EFFECT OF SULFUR TRIOXIDE CONTENT ON CONCRETE STRUCTURES USING FLORIDA MATERIALS

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6. Abstract

In this study, several ASTM Portland cements were used to address effects of increasing sulfur trioxide content of cement on the performance and durability of concrete. The cements were analyzed for their mineralogical content using x-ray diffraction. Several other characterization techniques were used including: calorimetric studies, fineness, quantitative x-ray analysis and oxide chemical composition. The findings indicate that increasing sulfur trioxide content increases expansion in lime and sulfate. The amount of expansion experienced by mortar appears to be dependent on the mineralogical composition of cements. Additionally, increasing SO_3 content increases strength loss for mortar exposed to sodium sulfate solution. Drying shrinkage measurements indicate that increasing sulfur trioxide beyond 3% increases the drying shrinkage for all cements. Concrete Strength data indicate that for cements low in alkali and aluminate content, increasing the SO_3 to 3.6% increases the strength loss at 180 days. Additionally, deterioration appears to be dependent on tricalcium silicate content of the cement. For cements moderate in tricalcium aluminate and alkalis, increasing tricalcium silicate content rendered cements less tolerant to higher sulfur trioxide content. It is recommended that SO_3 content should not be allowed to increase above the current specified limits.

17. Key Words
Sulfur trioxide content, optimum gypsum, durability in sodium sulfate environment, strength loss, ASTM C1038, ASTM C1012, expanion in lime, expansion in sulfate, setting time,open-circuit potential, surface resistivity, mineral admixtures.

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EXECUTIVE SUMMARY

Introduction

The objective of the current study was to determine the effect of sulfur trioxide content on the durability of structural concrete. Towards satisfying the above objective, several approved Florida Department of Transportation [FDOT] cement suppliers were contacted for material collection. The selected cements had similar fineness but variable mineralogical content. In order to increase the sulfur trioxide content of the as-received cements additions of gypsum were done to increase the SO_3 content to different levels. Two levels were fixed for all cements; namely, 3.0 and 3.6%. However, additional doping levels were also used for expansion measurements.

The as-received cements and mineral admixtures were subjected to several characterization tests that include mineralogical x-ray diffraction for cement phase quantification (Rietveld refinement). Other characterization tests were namely, x-ray spectroscopy for oxide chemical composition of mineral admixtures and cements, differential scanning calorimetric test and Blaine fineness. Durability tests for mortar and concrete included: mortar expansion measurements in lime and sulfate, mortar strength measurements in lime and sulfate, drying shrinkage, concrete strength measurements in lime and sulfate, setting times for concrete, surface resistivity for concrete and open circuit potential for steel rebars in different concrete mixes.

Results and Recommendations

The findings of this study indicate that there is a need to maintain low SO_3 content for cements for better long term concrete durability. The results of strength measurements conducted for a period of 360 days indicate that increasing the SO_3 content beyond 3.0% results in a significant strength loss when the cementitious system is exposed to sodium sulfate environment. Loss in strength between 1,000 to 3,000 psi was documented in this study for all cements studied here. The rate of strength loss at elevated SO_3 content was more pronounced the higher the tricalcium silicate content of the cement. Moderate alkali and tricalcium aluminate content cements showed lower strength loss or expansion on sulfate exposure at ambient temperatures. The study also indicated that ASTM C1038, might not assess accurately durability of the cementitious system at longer ages.

Expansion measurements indicate that increasing SO_3 content of cements increases expansion. This was the case for cements of lower alkali and tricalcium aluminate content. The effect seems to be more significant with increasing tricalcium silicates of the cements. The results also indicate that incorporation of mineral admixtures in the concrete and mortar improves significantly durability of a cementitious system with high sulfur trioxide content.

Since the findings of this study indicate that increasing SO_3 content accelerates the rate of deterioration for most of the cements considered in this study, it is recommended that a limit on the maximum allowable SO_3 content in cements has to be enforced with no provisions. It is also recommended that a study needs to be initiated with the objective of addressing the roles of alkalis and tricalcium aluminate content of cements on the long term durability of concrete.

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Disclaimer

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CHAPTER I

INTRODUCTION

Lately, the Florida Department of Transportation had to shut down several cement production facilities due to elevated levels of sulfur trioxide content in cements. State approved cement suppliers are encountering problems with their product; namely, sulfur trioxide content of elevated levels exceeding limits set by ASHHTO and ASTM standards. Sources of sulfur trioxide in cements are various and include: raw feed, fuel and gypsum. These sources can render clinker with high sulfate content. In order to control the setting behavior of concrete, the common practice is to intergrind gypsum with clinker in cement production. Gypsum primary function is to control the early hydration of aluminates.

Sulfur trioxide content in clinker or cement can be of variable reactivity depending on its source and kind. If it is nonreactive, and in order to control tricalcium aluminate hydration, cement producers are promoted to increase gypsum content. This can result in the production of cements with marginally higher sulfur trioxide content than the maximum limits set through state and national standards.

Though current standards have maximum set limits on sulfur trioxide content in Portland cement, they allow the use of cements with optimum sulfur trioxide content that can exceed the set maximum. Optimum sulfur trioxide content is established based on maximum strength. However, recent research indicates that optimum sulfur trioxide content for strength and durability might be different and also different from that for placement.

When manufacturers supply cements under those provisions, they must, upon request, provide additional data to the purchaser. Currently, Concrete Suppliers to the State of Florida are requesting provisional acceptance. However, the Florida Department of Transportation, being the user in this case, is lacking documented scientific data pertaining to the effect of higher sulfur trioxide content on concrete made with Florida materials and Florida mixes for Florida aggressive environments. Assessing those effects is critical prior to accepting cements under such provision. Furthermore, identification of additional data to be required by the state agencies, from cement suppliers, needs to be established to ensure sound structural concrete.

Due to the wide extent of the problem in the State of Florida and its timing, it is critical that this issue be addressed, timely, so that the opinions of the Florida Department of Transportation is based on documented research and scientific findings. The purpose of the proposed research is to address the effect of higher sulfur trioxide content and its effect on Florida's concrete properties and durability.

CHAPTER II

LITERATURE REVIEW

The main source of sulfates in Portland cement is calcium sulfate. Various forms of calcium sulfate (anhydrite, hemihydrate, dihydrate; sulfate-bearing industrial by products) are incorporated in Portland cement in order to control the setting characteristics. Sulfates may be added in several forms; that is, natural or industrial-grade calcium sulfate dihydrate (gypsum) or anhydrite. Additional sulfates can also originate from clinker, during clinkering process, either from raw feed or from products of fuel combustion. If sulfates form during clinkering, they can exist as: alkali sulfates, double salts and occasionally in the form of calcium sulfate anhydrite or other phases [1]. Common clinker sulfates are: arcanite, K_2SO_4, calcium langbeinite, $KC_2\hat{S}_3$, and aphthitelite $K_3N\hat{S}_4$. Lately, and due to stricter environmental regulations on sulfur emission, clinker sulfates present in Portland cements appear to be rising.

The chemical requirements for Portland cement, ASTM C 150, allow wide variations in chemical composition. The only limits placed on all cement types are MgO, SO_3, and alkalis (optional). The phenomenon of optimum sulfate levels in Portland cements has occupied researchers for decades. Michaelis, in 1870, identified the influence of 2% inter-ground raw gypsum on regulating the setting time of cements [2]. This discovery became of greater significance when the effect of gypsum on mortar strength was also observed.

Research conducted on the effect of gypsum content on the setting time showed that there is no advantage in gypsum additions beyond 2% $CaSO_4$. This work was conducted on one type of clinker ground with variable gypsum content. The increment of variation was 0.5% and the range studied was from 0.5- 7%. Maximum retardation was reported at 1.5% $CaSO_4$; however, gypsum additions above this level did not affect initial setting time. In 1920, ASTM adopted a limit of 2.0% SO_3; however, the recommended limit increased consistently since its adoption. This may be due to several factors that include higher sulfur fuels used in burning clinker, and increased cement fineness [2].

Several researchers observed a relationship between gypsum content and strength. One of first studies to address the effect of gypsum on cementitious system strength was published in 1924. The researchers also observed that gypsum interground 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 that has been confirmed by others [2].

ASTM Committee C-1 Subcommittee B conducted a study in 1931 on the effect of SO_3 content in cements of variable tricalcium aluminate content. The findings indicated a lower SO_3 content (1.75%) for cements of tricalcium aluminate content of 8%. This limit could be increased to 2.5% if C_3A of cements is higher (11-16%). Kanare et al. [2] indicated that optimums determined in this work varied depending on the property and age at which it has been assessed. A close look at data generated by the ASTM study indicated 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. Based on the results of this research in addition to others, Kanare et al [2] indicated that an optimum might only exist for a specific set of conditions that are well defined and include: cement fineness, form and reactivity of calcium sulfate, curing conditions, temperature during storage, and age of testing. Additionally, an optimum for strength does not necessarily identify one for volume stability.

In 1946, William Lerch [3] published a study on the effects of gypsum content on cement hydration. Twelve commercial clinkers covering a wide range of chemical composition that is generally encountered in Portland cements were selected for this study. Various SO_3 contents with fineness held uniform at about 1900 sq. cm. per gram were used. Additionally, five of the clinkers were ground to different fineness while maintaining SO_3 content fixed at 1.8 %. The main findings of this study indicate that gypsum content affect several cement properties; namely, heat of hydration, setting behavior, strength, drying shrinkage and expansion. As for initial hydration, gypsum was found to act as a retarder or an accelerator depending on the composition of the cement. The alkali and tricalcium aluminate content were found to be of significance on the level of gypsum allowed in cements. Another property that seems to affect gypsum content was cement fineness.

Lerch [3] definition of properly retarded cement was based on the shape of the heat of hydration curve during the first 30 hours of reaction with water. Properly retarded cement, according to Lerch, is “one that contains the minimum quantity of gypsum required to give a heat-liberation curve that shows only 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 would develop the highest strength and the lowest contraction”.

As for the influence of the alkalis and C_3A content of cements on the gypsum requirements, the results showed that cements of low alkali but high C_3A content require larger additions of gypsum than those of low alkali and low C_3A content. For cements of the same C_3A content, those high in alkalis appear to react more rapidly with gypsum. Therefore, for those cements, higher gypsum additions for proper retardation are required than for lower alkali cements. The results also indicate that the type of alkali was also significant. The presence of alkalis in the aluminate phases of cements appeared to render those phases more reactive with water than aluminates that are alkali free. Cements containing Na_2O required larger gypsum additions than cements containing the same equivalent quantity of K_2O. As to the effect of fineness, it was concluded that increasing the fineness of cements increases gypsum requirement. It was indicated that increasing fineness resulted in a corresponding increase in the quantity of aluminate phases available for reaction with the water at early ages and thereby increases the required amount of gypsum for proper retardation.

For cements of low C_3A and alkali content, mixing and normal setting can occur, without gypsum addition. This was found to be due to the formation of an amorphous hydrated calcium ferrite that precipitated on the surface of cement particles. The amorphous material seals the surface of cement particles and retards subsequent hydration. However, if gypsum was added to those cements, then a crystalline calcium sulfoferrite hydrate was formed which did not seal the surface of cement particles and consequently accelerated hydration.

The results of the physical tests showed that strength, drying shrinkage and expansion depend on the amount of gypsum incorporated in cement. Generally speaking, the findings followed the same conclusions as those obtained from the heat of hydration and setting behavior. For cements low in C_3A and alkalis, larger additions of gypsum did not result in strength increase or reduction in contraction. However, for high C_3A or high alkali content cements, strength, contraction and expansion benefited from larger additions of gypsum.

The most important conclusion of Lerch's work [3] was that there is no global optimum for gypsum content, and that optimum depends on cement composition, fineness and the property. Lerch's work was faulted in some areas [2]; namely, using a variable w/c ratio, using Bogue determined phase content which can be significantly different from the actual phase content, not indicating that optimum gypsum content for strength is age dependent, and finally the study did not include high alkali sulfate clinkers.

Other properties of gypsum that were found to affect concrete hydration process and properties included fineness and form. Panigrahy et.al. [4] studied gypsum differential comminution when ground in different mills. In this study, two types of industrial cement mills were used; namely, ball mill (BM) and vertical roller mill (VRM). Identical clinker and gypsum mixes were ground to the same Blaine fineness and the setting time of cements produced from those mills was studied. For all cases studied, it was found that cements produced from VRM had lower setting time than those produced by BM. An explanation for the observed trends was offered through X-ray diffraction studies. The diffraction patterns showed, consistently, lower peak intensity for gypsum in BM cements compared to those produced from VRM. No other crystalline calcium sulfate phase(s) could be identified on the spectra. This lead to the conclusion that BM cements contained a significant portion of calcium sulfates in an amorphous form. It was concluded that differential amorphism of gypsum was caused by grinding. Additionally, the degree of crystallinity of gypsum, as determined by X-ray diffraction (XRD), changed with the type of grinding mill.

This in turn caused changes in the setting times of similar cements ground to identical Blaine fineness.

Goswami et al [5] studied the effect of different forms of calcium sulfate on cement properties. It was found that calcium sulfate, added to clinker in the form of gypsum, could dehydrate to different degrees depending on the type of mill used in the grinding process. Grinding to similar fineness but in different types of industrial mills was found to subject gypsum to different degrees of dehydration to hemihydrate. Additionally, it was found that hemihydrate had an effect on ettringite formation during the early stages of cement hydration. This was accompanied by a 10% reduction in strength and retardation in the setting time. It was suggested that the fall in strength was due to re-hydration of part of the hemihydrate present in the cement.

The above findings on the effects of gypsum form and fineness on setting behavior of cements were shared by other investigators [2]. An additional concern that was reported is the possible presence of large inert gypsum particles in commercial cements. The presence of such particles might influence work conducted on the optimization of gypsum content in commercial cements.

As mentioned earlier, gypsum addition is not the only sulfate source in Portland cements. Sulfates can also exist in clinker during the clinkering and manufacturing process. Several studies have been conducted on the effects of alkali sulfates, their role and interaction with gypsum and their effects on cement hydration, flow and strength development. Tang et al [6] studied the influence of sulfate sources and different types of sulfates on Portland cement hydration. In this work, cements were synthesized by blending a Type I low alkali Portland cement clinker with sulfate salts. A quantitative X-ray diffraction method was developed to measure the rate of C_3A and C_4AF consumption as a function of hydration time. The results indicated a strong dependence of aluminate phase consumption on the rate of solubility of sulfates. Sulfate solubility depends on the cation type. Differences were also observed regarding how gypsum was introduced to the cement. It was found that interground gypsum was more effective in controlling initial hydration of the aluminate phases than interblended gypsum. Tang et al did not agree that gypsum content for high alkali cements need to be increased in all cases. Rather, they emphasized that the solubility, reactivity and physical distribution of alkali sulfates was as equally important.

The study showed that there is an approximate inverse correlation between initial aluminate consumption and initial mini-slump of pastes. The data for the paste compressive strength showed the positive effect of soluble alkali on 1-day strengths, but at 7 and 28 days, there was insignificant 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.

Osbaeck et al [7] studied the effect of alkalis present as sulfates and as constituents of clinker minerals on the hydration properties of Portland cement. In this study, a series of laboratory-burned clinkers were prepared that differed only in content and distribution of alkalis. The clinker was ground to cement fineness with different gypsum content. The results indicate that soluble alkali sulfates affected strength. They concluded that this effect was dependant on gypsum content of cement.

Increased SO_3 levels in clinker of the same alkali content imply that a greater fraction of the alkalis will be present in the sulfate form. Increasing alkali sulfates was found to result in an increase in early strength and a decrease in later strength. This effect was modified through the addition of gypsum. It was also found that the effect of alkali sulfates on increasing early strength was absent when gypsum content was increased to above optimum values. Similarly, high gypsum content tends to diminish the negative effect of alkalis on later strength.

This behavior was assumed to occur due to the effect of alkalis on entraining air in mortar through the premature precipitation of structures such as syngenite, ettringite and gypsum. Such an indirect effect of alkalis would introduce a general reduction of strength at all ages, but most pronounced at later age. The favorable influence of higher gypsum content, on the later strength development of the alkali rich cements, was explained as follows: in a system rich in alkali sulfates, gypsum removal is rapid and in order to counteract this effect, higher gypsum content is required in high alkali sulfate cement. Additionally, this research indicated that gypsum effect on strength might be related to its impact on tricalcium silicate and aluminate hydration.

