Intensity Ratios for ettringite and gypsum as measured by the X-Ray diffraction analysis done on pieces from the outside perimeter of bars at the age of 480 days for the 3.0% sets and 3.6% sets respectively.

Table 13. Relative Intensity Ratios of Ettringite and Gypsum for the 3.0% SO₃ Content Mortar Bars at the Age of 480 Days in Sulfate

	Mortar bars at 480 days in Sulfate Solution			
	C-3.0	D2-3.0	E-3.0	P-3.0
Ettringite Intensity Ratio	0.268	0.296	0.252	0.306
Gypsum Intensity Ratio	0.368	0.455	0.450	0.292

Table 14. Relative Intensity Ratios of Ettringite and Gypsum for the 3.6% SO₃

Content Mortar Bars at the Age of 480 Days in Sulfate

	Mortar bars at 480 days in Sulfate Solution			
	C-3.6	D2-3.6	E-3.6	P-3.6
Ettringite Intensity Ratio	0.330	0.281	0.268	0.308
Gypsum Intensity Ratio	0.407	0.495	0.534	0.469

Figures 35, 36, 37, and 38 illustrates also the relative intensity ratios of the sets of bars
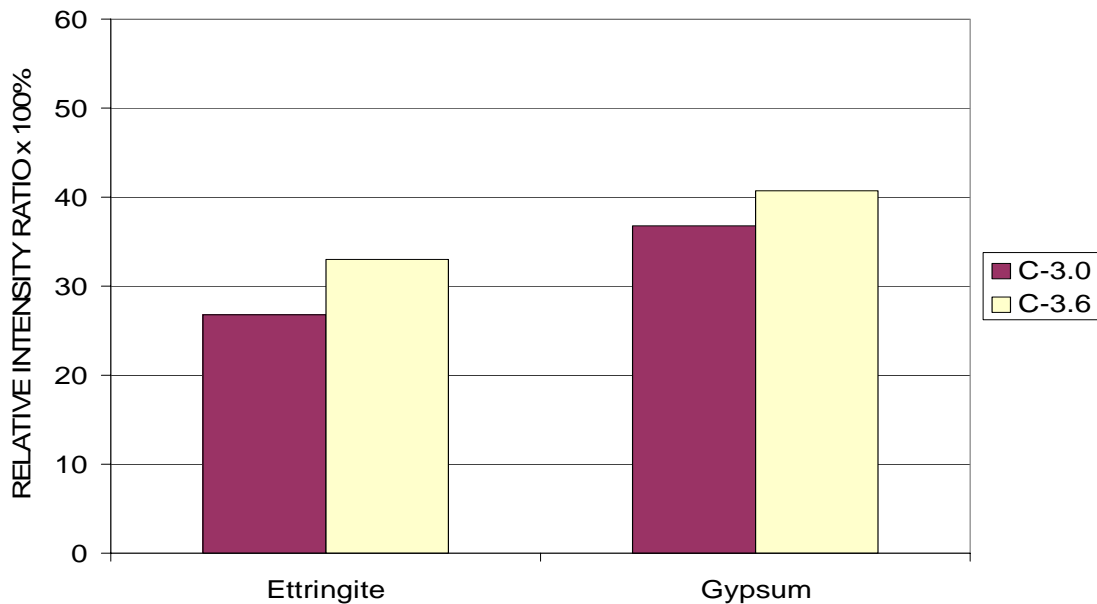
for the C, D2, E, and P cements respectively.