Jelenic et al [8] 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 initiated in order to find out whether the effects observed on pure systems maybe applicable for the determination of optimum gypsum content in Portland cement of high alkali sulfates. The findings of this study was in agreement with Lerchs [3]; namely, for a clinker rich in alite, moderate in C_3A, and low in alkalis, maximum strength tends to shift to lower values of SO_3 as 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 higher values of SO_3 was noticeable. They found that for clinker rich in alkalis and sulfates, gypsum had a remarkable effect on accelerating alite hydration at all ages. For low alkali clinker, the accelerating effect was noticed up to the age of 28 days but not at 90 days. It was concluded that the differences in the optimum SO_3 content is influenced not only by the difference in C_3A content of clinkers, but also by the difference in alkalis, as well as the amount of the primary water soluble sulfates.

Additionally, it was found that only a part of the SO_3 content appears to be used in ettringite formation. However, since there was no monosulfoaluminates detected and the total SO_3 content determined by chemical analysis was significantly higher than that used in ettringite formation, it was concluded that a significant amount of sulfates must be incorporated in C-$(S,\hat{S})$-H. The amount of SO_3 incorporated in the C-$(S,\hat{S})$-H was found to be dependent on the total sulfate content. Increasing total SO_3 content of cement appeared to increase the amount of sulfates incorporated in the gel. It was found that increasing sulfate content of C-$(S,\hat{S})$-H resulted in 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 due to difference in the composition of the liquid phase in the system. For the clinker rich in alkalis and sulfates, it is expected that the liquid phase will consequently contain higher alkali and sulfate concentrations. Also, this system is expected to have a higher amount of glassy phase.

The authors also noticed differences in the morphological characteristics of the ettringite formed by the two clinker samples. Ettringite coatings on C_3A grains appeared to be influenced by the amount of the gypsum added. For a higher SO_3/C_3A ratio, the retardation of C_3A hydration was found to be more effective due to a faster reaction that presumably generates a denser coating.

Jawed et al [9] in their review on alkalis in cement, stated that there is a worldwide trend towards higher alkali content in cements. This is due to various factors including changes in clinkers pyproprocessing technology, energy conservation, limited availability of low-alkali raw feed, 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. Alkalis in clinker can be divided to: alkali sulfates, alkali aluminates and aluminoferrites, and alkali silicates. Also in some cases, alkalis may occur in the form of carbonates.

SO_3 content of clinker makes prior demand on the alkalis with the resulting quantity of alkali sulfate determined by the ratio of total clinker sulfate to total alkali. The remaining sulfates form double salts or anhydrite. Alkalis that remain is then distributed between silicates, aluminates, and aluminoferrites phases.

Aluminates and ferrites are known to accommodate about half or more of the available alkalis. The introduction of alkalis into clinker minerals is also known to modify the crystal structure of C_3A. The cubic crystal structure of tricalcium aluminate is modified through the introduction of 2.8% equivalent Na_2O or 1.8% equivalent K_2O to an orthorhombic lattice. This structure transformation is accompanied by a change in hydraulic reactivity.

It was also reported, in this review, that gypsum introduction to alkali containing raw feeds appears to have a positive effect on the clinkering process. Positive effects include: a decrease in clinkering temperature, an increase in C_3S content, and formation of well-developed alite and belite crystals. Different alkali containing raw materials require different amounts of gypsum. It was reported that the use of a proper amount of gypsum results in higher kiln output and a reduction in fuel consumption.

Alexander et al [10] conducted a study on the influence of SO_3 content of cement on creep, drying shrinkage, and strength of concrete. Three commercial cements were used and each was produced at four different levels of SO_3 . Creep and drying shrinkage were found to be very sensitive to SO_3 content. An optimum appeared to exist for those two properties, which was higher for creep than drying shrinkage. The optimum SO_3 content was found to be independent of the duration of the creep test. However, the established optimum for creep was found to be high (3-4%). This appeared to be the case even for cements of moderate fineness and low alkali and tricalcium aluminate contents. For compressive strength measurements at different ages and variable SO_3 content, the findings indicated that compressive strength was independent of or linearly related to SO_3 content. Concrete elastic modulus was not affected by SO_3 content of cement.

Alexander et al [11] also studied the long-term effects of SO_3 content of cements on strength of normal and high strength concrete. In this study, six different cements were used, with each manufactured at four different SO_3 levels. Several mixes were prepared. The design of concrete mixes was done using constant w/c ratios or a specified nominal strength. The cements used had a wide range of C_3S (48-60%) and C_3A (2-15%) content. However, phase content was only determined through bogue calculations. Cements fineness appeared to be reasonably constant (335-365 m^2/Kg). Similar to the findings of their previous study, a well-defined optimum SO_3 content for strength appears to be the exception rather than the rule. The relationship between strength and SO_3 content at 28 days appears to be unchanged at 1 year. There appears to be a relationship between the C_3A and SO_3 content of cement and concrete strength. This relationship was found to be influenced by the w/c ratio used in mixing concrete.

Several researchers investigated the effect of SO_3 on the hydration of the silicate phases. One common indication among the findings of different researchers is that any level of gypsum, which keeps the hydration liquid saturated at early ages, will result in accelerating alite hydration [2]. 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. The general findings from the literature indicate that sulfate substitution for silica sites would typically result in a gel that is intrinsically inferior [2]. While gypsum presence appears to increase the amount of gel produced, gel formed in the presence of gypsum appears to be of inferior quality especially at later age.

Bentur [12] studied the effect of gypsum on the hydration and strength of C_3S pastes prepared with variable gypsum content. The main objective of this study was to clarify the nature of gypsum interaction with C_3S and its hydration product C-S-H. Constant water to solid ratio of 0.43 was used and the gypsum content was varied from 0 to 9%. Pure tricalcium silicate was synthesized and the gypsum used was analytical grade. The effect of gypsum content on the compressive strength appears to change 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 at a maximum with 2% gypsum. This trend was sustained at longer hydration times (28 and 90 days). For pure C3S pastes, the strength at 90 days was equal to the paste with 2% gypsum, and higher than those attained by mixes of higher gypsum content.

On studying the effect of gypsum content on the calcium oxide to silica ratio (C/S) of the paste, it was found that in pure C_3S pastes, the ratio decreases as hydration advances; however, beyond 70% hydration, it tends to stabilize. In the pastes containing gypsum, the C/S ratio increases up to approximately 60% hydration but decreases as hydration continues.

Bentur also found that in 70% hydrated pastes, the C/S ratio increases with sulfate to silica ratio ($\hat{S}/S$). It was explained that this trend is indicative of a chemical change occurring in the CSH gel. Such chemical change affects the mechanical quality of C-S-H gel. This effect appears to be critical or of significance after a certain period of hydration. This was thought to be due to the slow nature of the reaction between sulfates and C-S-H gel.

This research indicates that the nature of the interaction of gypsum and tricalcium silicate is a quality/quantity relationship. Increasing gypsum content not only increases the amount of hydrated C_3S but also the substitution of silicates by sulfates in the gel. The later appears to affect the C/S ratio of the gel, which in turn is related linearly to the intrinsic strength of the gel. Optimum gypsum content was therefore defined in terms of optimizing the gel quantity and quality.

Menetrier et al [13] studied also the effect of gypsum on tricalcium silicate hydration. Tricalcium silicate was mixed with 2.5% gypsum and the hydration products were analyzed at selected times. Incorporation of gypsum was found to increase the dissolution rate of anhydrous tricalcium silicate. Additionally, microscopy studies revealed a significant incorporation of sulfates in amorphous C-S-H. It appears that in addition to modifying the chemical constituents of the silicate gel, gypsum presence affects the gel morphology. It was observed that in the presence of gypsum, and during the first few minutes of hydration, C-S-H "honeycomb" was less developed.

Reviewing data published on the role of gypsum in cement hydration appears, therefore, to indicate that the most important effect of gypsum is to accelerate C_3S hydration in addition to its important role in retarding C_3A and C_4AF hydration.

Shalom et al [14] studied the effects of aluminate and sulfate contents on the hydration and strength of Portland cement pastes and mortars. Three cements were used of similar silicate content but variable tricalcium aluminate content. Additionally, one of the cements was used to vary gypsum content through doping. Bound water was determined and used as a measure of the binder quantity. Another ratio that was used in data analysis was Free Lime to Bound Water Ratio (FLWR). FLWR is a measure of the chemical constitution and quality of the gel. It was indicated that the presence of gypsum and aluminate would influence hydration through the formation of sulfoaluminates, or indirectly, through their effect on tricalcium silicate hydration rate and quality of its hydration products.

It was also found that for cements hydrated for similar time, higher compressive strength was associated with the higher FLWR but not bound water. It was suggested that in these cases high FLWR indicates the existence of a high quality gel. According to this explanation, high FLWR implies low Bound Lime to Bound Water Ratio (BLWR) and since bound water is proportional to the amount of hydrated silicates, then low BLWR would therefore imply a low CaO/SiO_2 ratio in gel. A low lime to silica ratio is indicative of a large proportion of double-layered structure of tobermorite in the gel. Such formation was found to lead to higher strength. It was concluded that an optimum combination of both parameters, expressing quality and quantity of gel, would ultimately lead to the highest compressive strength.

The role of gypsum on the compressive strength of Portland cement clinker was also addressed by Soroka et al [15]. The research focused on studying the effect of added gypsum on paste prepared from the same clinker but with a different initial porosity. The findings indicate that there was improvement in compressive strength with additions of gypsum. The higher strength was found to be due to lower porosity and better quality gel. 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 also due to the pressure generated by ettringite formation. The findings of this study seem to contradict Bentur findings [12]. Additionally, it fails to explain the retrogression in strength observed in adding gypsum to tricalcium silicate paste [16].

Soroka et al [16] conducted another study on the effect of gypsum on properties and internal structure of Portland cement pastes. A clinker of low tricalcium silicate content was used in this study. The clinker was ground to three different fineness values. Gypsum was blended with cements at different levels and up to 5%. Pastes were prepared at a constant water to cement ratio of 0.30. The results indicate that there is optimum gypsum content with respect to drying shrinkage and strength. Optimum gypsum content appeared to be dependent on cement fineness, an observation that is consistent with the findings of others. Only minimal accelerating effects were observed in regards to degree of hydration on gypsum additions. However, for gypsum content above optimum, there was a significant retardation in the rate of hydration. It was stipulated that the retardation effect might explain strength retrogression that was observed with gypsum additions above the optimum.

The effect of gypsum content was found to be neither due to pore size refinement nor to an increase in the density of the hydration products.

Skalny et al [17] investigated the mechanism of retardation of the C_3A dissolution rate by $CaSO_4$ and concluded that the retardation of C_3A-H interaction in the presence of gypsum is due to the formation of an aluminum rich layer on the surface of tricalcium aluminate particles. This layer would subsequently adsorb calcium ions, which due to their positive charge would attract sulfate ions. This mechanism was offered to explain the retardation of aluminate hydration. It was suggested that ettringite formation is not the primary mechanism by which tricalcium aluminate hydration is retarded at high gypsum concentrations.

Collepardi et al [18] studied the hydration of tricalcium aluminate in the presence of lime and sulfates of calcium or sodium. The results of this work confirmed the mechanism by which gypsum retards C_3A hydration is based on ettringite coating C_3A grains. Several preparations with variable gypsum to tricalcium aluminate ratios were tested. Additional mixes incorporating lime and sodium sulfate were also included in the study. Calorimetric, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) coupled with x-ray diffraction (XRD) scans were conducted on the mixes.

The heat of evolution curves indicated that lime and gypsum decrease the amount of heat liberated. Incorporation of sodium sulfate did not generate any reduction in the heat of hydration peak. The findings of the calorimetric studies indicate that gypsum is more effective as a retarder than lime. A combination of lime and gypsum appears to be more effective in retarding tricalcium aluminate hydration. DTA data indicated that ettringite was present at 15 minutes of hydration of tricalcium aluminate in the presence of gypsum. The amount of ettringite appeared to increase up to 24 hours of hydration. At 24 hours, monosulfoaluminates started to appear in the X-ray scans. Similar trends were reported for gypsum and lime mixes. Additionally C_3AH_6 did not form. In mixes incorporating sodium sulfate, neither ettringite nor gypsum was present.

The results presented indicate that retardation of tricalcium aluminate in the presence of lime and gypsum is primarily due to ettringite formation. It was also proposed that these formations occur by a through-solution mechanism and that the triclaium aluminates act as a nucleation site for those crystals. It is also suggested that ettringite is much more effective in retarding the hydration of tricalcium aluminate than C_4AH_x . It was also found that gypsum and ettringite are more effective in retarding C_3A hydration than either one alone. This was explained by the finer morphology of ettringite in the presence of lime compared to those formed in its absence. It was concluded that the finer ettringite morphology was more effective in retarding C_3A as such morphology can fit better the irregularly shaped C_3A particles. It was also concluded that the finer ettringite morphology is capable of generating expansion through attracting large number of water molecules.

Rilem Committee 68-MMH [19], in their report on hydration of tricalcium aluminate and tetracalcium aluminoferrite in the presence of calcium sulfate [8], summarized the state of knowledge as follows:

"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."

The effect of temperature is another important parameter that is considered to affect optimum gypsum content for proper retardation. This effect might be expected due to the role of temperature on accelerating the hydration of C_3A. It is also expected that the mixing and curing temperatures would be significant on determining optimum gypsum content for adequate retardation. These effects of temperature on C_3A hydration are compensated for by the similar strong effect of temperature on increasing the rate of hydration of C_3S. This counter effect results in mild effects of an increase in temperature on optimum gypsum content [2].

CHAPTER III

RESULTS AND DISCUSSION

Introduction

The objective of the current study is to address the effect of higher sulfur trioxide content in Portland cement on the properties and durability of concrete. Towards satisfying the above objective, four ASTM Portland cements were used in this investigation. The results of the study will be presented in this chapter.

3.1 Characterization of the As-Received Materials

3.1.1 Blaine Fineness

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

Table 1. Blaine Fineness of As-Received Cements

Cement	**1**	**2**	**3**	**4**
Blaine Fineness(cm^2/g)	3820	3800	3880	3840

3.1.2 Oxide Chemical Composition of As-Received Materials

Oxide chemical composition of as-received materials; namely, cement, fly ash and slag was determined using x-ray fluorescence spectroscopy. The results are presented in Tables-2 through 4 where it can be seen that cements 1 and 4 have higher sulfur trioxide content than cements 2 and 3. In addition, alkali content of cement 1 is marginally higher than that indicated in ASTM-C150. Cement 4 had the lowest alkali content among all cements. In addition, Cements 1 and 3 share higher potassium oxide content while cements 3 and 4 have traces of sodium oxide.

Oxide chemical analysis on mineral admixtures indicate that slag is high in its alumina content and fly ash can be classified as Class F in accordance with ASTM C-618.

Mineralogical phase content for the as-received cements determined through Bogue calculations and x-ray Rietveld analysis are depicted in Tables 5 and 6 respectively. The results indicate the discrepancy between both quantification techniques. This finding is not surprising as it is well established that cement compound content as determined through Bogue calculations are essentially an approximation. X-ray quantification of the as-received cements reveals differences in the phase content of the as-received cements. First, tricalcium silicate content for cements 1 and 2 is similar and at about 54 % approximately while for cements 3 and 4 it is 61 and 67% respectively. However, all cements share similar tricalcium aluminate content of approximately 3 (+/- 1%) except for cement 1 which has more than double this amount. Additional differences exist in the form and content of calcium sulfate as will be discussed later. Fly ash mineralogical analysis indicates the presence of four crystalline phases; namely, quartz, mullite, hematite and magnetite.

Table 2. Oxide Chemical Composition of As-received Cements

Analyte	Cement 1	Cement 2	Cement 3	Cement 4
SiO_2	20.78	21.15	20.55	20.52
Al_2O_3	5.47	4.78	4.4	4.92
Fe_2O_3	4.15	3.76	3.61	3.7
CaO	63.14	64.41	64.6	64.31
MgO	0.85	0.95	2.47	1.71
SO_3	2.88	2.58	2.54	2.81
Na_2O	0.26	0.18	0.03	0.01
K_2O	0.6	0.34	0.54	0.41
TiO_2	0.32	0.33	0.22	0.27
P_2O_5	0.18	0.07	0.05	0.03
Mn_2O_3	0.03	0.03	0.05	0.04
SrO	0.05	0.12	0.02	0.04
Cr_2O_3	0.02	<0.01	0.02	<0.01
ZnO	0.02	0.02	0.03	<0.01
L.O.I. (950°C)	1.3	1.15	0.99	1.08
Total	100.04	99.84	100.12	99.83
Alkalies as Na_2O	0.65	0.4	0.39	0.27
Free CaO	0.44	1.05	2.31	0.92

Table 3. Oxide Chemical Composition of Class F Fly Ash

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

Table 4. Oxide Chemical Composition of Slag

Analyte	Weight Percent (w/o)
SiO_2	34.01
Al_2O_3	12.93
Fe_2O_3	0.57
CaO	42.99
MgO	6.04
SO_3	1.84
Na_2O	0.16
K_2O	0.30
TiO_2	0.49
P_2O_5	<0.01
Mn_2O_3	0.03
SrO	0.05
Cr_2O_3	<.01
ZnO	<.01
L.O.I. (950°C)	0.43
Total	99.24
Alkalies as Na_2O	0.36

Table 5. Mineralogical Phase Content of Cements (Bogue Formulae)

Compound	Cement 1	Cement 2	Cement 3	Cement 4
C_3S	48	57	65	60
C_2S	23	18	10	14
C_3A	7	6	6	7
C_4AF	13	11	11	11
C_3S/C_2S	2.1	3.2	65	4.3

Table 6. Rietveld X-Ray Mineralogical Analysis of Cements

Compound	Cement 1	Cement 2	Cement 3	Cement 4
C_3S (%)	51	54	61	67
C_2S(%)	28	25	19	15
Cubic C_3A (%)	8	4	3	2
C_4AF (%)	10	13	12	14
MgO (%)	0	0	1.8	0.0
C_3S/C_2S (%)	2.3	2.2	3.2	4.5

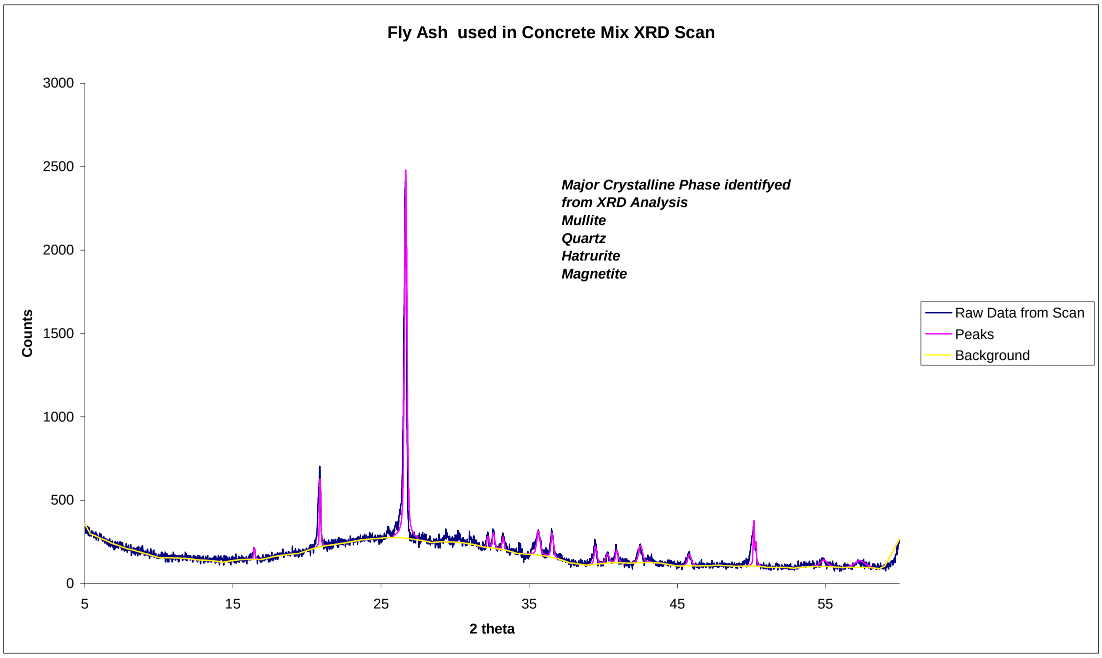


Figure 1. X-Ray diffraction pattern of Class F fly ash

3.1.3 Differential Scanning Calorimeter Data for Sulfate Phases

Different forms of calcium sulfate have different solubilities and therefore are expected to affect the initial hydration process. In addition, presence of highly soluble syngenite is also expected to affect the initial hydration process. Differential scanning calorimetric studies on the as-received cements indicate the presence of syngenite in cements 1 and 4. In addition, the results depicted in Table-7 show that calcium sulfate present in Cements 1 and 2 are equally distributed between gypsum and hemihydrate. For cement 3 and 4, calcium sulfate is primarily present as hemihydrate. Cement 4 also contains appreciable amounts of anhydrite.

Table 7. Differentials Scanning Calorimetric Analysis

Compound	1	2	3	4
Gypsum	1.5	1.5		0.3
Hemihydrate	1.5	1.6	2.1	1.8
Syngenite	0.3			.4
Anhydrite*			0.5	1.3

*= Determined through x-ray diffraction

3.2 Mortar Durability

3.2.1 Optimum Sulfur Trioxide Content and Expansion in Lime

Optimum SO_3 content was determined in accordance to ASTM C563. Table -8 shows the optimum sulfur trioxide content as determined per ASTM C563 for the four as-received cements. The results indicate that all cements have sulfur trioxide content below the determined optimum. Following optimum determination, expansion of mortar bars was monitored per ASTM C-1038. Several doping levels were used in this test in excess of the optimum SO_3 content determined previously. Increasing the SO_3 content beyond 3% is allowed per ASTM specification C150 provision (d), provided the cement satisfies the expansion criteria set per ASTM C1038. In order to address the extent of applicability or limitation of such provision, all cements were doped with SO_3 above the optimum and expansion was monitored as a function of time. The results are depicted in Figures 2 through 5.

Table 8. Optimum SO_3 Content of Cement

Cement	Optimum SO_3 Content (w/o)
Cement 1	2.97
Cement 2	2.78
Cement 3	2.86
Cement 4	2.92

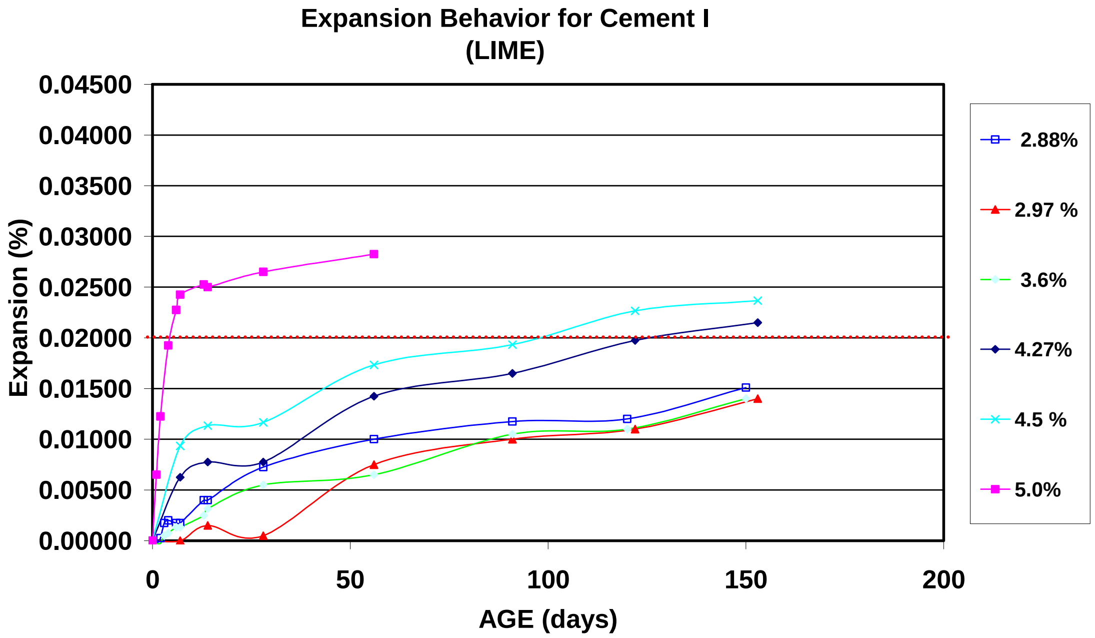


Figure 2. Expansion behavior of cement 1 at variable SO_3 content

From Figure 2 it can be seen that increasing the SO_3 content of the as-received cement up to 4.5% did not generate failure as defined in ASTM-C1038. Increasing the SO_3 content to 3.6% did not generate adverse expansion in lime for cement 1. On increasing the doping level to 4.2, it can be observed that the mortar experienced expansion above the as-received SO_3 content. At a doping level of 5% SO_3, cement 1 did not pass ASTM C-1038 expansion criteria.

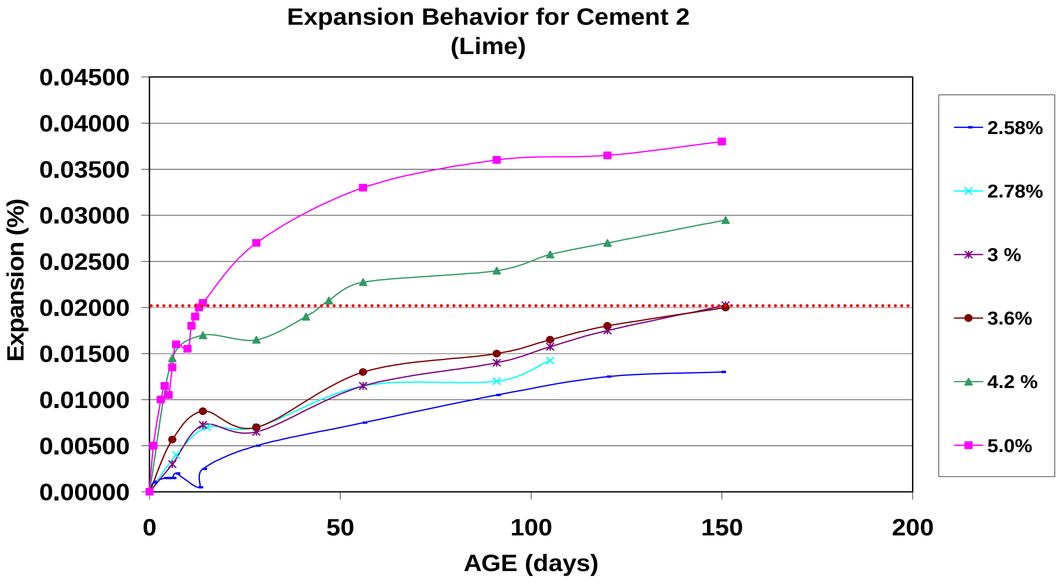


Figure 3. Expansion behavior of Cement 2 at variable SO3 content

For cement 2, increasing the SO_3 content generated an increase in expansion for all levels of doping. However, increasing the SO_3 content up to 4.2% did not result in failure. It is interesting to note that the expansion at 3.6% SO_3 is distinctively higher that that experienced by cement 1. However, the expansion assessed at this level of doping, for both cements, is far less than the specified limit.

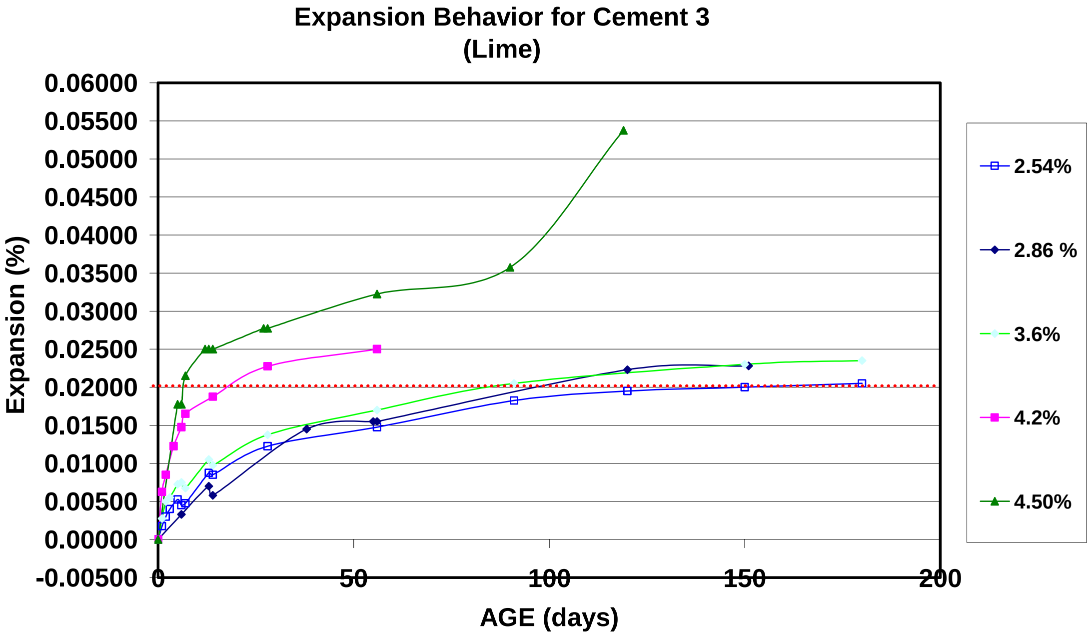


Figure 4. Expansion behavior of cement 3 at variable SO_3 content

For cement 3, increasing the SO_3 content from the as-received to 4.2% increased expansion in lime; however, such an increase did not generate failure in accordance with ASTM C 1038 criterion. Failure occurred at an SO_3 content of 4.5%. Additionally, it is observed that while increasing the SO_3 content to 3.6% did not generate significant variation in the expansion behavior, expansion for this cement is higher than those experienced by cements 1 and 2.

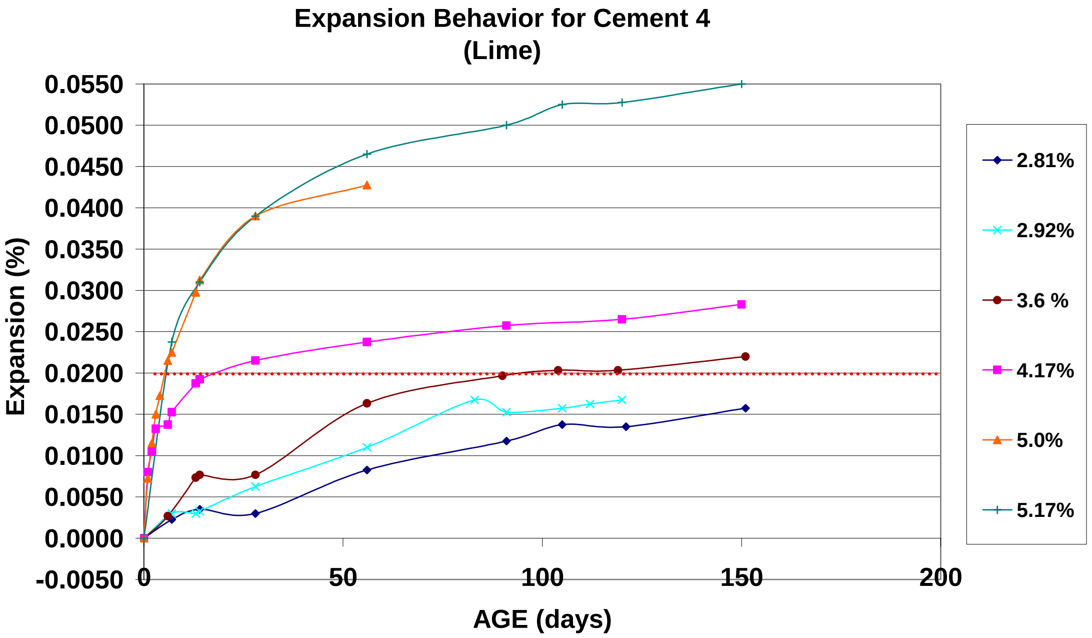


Figure 5. Expansion behavior of cement 4 at variable SO_3 content

For cement 4, increasing SO_3 content in small increments resulted in clear increase in expansion. The behavior is similar to that experienced by cement 2. Again, increasing the SO_3 content up to 4.17 did not generate failure according to the criteria set by ASTM C-1038.