Figure 35. Relative Intensity Ratios of Ettringite and Gypsum for the C-3.0 and

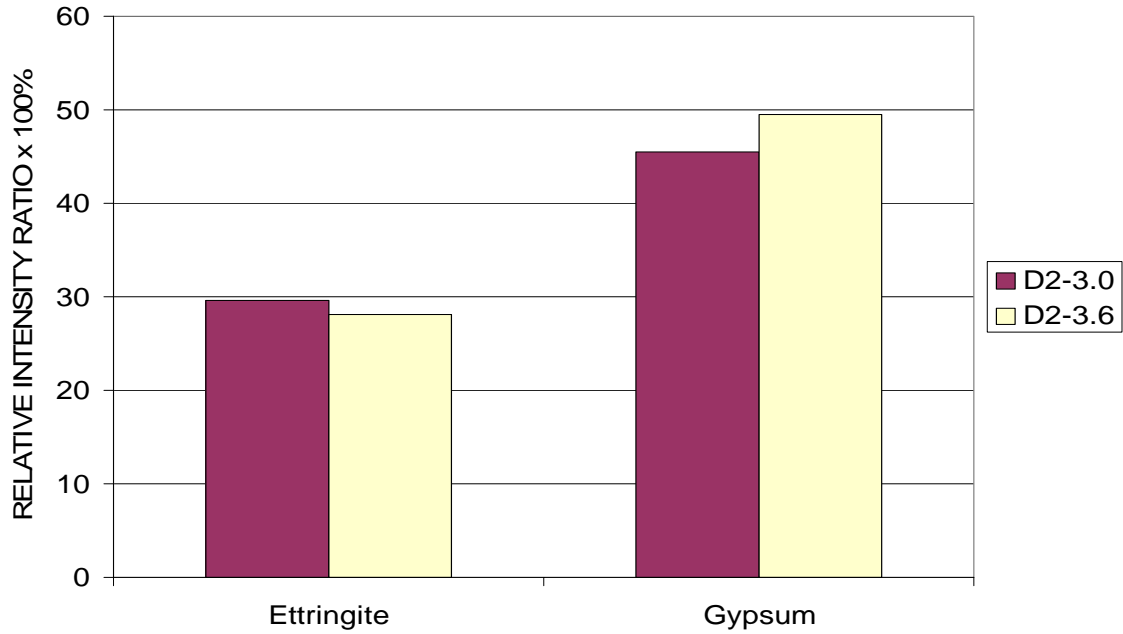**C-3.6 Mortar Bars at the Age of 480 Days in Sulfate**