In conclusion, the results indicate that increasing the cement SO_3 content up to an SO_3 content of approximately 4.2% did not generate failure for any of the cements studied here. In one case, for cement 1, even a doping level of 4.5%, did not generate failure. For this cement, the expansion measured at 4.5% SO_3 was comparable to expansion values experienced by the other three cements at an SO3 content of only 3.6%. It appears that for cement 1, with higher alkali and tricalcium aluminate content, higher levels of sulfure trioxide content are required to generate the same expansion in lime. Previous research indicates the effects of high alkali content on suppressing expansion under ambient conditions. However, if concrete, during its service, is exposed to cycles of wetting and drying or elevated temperatures, cements of high alkali and sulfate contents are susceptible to experience failure due to internal sulfate attack or delayed ettringite formation. For cement systems that are high in alkalis and tricalcium aluminate content, ASTM C1038 might not be adequate to provide durability assessment at longer ages.

3.2.2 Expansion Behavior of Doped Cements in Sodium Sulfate Solution

Durability assessment was conducted through expansion and strength measurements at selected times. The first sets of experiments were conducted on the as-received cement mortars. In addition, as-received cements were doped to increase the total sulfur trioxide content to 3.0 and 3.6%. The results are depicted in Figures 6 through 10.

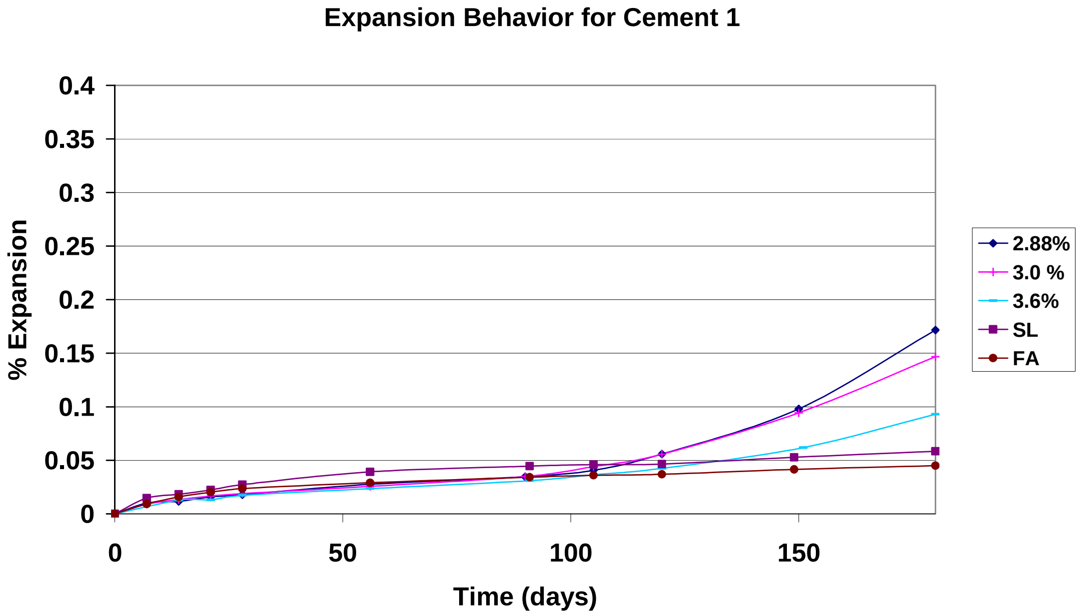


Figure 6. Expansion Behavior of cement 1 at variable SO_3 content

For cement 1 with highest tricalcium aluminate and highest alkali content, Figure-1 reveals that increasing the SO_3 content to 3.0 and 3.6 results in extending the induction period. For the period reported here of 180 days, it appears that increasing the SO_3 content decreases the expansion experienced by the mortar in sulfate solution. Incorporation of mineral admixtures as a replacement for cement results in a clear reduction in expansion.

Figure 7 shows the expansion behavior for cement 2. This cement has similar tricalcium silicate content as cement 1 but the later has double the tricalcium aluminate content of the former. The results presented in Figure 7 indicate a different expansion behavior with increasing the SO_3 content. It can be seen from Figure 7 that there is an increase in expansion with increasing SO_3 content of the cement.

Increasing the as-received SO_3 content to 3.0 and 3.6 % results in a corresponding increase in expansion by a factor of 2 and 3 respectively. However, similar to Cement 1, use of pozzolanic admixture modified the expansion behavior. At 180 days, fly ash mortar shows similar expansion to the as-received cement.

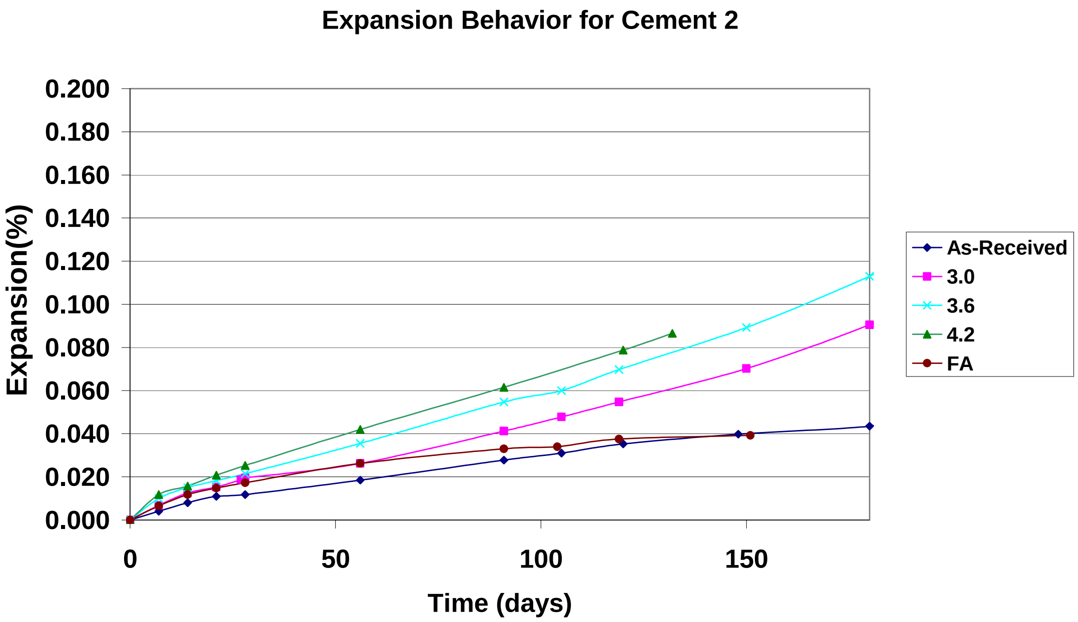


Figure 7. Expansion behavior of cement 2 at variable SO_3 content

For cements 3 and 4 with higher tricalcium silicate content, incorporation of mineral admixtures reduced the expansion, especially for cement 4. However, the effect of increasing the SO_3 content on the expansion behavior for those two cements was different. In the case of cement 3, increasing the SO_3 content up to 3.6%, did not generate significant variation in expansion behavior. Further increase of SO_3 content to 4.0% increased the expansion at 180 days substantially.

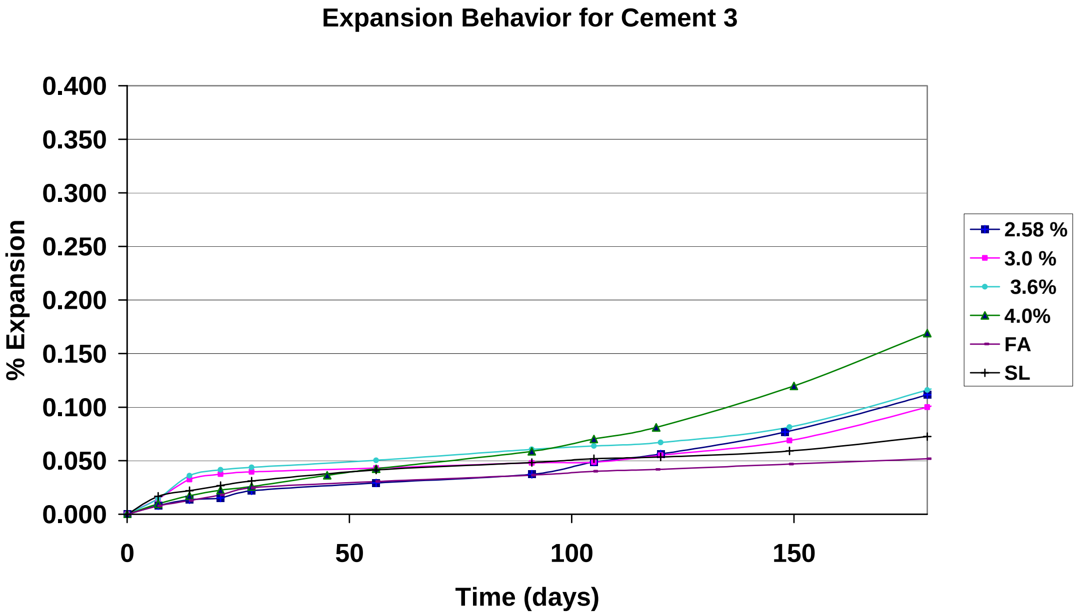


Figure 8. Expansion behavior of cement 3 at variable SO_3 content

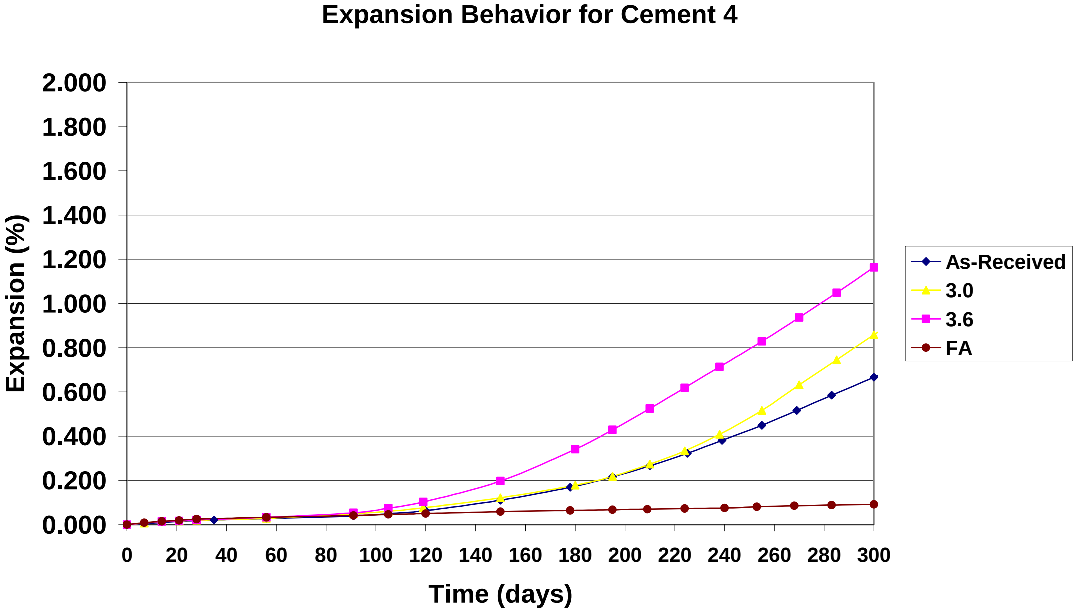


Figure 9. Expansion behavior of cement 4 at variable SO_3 content

Increasing the SO_3 content for cement 4 initiated an increase in expansion for all levels of doping above the as-received SO_3 content. The increase in expansion associated with increasing the SO_3 content to 3.0 was not significant up to 180 days as can be seen from Figure 9. However, at 300 days the increase in expansion with increasing the SO_3 content to 3.0 and 3.6 is apparent. Blending cement with fly ash appears to have a significant effect on reducing the expansion. Increasing the SO_3 content to 3.6% increases expansion by a factor of 2; however, fly ash incorporation results in reduction in the expansion by a factor of 5. Figure 10 shows additional doping levels for Cement 4. It can be seen that there is a continuous increase in expansion with SO_3 content and at 5.17%, the increase in expansion at 180 days is 5 fold compared to the as-received mix.

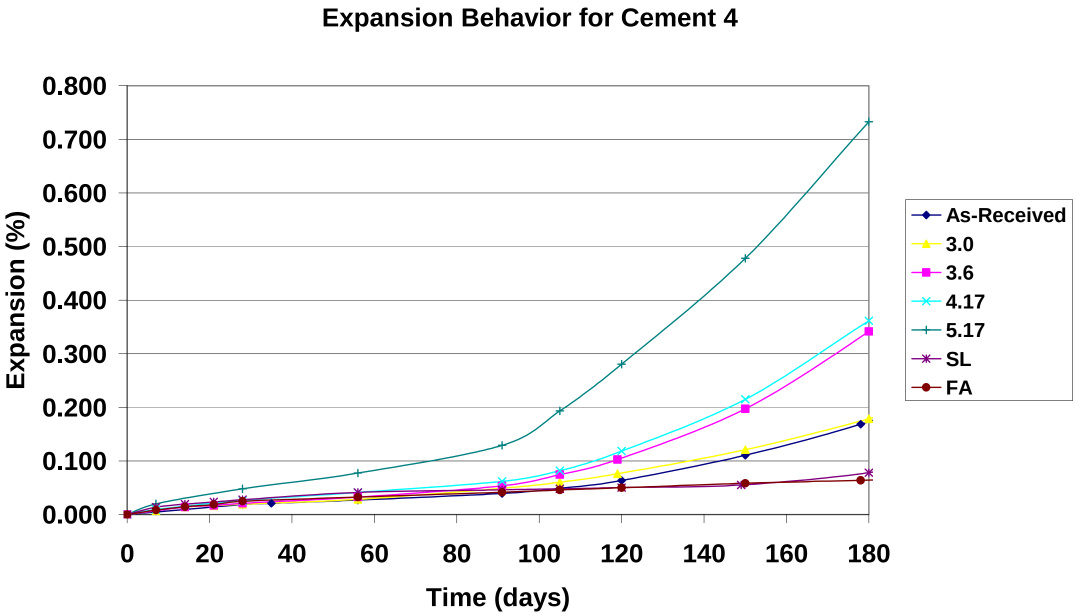


Figure 10. Expansion behavior of cement 4 at variable SO_3 content

In conclusion, it can be seen that increasing the SO_3 content of the cements studied here had variable effect on their durability assessed by expansion in lime and sulfate. Among the cements studied here, only cement 1 did not show changes in expansion behavior on increasing the SO_3 content to 3.6%. However, all other cements experienced increase in expansion on increasing the SO_3 content to 3.6%. Among those cements, Cement 4 had the worst tolerance to increasing the SO_3 content. Cement 4 had the lowest tricalcium aluminate and alkali content while the highest tricalcium silicate content among the cements studied here. It is to be noted that sulfate expansion is not the only deterioration mechanism operating in a high sulfate system. The nature of tricalcium silicate hydrate gel has been reported to affect the performance of cements with higher SO_3 content. Increasing the SO_3 content has been shown to result in a gel of inferior properties of that is higher in its C/S ratio and porosity [12].

3.2.3 Compressive Strength

The effect of increasing the SO_3 content on durability of Portland cement was also assessed through compressive strength measurements. Data were collected for the as-received cements and also for cements with increased SO_3 content. Increasing the SO_3 content was achieved through doping with gypsum. Doping levels adopted here were for an SO_3 content of 3.0 and 3.6%. Mortar cubes were prepared in accordance with ASTM C-109 and C305. Two exposure conditions were used; namely, lime and 5% sodium sulfate solution.

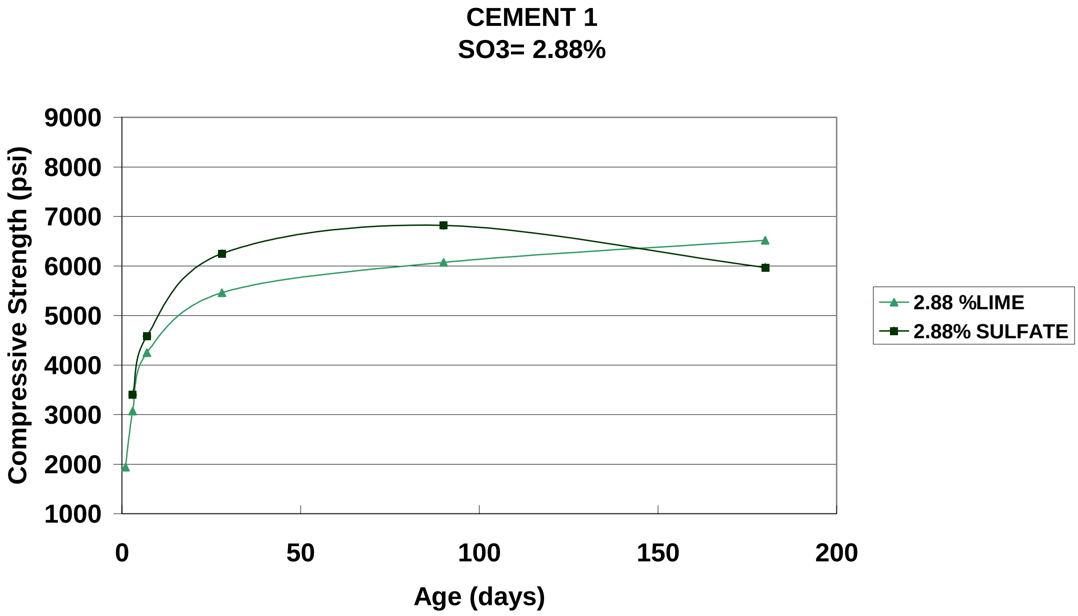


Figure 11. Variation of Compressive strength for cement 1

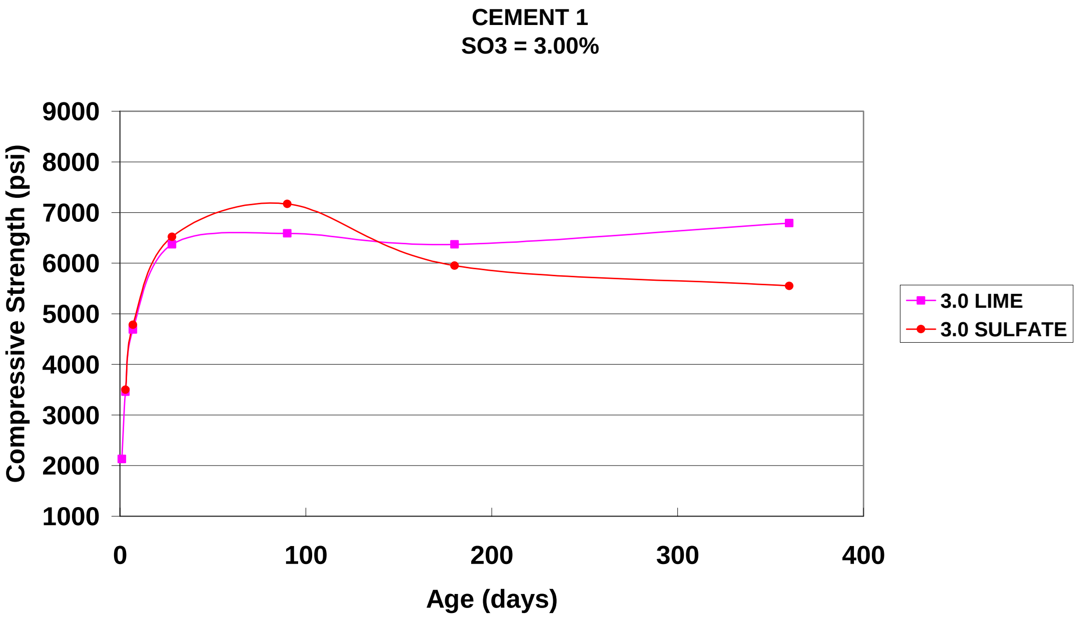


Figure 12. Variation of Compressive strength for Cement 1

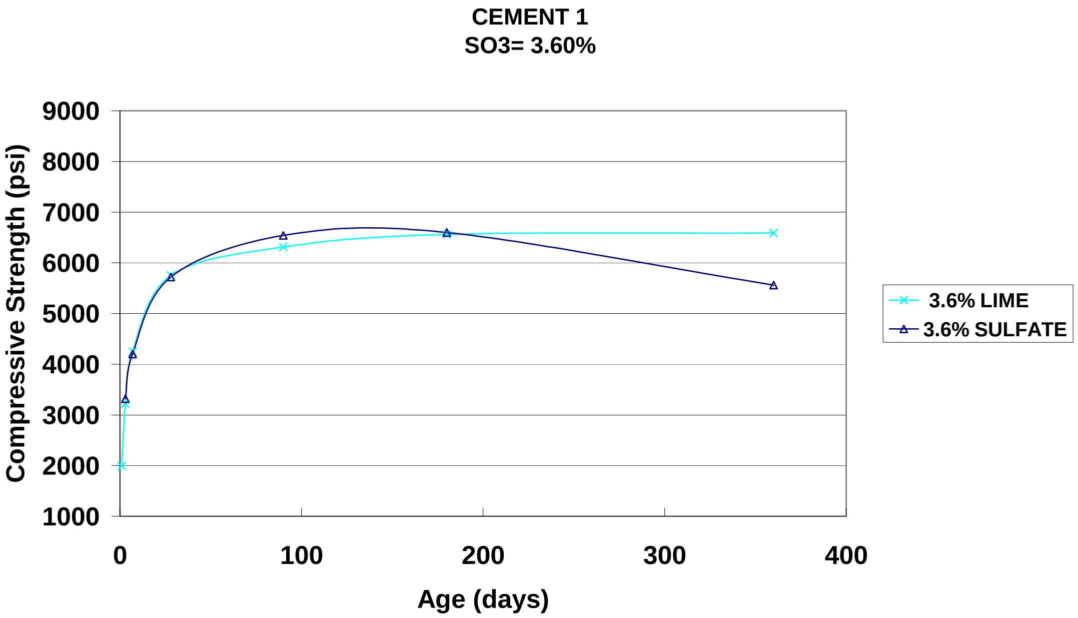


Figure 13. Variation of Compressive strength for Cement 1

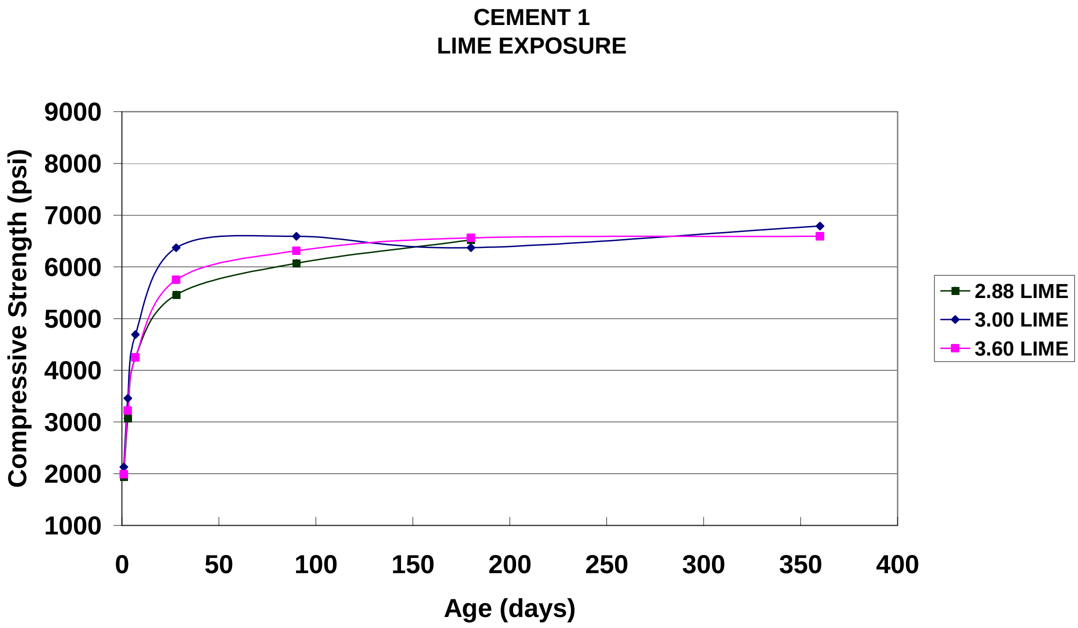


Figure 14. Variation of compressive strength for Cement 1

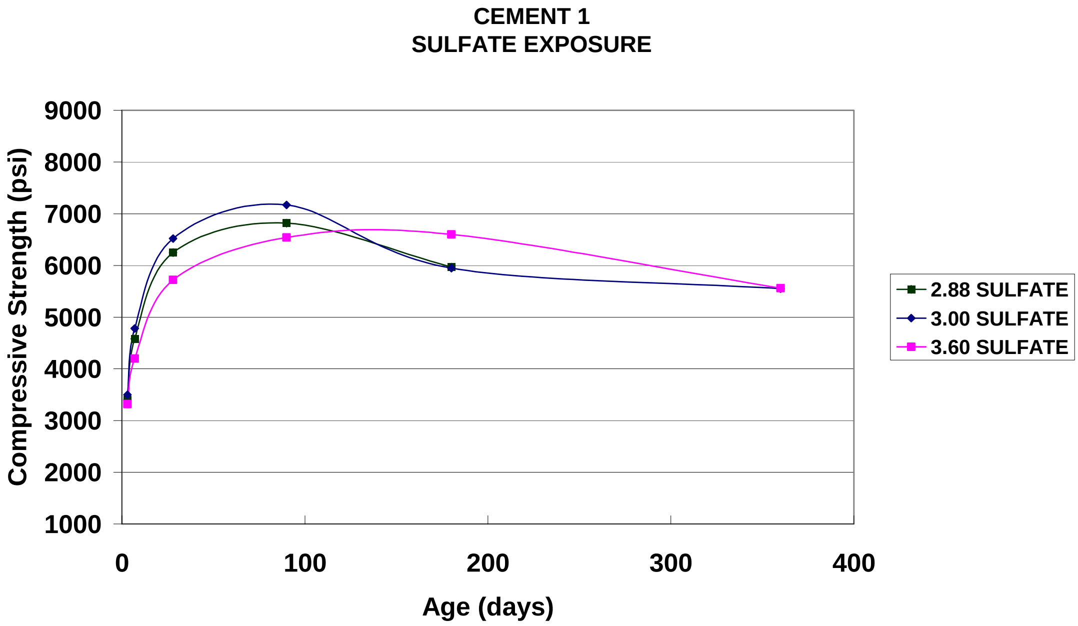


Figure 15. Variation of compressive strength for Cement 1

The results presented for cement 1 indicate that for lime exposure there is continuous strength gain with time, independent of the SO_3 content of the cement. It is also observed that for an SO_3 content of 3.0%, the early rate of strength gain was highest. On sulfate exposure and for SO_3 content up to 3.0%, there appears to be a drop in strength at 180 days of more than 1,000 psi compared to lime exposure.

Further increase in SO_3 content to 3.6%, delayed the initiation of strength drop to 360 days. However, the magnitude of strength drop was similar to that experienced by cement 1 with a doping level of 3.0%. It appears that increasing the SO_3 content for cement 1 from 3.0% to 3.6% delayed the initiation of deterioration.