Figure 36. Relative Intensity Ratios of Ettringite and Gypsum for the D2-3.0 and

D2-3.6 Mortar Bars at the Age of 480 Days in Sulfate

Figure 37. Relative Intensity Ratios of Ettringite and Gypsum for the E-3.0 and

E-3.6 Mortar Bars at the Age of 480 Days in Sulfate

Figure 38. Relative Intensity Ratios of Ettringite and Gypsum for the P-3.0 and P-3.6 Mortar Bars at the Age of 480 Days in Sulfate
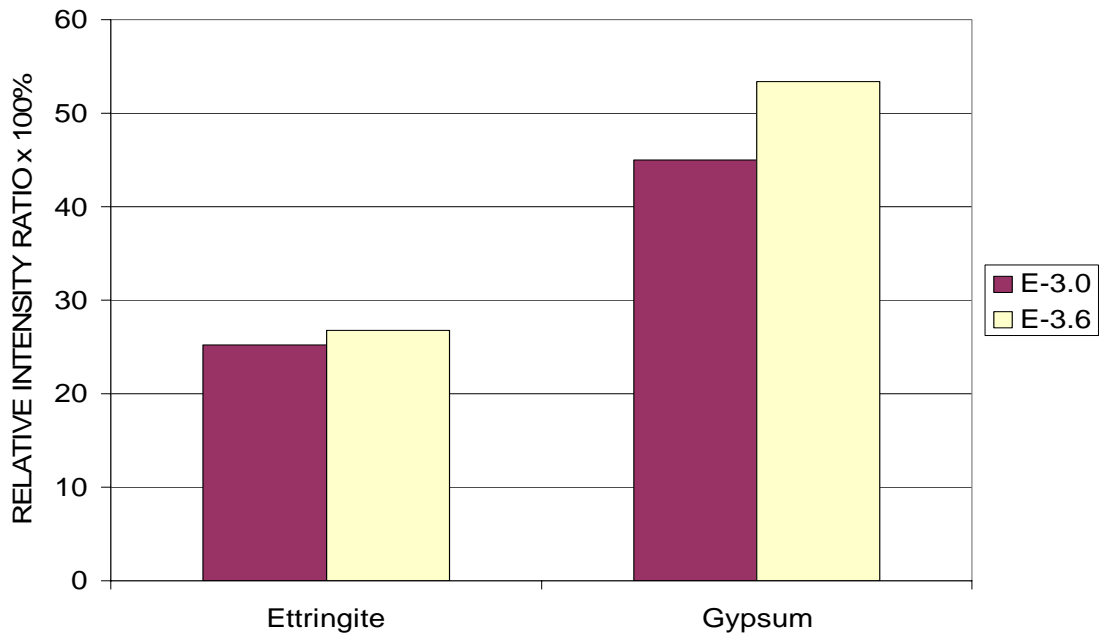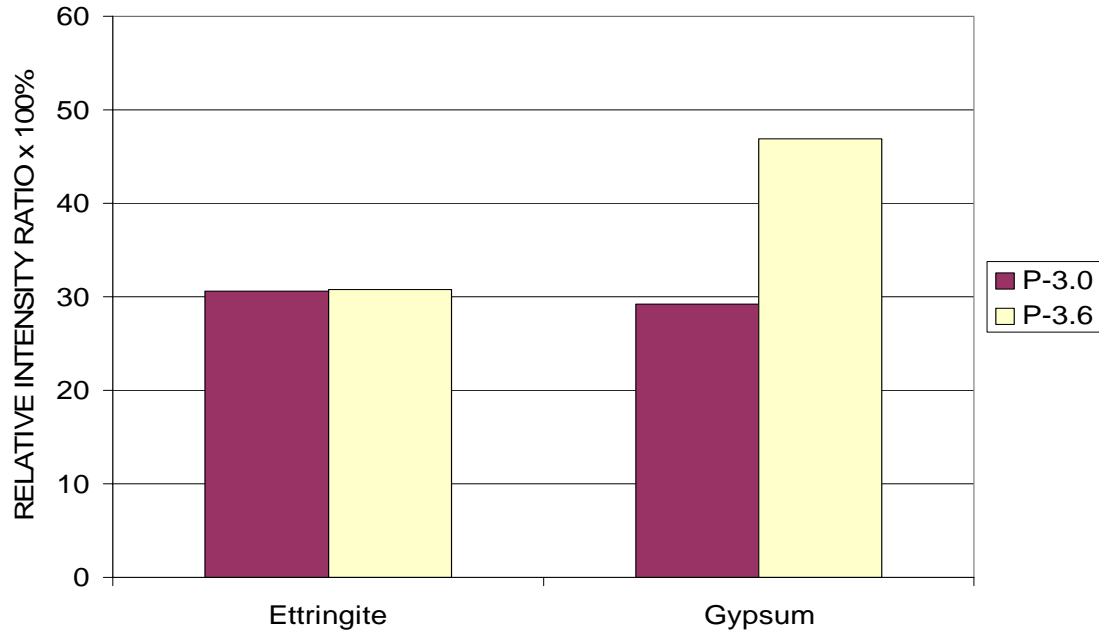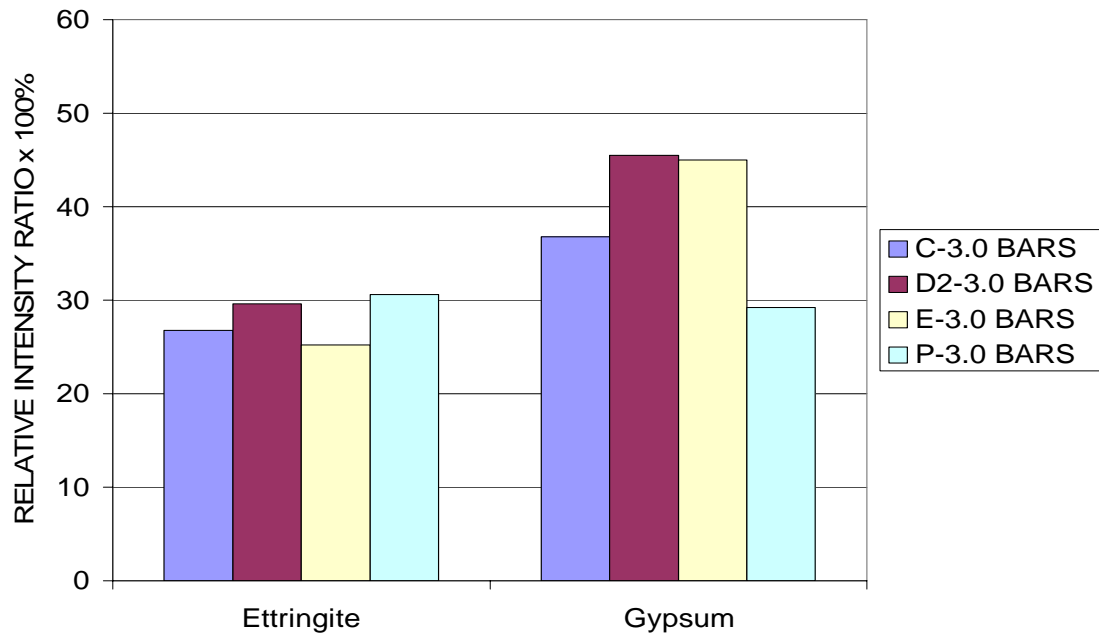