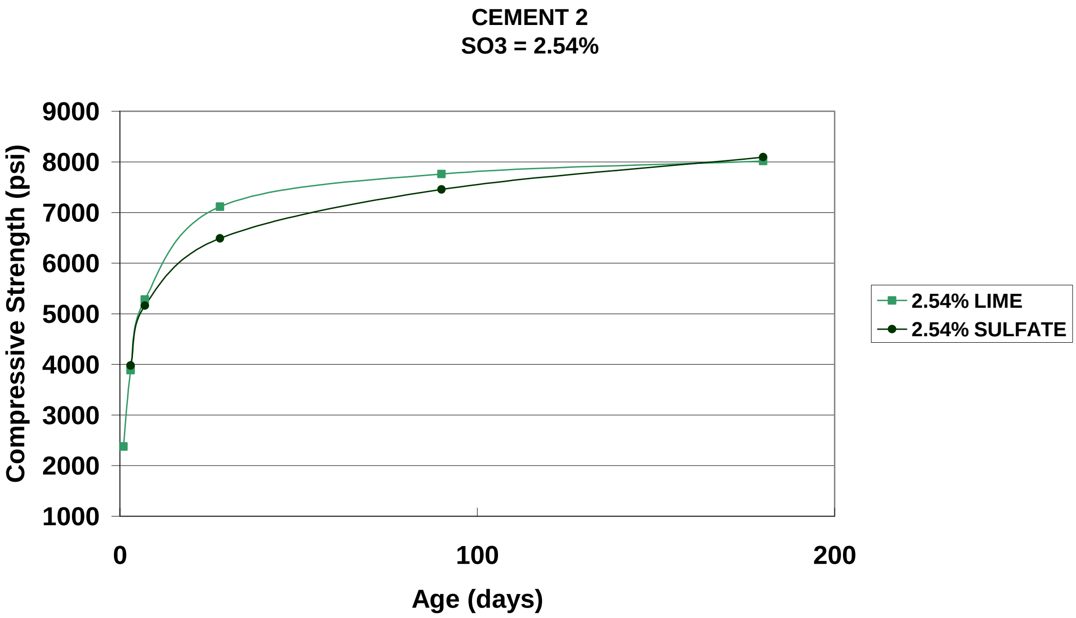


Figure 16. Variation of compressive strength for cement 2

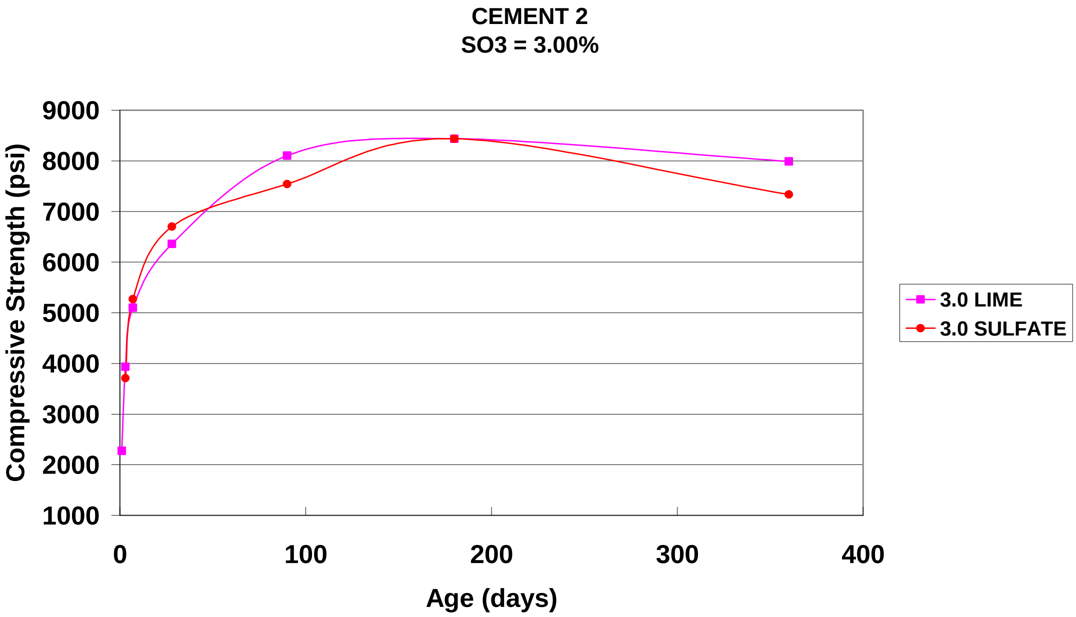


Figure 17. Variation of compressive strength for cement 2

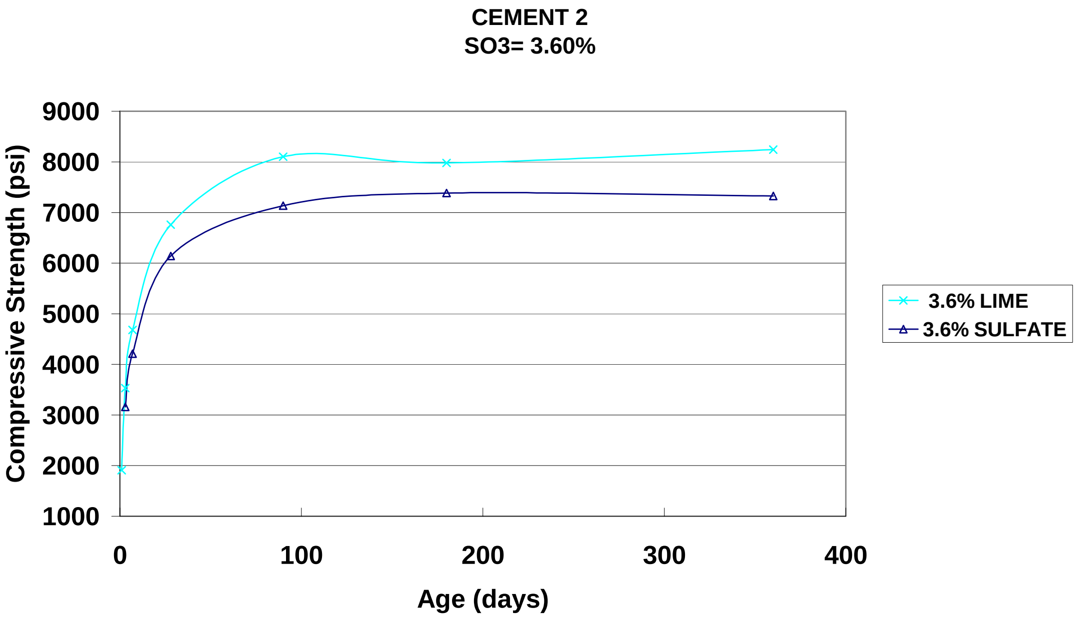


Figure 18. Variation of compressive strength for cement 2

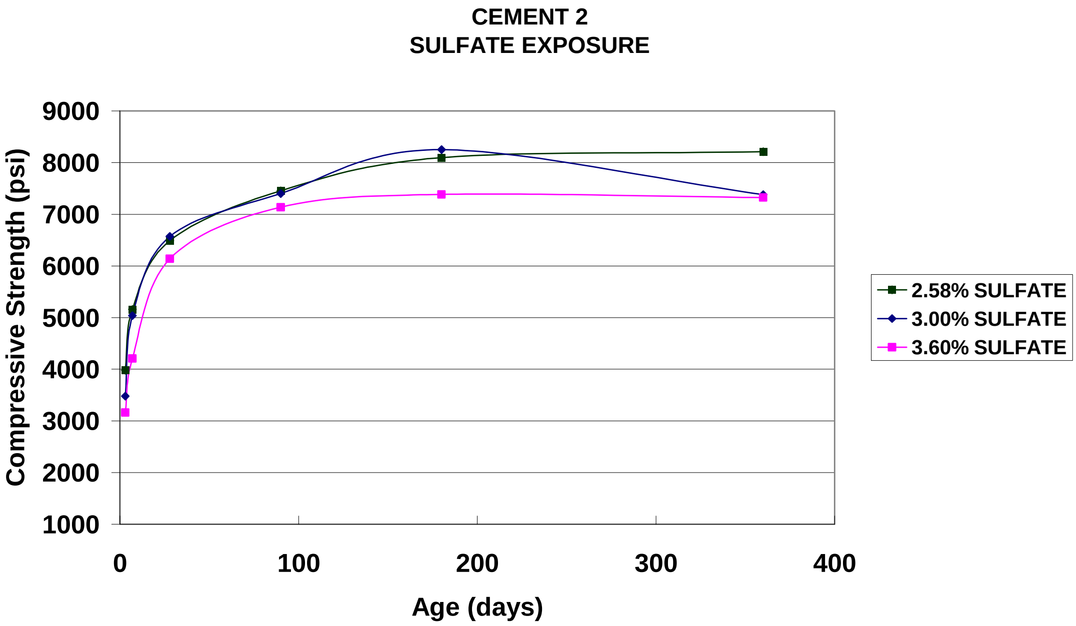


Figure 19. Variation of compressive strength for cement 2

Comparing the strength behavior in lime and sulfate indicates that for cement 2, and for SO_3 content up to 3.0, the variation in compressive strength in lime versus sulfate seems to be very similar up to 180 days of exposure. However, at an SO_3 content of 3.6%, the strength in sulfate is approximately 500 and 1,000 psi lower than in lime at 180 and 360 days respectively. For mortar with an SO_3 content of 3.0%, strength in lime compared to sulfate exposure reveals similar differences but of lower magnitude. For cement 2, increasing the SO_3 content above the as-received condition, did not yield favorable behavior in sulfate environment. The strength behavior for Cement 2 in the as-received condition showed continuous increase with exposure to lime or sulfate up to 180 days. Sulfate exposures up to 360 days did not show any detrimental effects on this cement. On increasing the SO_3 content to 3.0%, a drop in strength was observed for mortar exposed to sulfates at 360 days. On further increase of SO_3 content to 3.6%, mortar specimens exposed to the sulfate environment were approximately 600 to 1,000 psi lower in strength than those in lime. This appears to be the case from 7 days to 360 days.

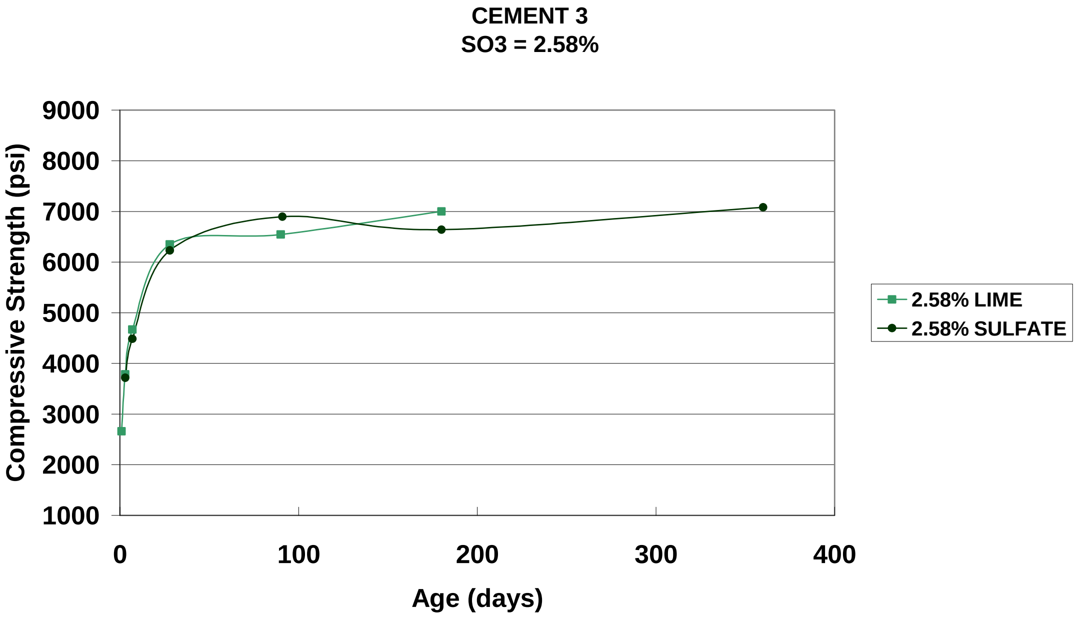


Figure 20. Variation of compressive strength for cement 3

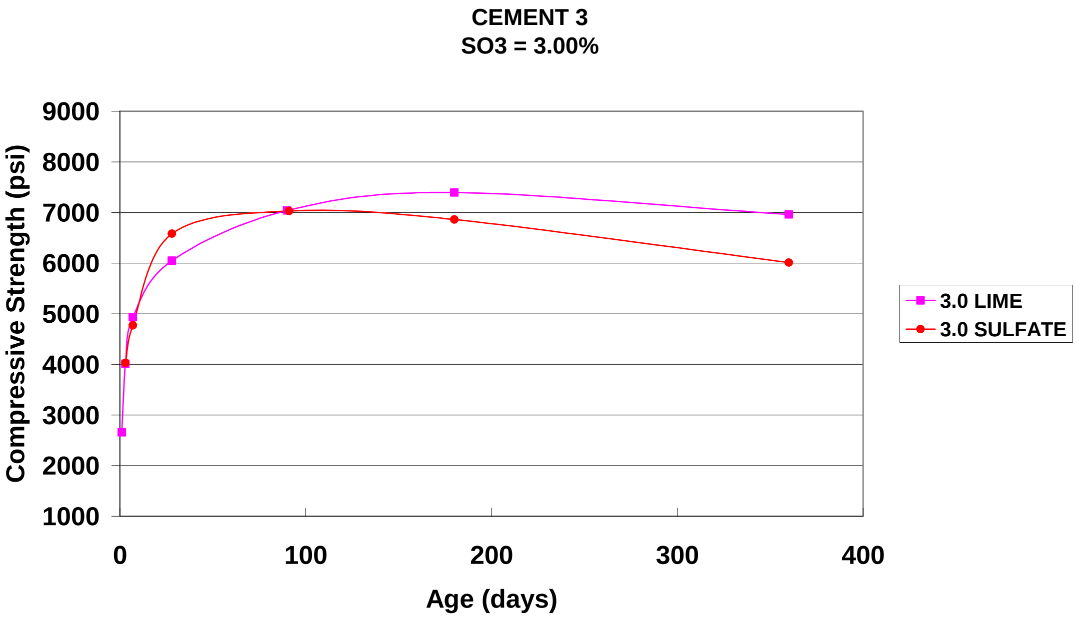


Figure 21. Variation of compressive strength for cement 3

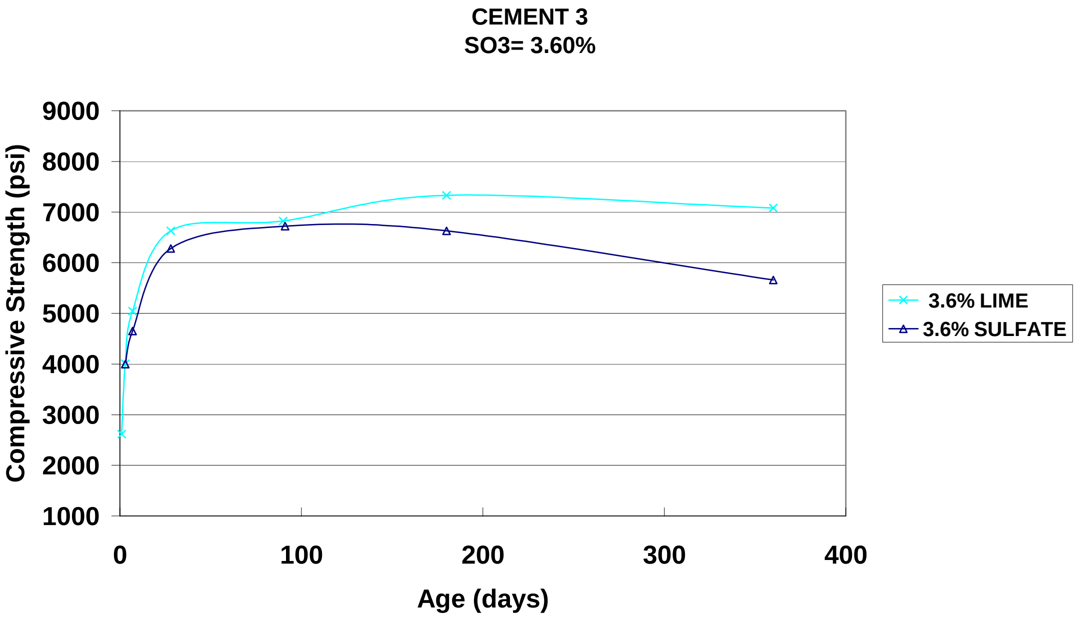


Figure 22. Variation of compressive strength for cement 3

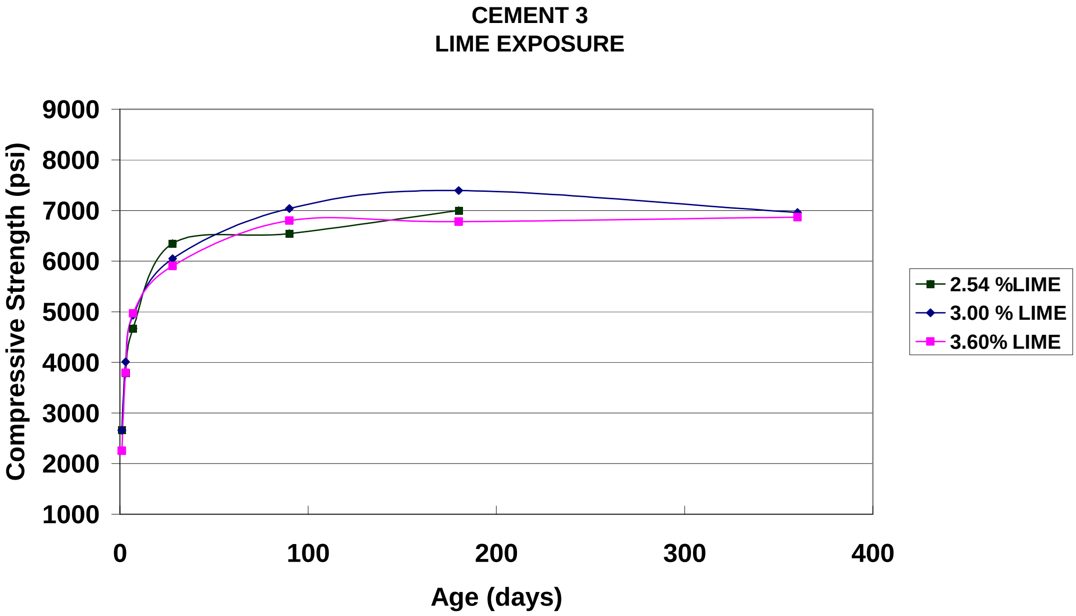


Figure 23. Variation of compressive strength for cement 3

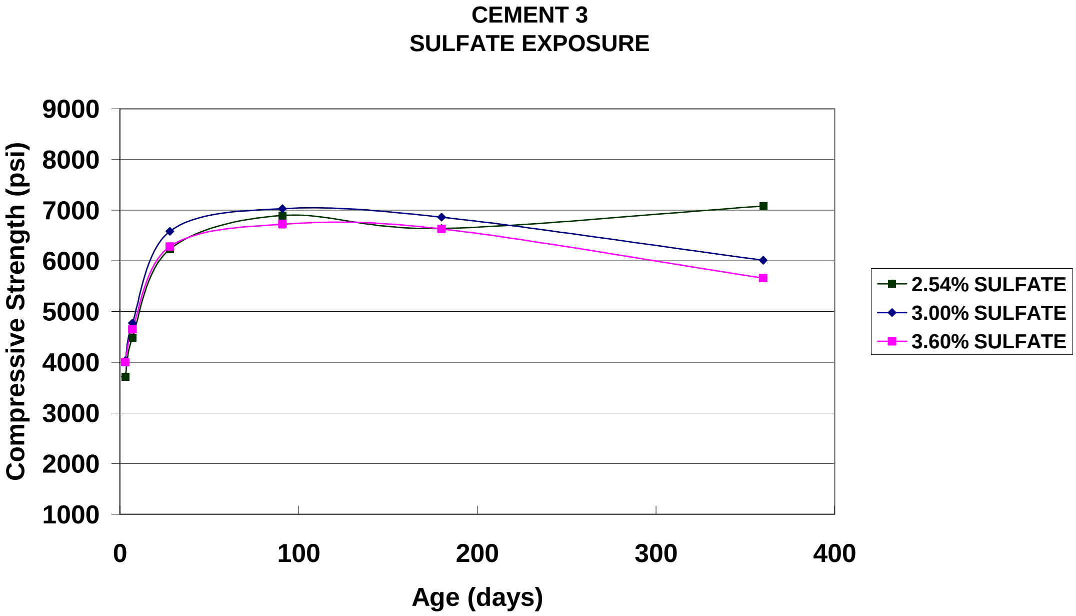


Figure 24. Variation of compressive strength for cement 3

Results for cement 3 depicted in Figures 20 through 24 indicate that for the cement in the as-received condition, strength gain continues up to 180 days for lime exposure. Sulfate exposure up to 360 days did not reveal any deterioration. The results indicate that increasing the SO_3 content to 3.0% results in reduction in the compressive strength of approximately 1,000 psi in comparison with the strength in lime. Increasing the SO_3 to 3.6% results in a higher strength drop as can be seen from Figure 22. First, mortar exposed to sulfates had lower strength values compared to those exposed to lime from an age of 7 days. At 180 and 360 days, specimens exposed to sulfate solution experienced a drop of 600 and 1,200 psi respectively when compared to those cured in lime.

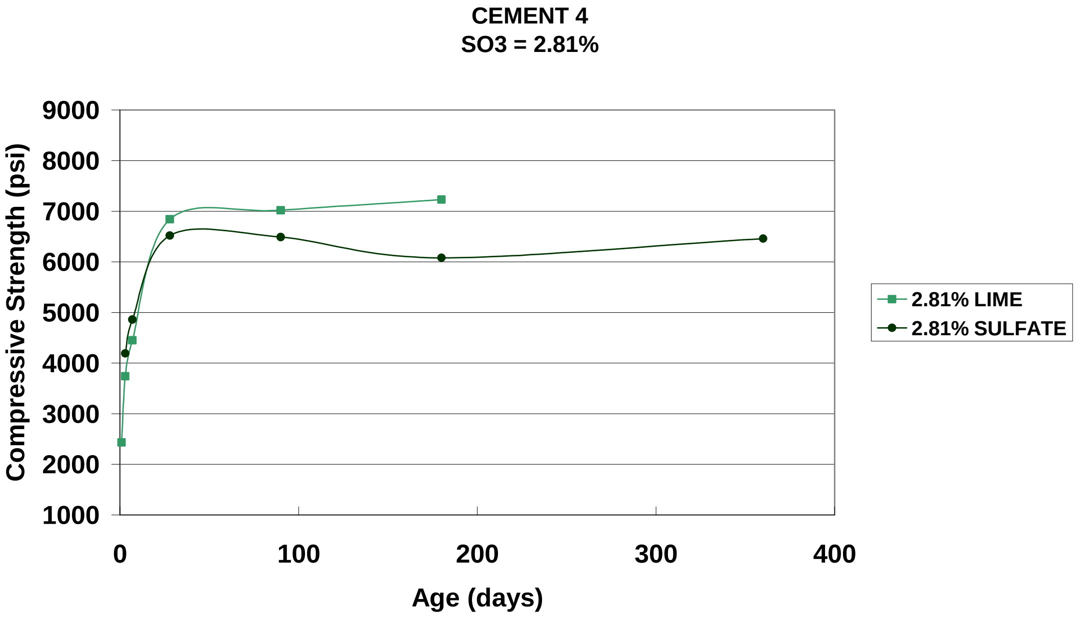


Figure 25. Variation of compressive strength for cement 4

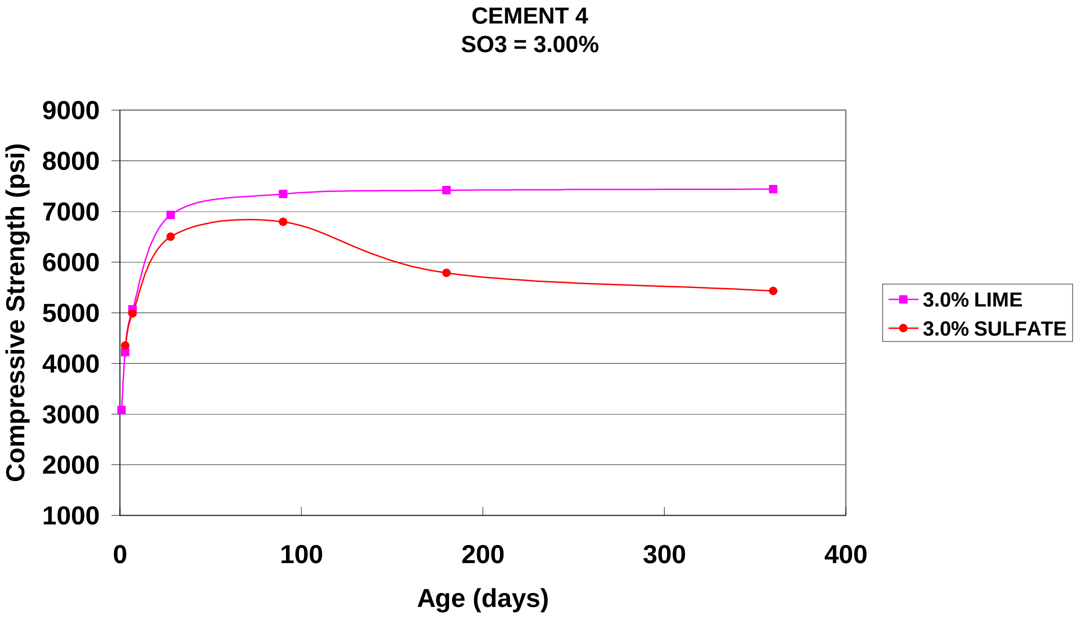


Figure 26. Variation of compressive strength for cement 4

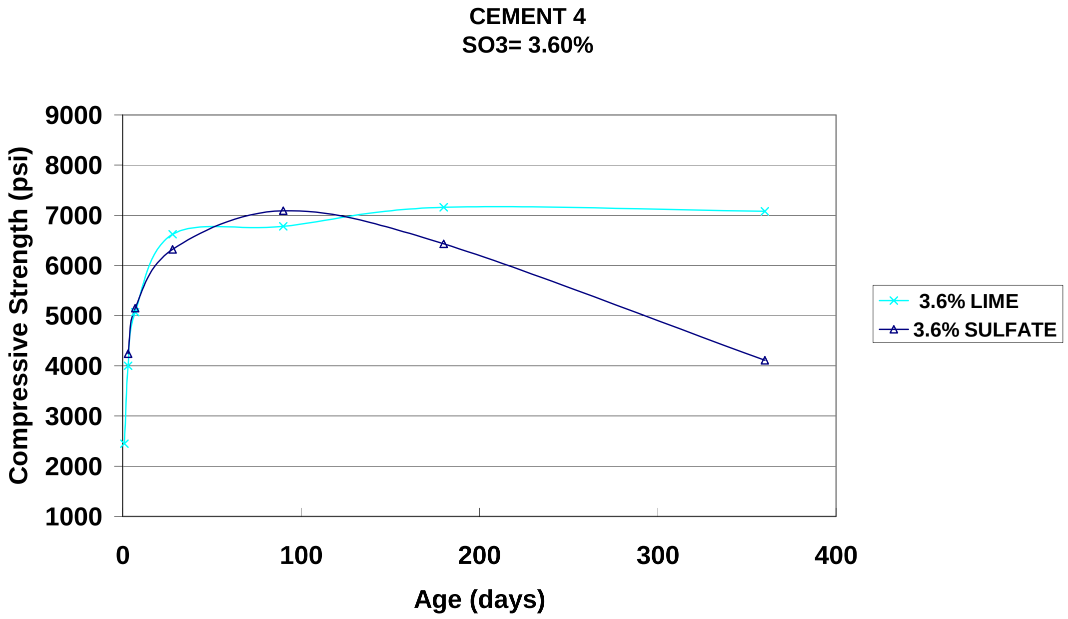


Figure 27. Variation of compressive strength for cement 4

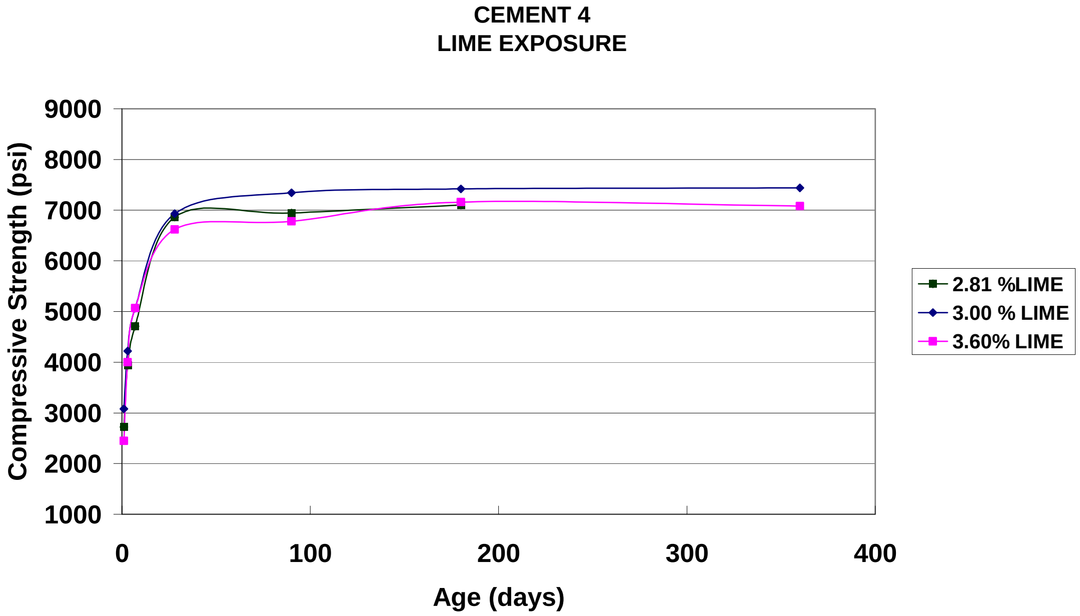


Figure 28. Variation of compressive strength for cement 4

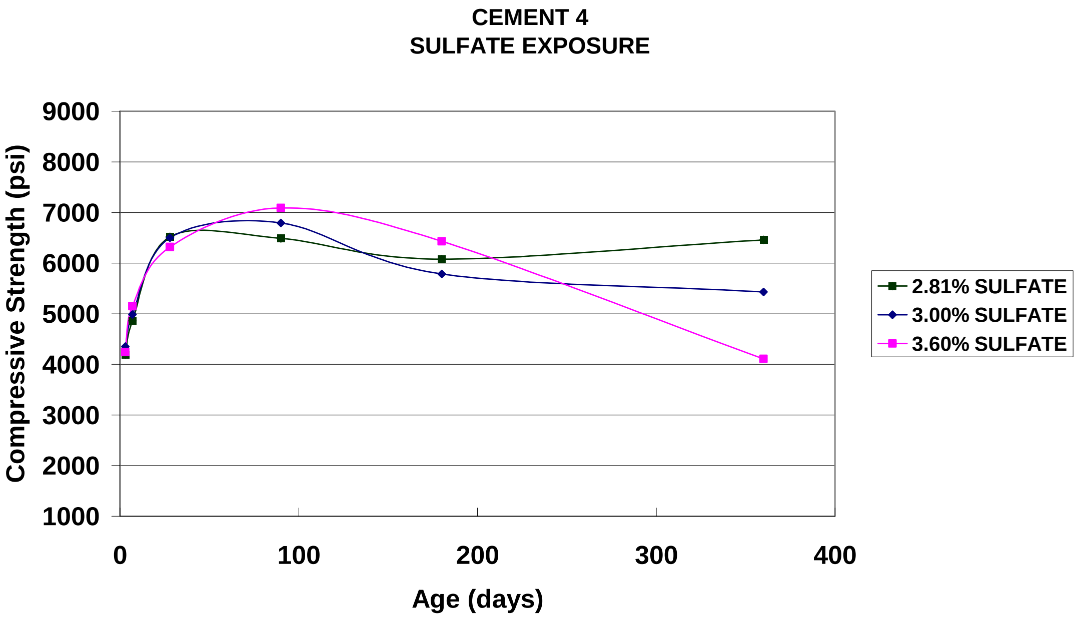


Figure 29. Variation of compressive strength for cement 4

Increasing sulfur trioxide content in cement 4 to 3% increased strength in lime. However, increasing SO_3 content in this cement had pronounced effects on the durability in sodium sulfate as can be observed form the presented data. On increasing the SO_3 content to 3.0% and 3.6% a corresponding drop in mortar strength ($\sigma_{lime} - \sigma_{sulfate}$) of 2,000 and 3,000 psi occurred.

It appears that for all the cements studied here, increasing the SO_3 content beyond 3% was detrimental on the behavior of cement in a sulfate environment. The response of individual cements to the increase in the SO_3 content appears to depend on their chemical composition. In spite of that all of the cements studied here showed a lower strength on exposure to sulfate compared to lime exposure of at least 1,000 psi at an SO_3 level of 3.6% and an age of 360 days. Observation of the deterioration process indicates that initiation of compromised behavior depends on cement composition. Though cement 1 experienced similar strength drop at 360 days of exposure to sulfate to cement 2, the initiation of deterioration was not apparent till 360 days. It is to be noted that cement 1 shares similar fineness and tricalcium silicate content with cement 2. However, cement 1 has higher tricalcium aluminate content and has marginally higher alkali content. Such observation should indicate that extended periods of time might be crucial in addressing durability behavior of cements of high alkali and or aluminate content.

If we consider the cements that share the same tricalcium aluminate content but variable tricalcium silicate content; that is cement 2, 3 and 4, and comparing sulfate exposure at different SO3 contents, the following can be concluded:

1. Increasing SO_3 content increases strength drop.
2. At an SO_3 content of 3.6%, increasing tricalcium silicate content of cement, increases the magnitude of strength drop.