Figure 39. Relative Intensity Ratios of Ettringite and Gypsum for the 3.0% SO$_3$ Content Mortar Bars at the Age of 480 Days in Sulfate
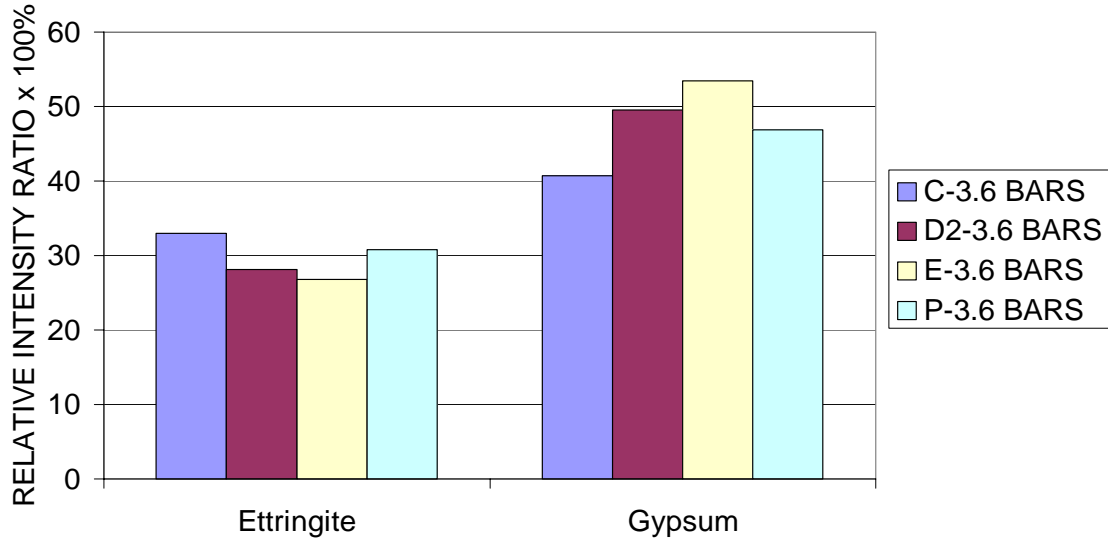
Figure 40. Relative Intensity Ratios of Ettringite and Gypsum for the 3.6% SO₃

Content Mortar Bars at the Age of 480 Days in Sulfate

Figures 39 and 40 compares the relative intensity ratios of ettringite and gypsum for the four types of cements in the two cases of 3.0% and 3.6% SO_3 content respectively. From the above figures, it can be seen that increasing the SO_3 content of cements C and E led to an increase in the amount of ettringite found in the bars. These results explain the expansion trend that was found for the C and E cements with the 3.6 bars having a higher expansion than the 3.0 bars.

Similarly, the results of the 3.6% set showed that the C-3.6 bars contained the highest amounts of ettringite followed by P-3.6 bars, then D2-3.6 bars, and finally the E-3.6 bars with the lowest amount. The expansion trend for the 3.6% set was exactly the same at that age, with the C-3.6 bars having the highest expansion, followed by P-3.6 bars, then D2-3.6 bars, and finally E-3.6 bars with the lowest expansion. The gypsum content of the D2 and E bars was higher than that of the C bars in both the cases of the 3.0% and 3.6%.

CHAPTER 4.

CONCLUSIONS AND RECOMMENDATIONS

It can be concluded from this study that there is an optimum SO_3 content for the lowest expansion and for the highest compressive strength of the portland cement mortars used, and exposed to sodium sulfate environment. This optimum was not the same for both expansion and strength. The optimum also differed from one cement to another and from one age to another for each cement.

For cements C, D2, and E with similar and low C_3A content, the compressive strength showed an optimum at 3.0% for ages up to 28 days except for E cement. In the case of the latter, the optimum was at the as-received SO_3 content. For cement P in lime, with a moderately high C_3A and alkali content, increasing the SO_3 content to 3.0% increased the strength; however, increasing it further to 3.6% decreased the strength. The effect became more pronounced as the SO_3 content was increased beyond 3.0%.

As for the expansion behavior, for cements with similar tricalcium aluminate content, increasing the SO_3 content beyond 3.0% results in an increase in expansion on exposure to sodium sulfate solution. For cement P with higher tricalcium aluminate and alkali content, increasing the SO_3 content to 3.6% did not increase the expansion in sodium sulfate solution.

The findings of this study did indicate that increasing the SO_3 content above 3.0% for all the cements studied here results in decreasing the durability of mortar exposed to sulfate environment.

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