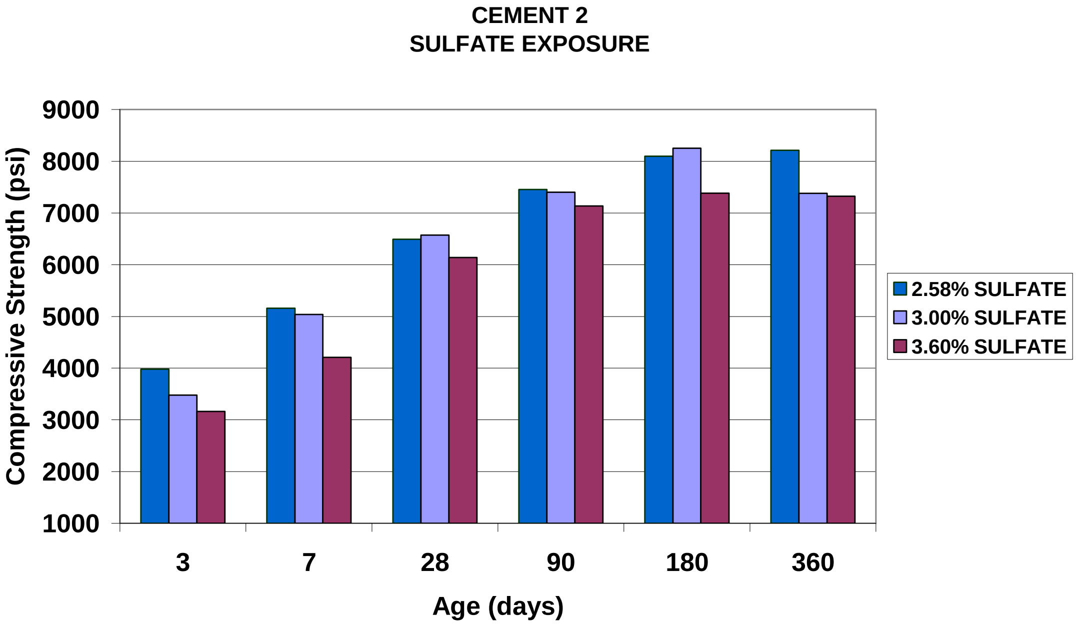


Figure 30. Compressive strength behavior for cement 2

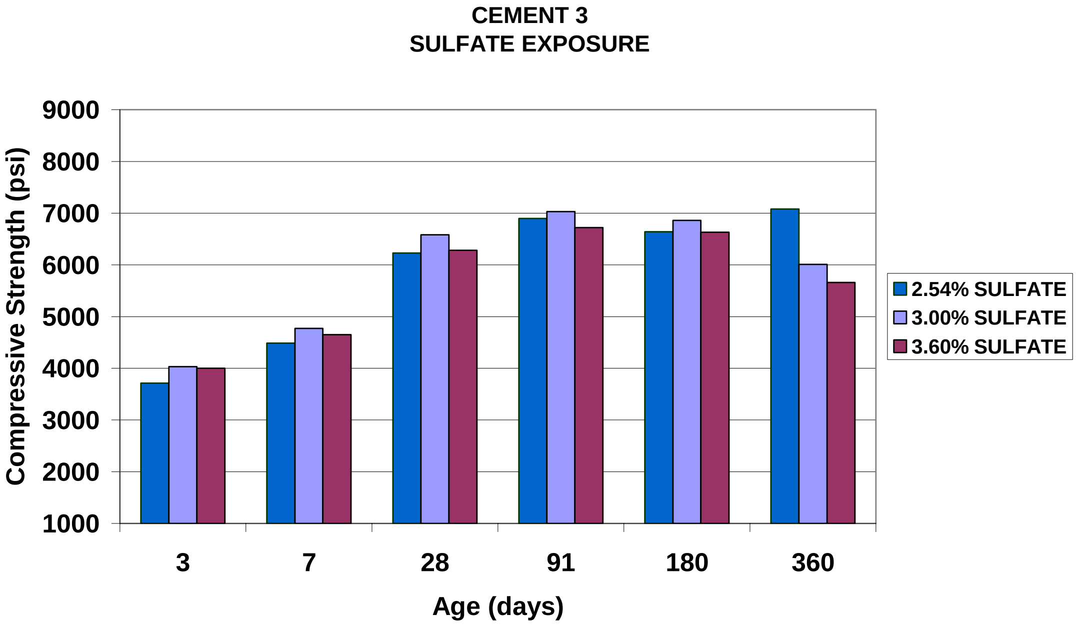


Figure 31. Compressive strength behavior for cement 3

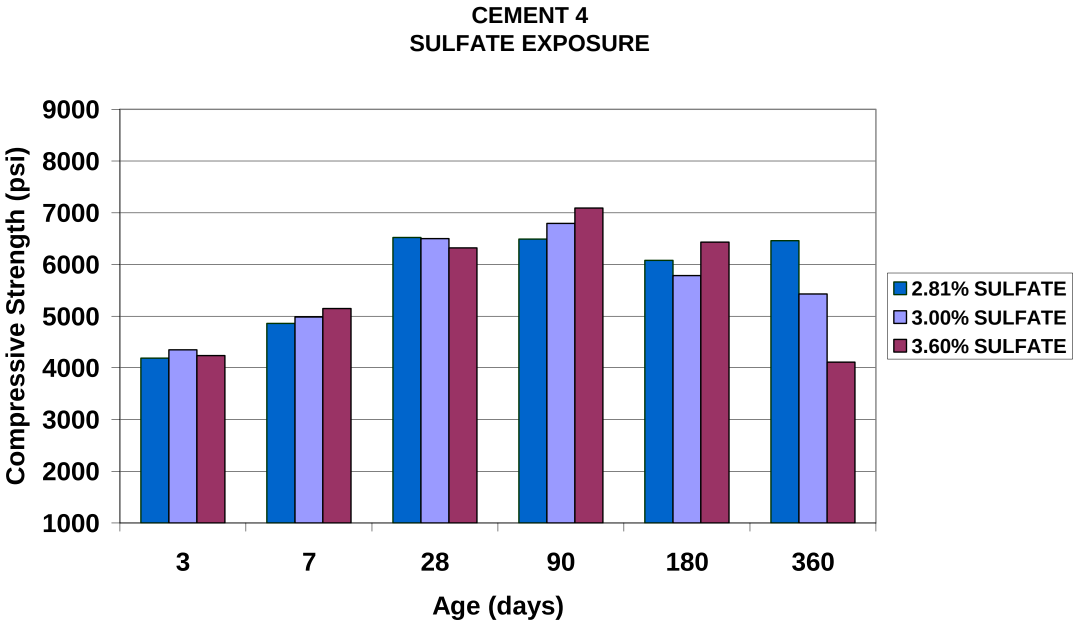


Figure 32. Compressive strength behavior for cement 4

Durability assessment through compressive strength behavior indicates that for all the cements studied in this investigation, increasing the SO_3 content above the as-received conditions yielded inferior performance for the cements. The data also indicate that the rate of deterioration is affected by tricalcium silicate content of cements.

3.2.4 Drying Shrinkage and Optimum SO3 Content

Drying shrinkage experiments were also conducted in order to address optimum SO_3 content for the cements studied here. Additionally, it is of interest to examine whether such optimum correlates with those determined through strength measurements. As mentioned previously, sulfur trioxide content affects the hydration process of tricalcium silicate. Tricalcium silicate hydration products are primarily responsible for drying shrinkage behavior of cementitious systems. The effect of varying SO_3 content on the drying shrinkage of cements is depicted in Figures 33 through 36. For cement 1, increasing the SO_3 content to 3% decreased the drying shrinkage to a minimum. Increasing the SO_3 content to 3.6% increased drying shrinkage up to 14 days but seems to have no effect at later ages. However, for cement 2, increasing the SO_3 content to 3.0 and 3.6% increased the drying shrinkage at all ages. Similar behavior was observed for cement 4 where it can be seen that the as-received SO_3 content had the lowest drying shrinkage. However, increasing the SO_3 content to 3% was not of significance. Increasing the SO_3 content for cement 3 to 3% did not affect the drying shrinkage significantly. In general, for all the cements studied here it appears that the as-received SO_3 content or an SO_3 content of 3.0% generated lowest drying shrinkage with the exception of cement 1. In this case, increasing SO_3 content to 3.0 decreased the drying shrinkage. Further increase in SO_3 content to 3.6% increased shrinkage at earlier age but generated no increase at later age. While cements 2, 3 and 4 share similar tricalcium aluminate content, cement 1 had the highest tricalcium aluminate and alkali content.

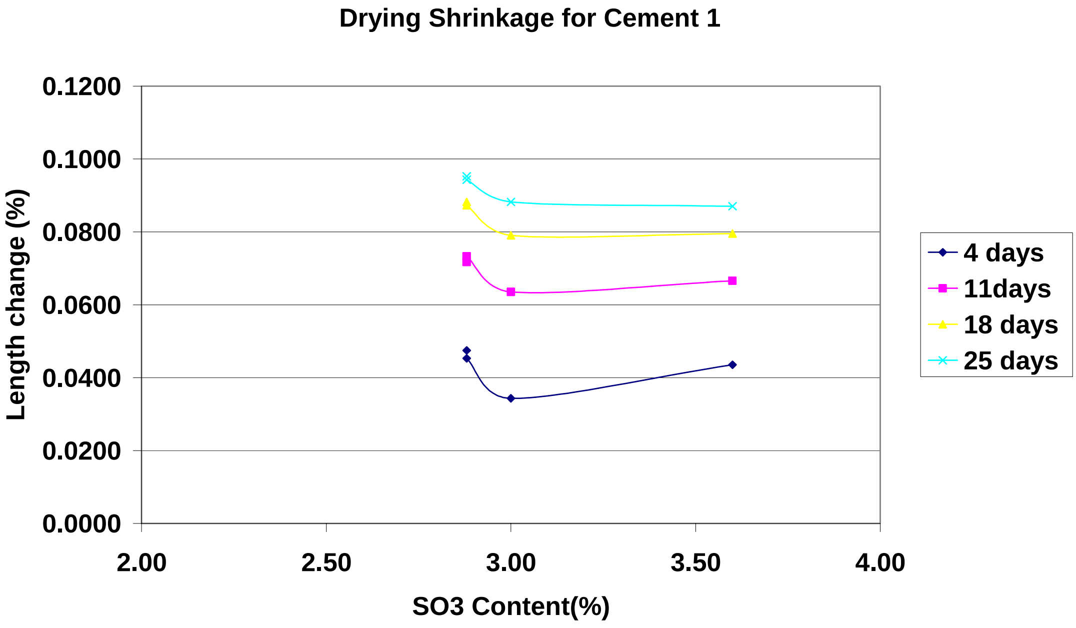


Figure 33. Variation of drying shrinkage with SO_3 content for cement 1

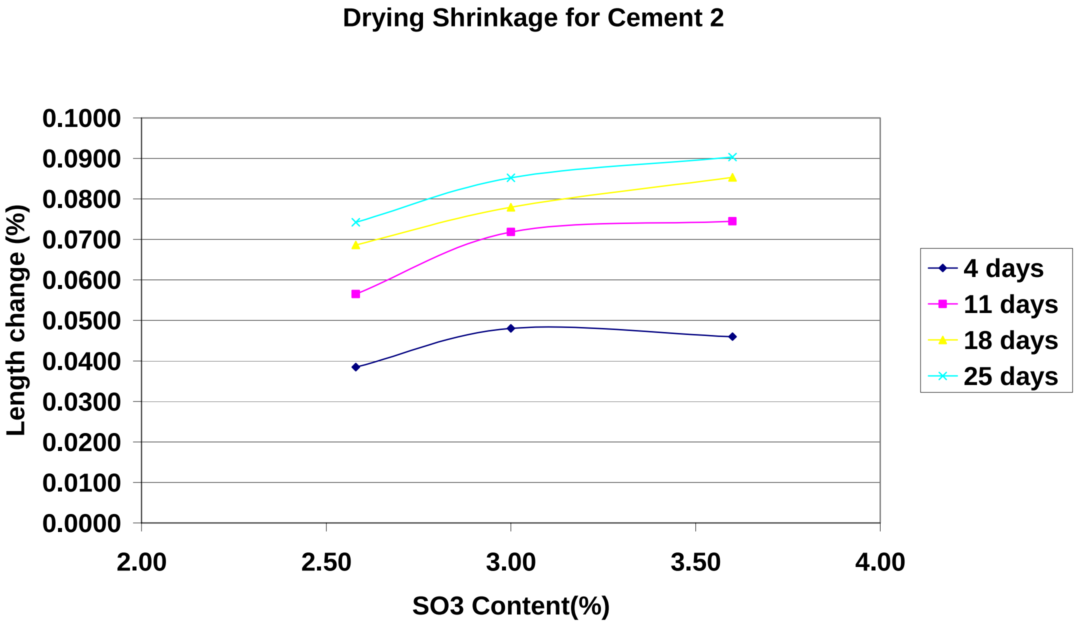


Figure 34. Variation of drying shrinkage with SO_3 content for cement 2

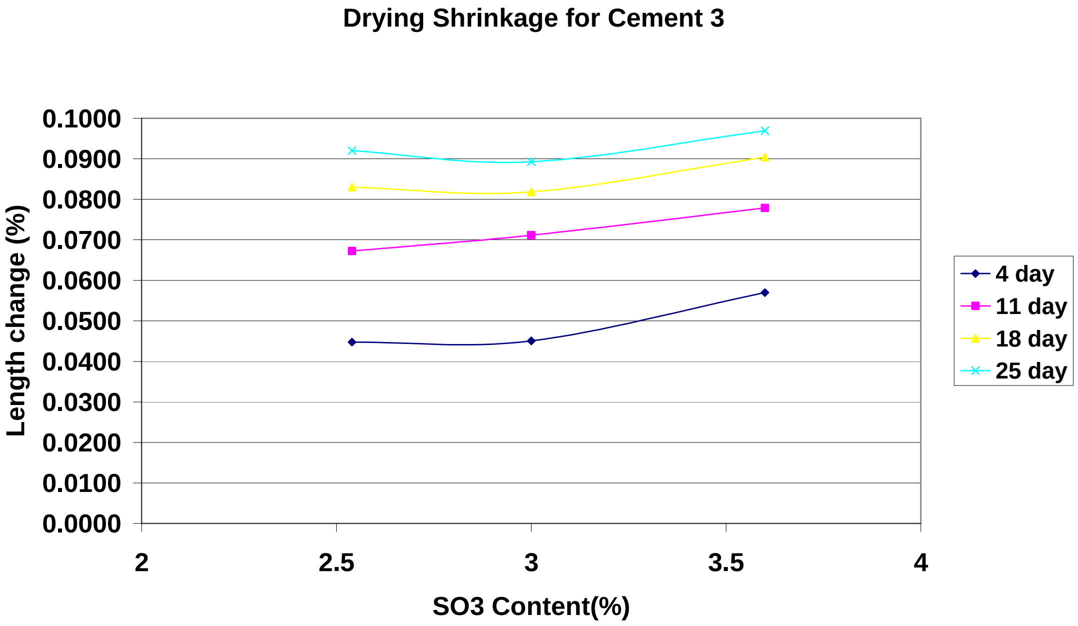


Figure 35. Variation of drying shrinkage with SO_3 content for cement 3

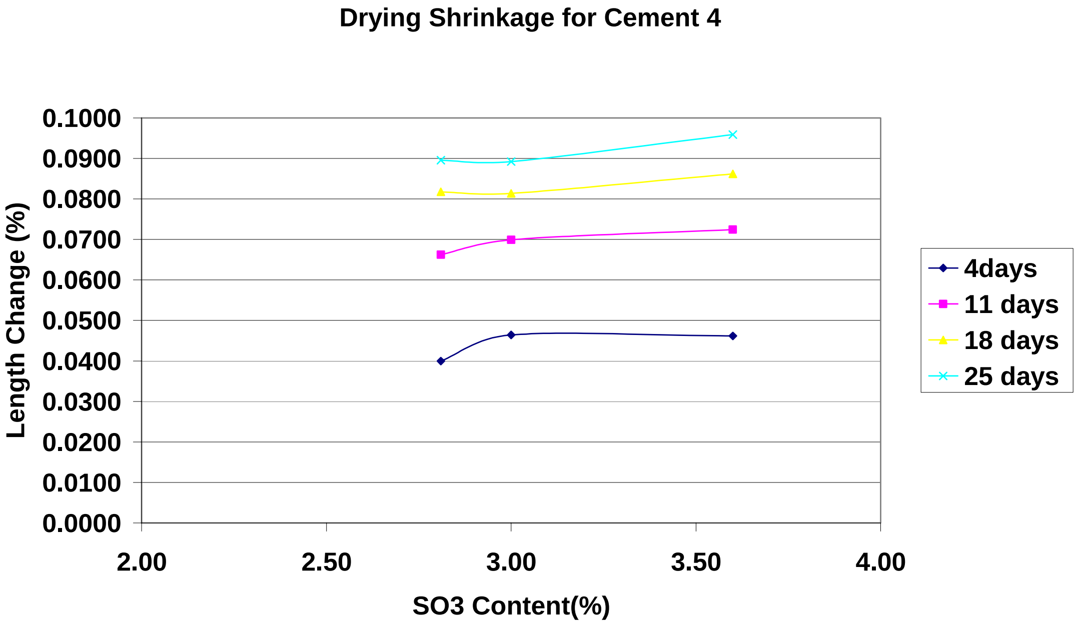


Figure 36. Variation of drying shrinkage with SO_3 content for cement 4

3.3 Concrete Durability

Several concrete mixes were prepared in order to address the effect of SO_3 content on concrete properties and durability. Class IV FDOT concrete mix was adopted for this investigation. The water to cement ratio was fixed and the slump allowed to vary. One hundred and fifty cylinders were prepared for a given SO3 content. Five different mixes were prepared for each cement; namely, as-received cement, cement doped to SO_3= 3.0%, cement doped to SO_3= 3.6%, cement doped to an SO_3 content of 3.6% and replacement level of 20% Class F fly ash, cement doped to 3.6% SO_3 and replacement of 50% by slag. For each of these conditions, the following properties were assessed: compressive strength in lime and 5% sodium sulfate solutions, surface resistivity, and open circuit potential for steel rebars embedded in concrete.

It is to be noticed that all aggregates have been graded and a specific grading curve was adopted for all concrete mixing. This procedure was adopted in order to maintain uniformity and eliminate any variations form aggregate grading. The results of all assessed properties on concrete are presented in this section.

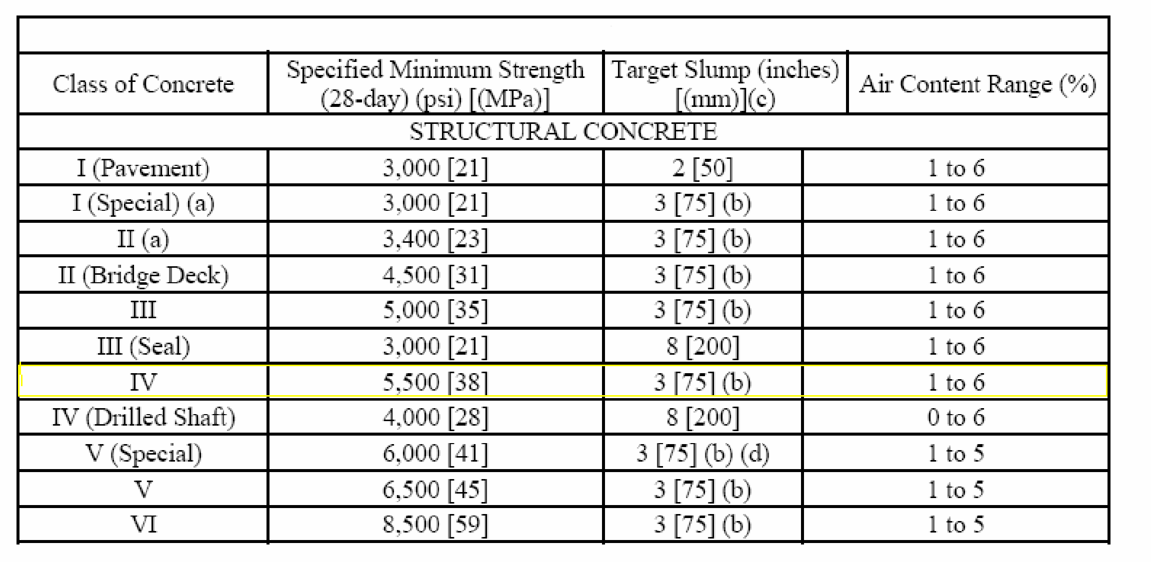
3.3.1 Concrete Mix Proportions

Mix proportions adopted in this study are presented in Table 9. Additionally, specifications for Class IV concrete mix are presented in Tables 10 and 11.

Table 9. Mix Proportions of Concrete

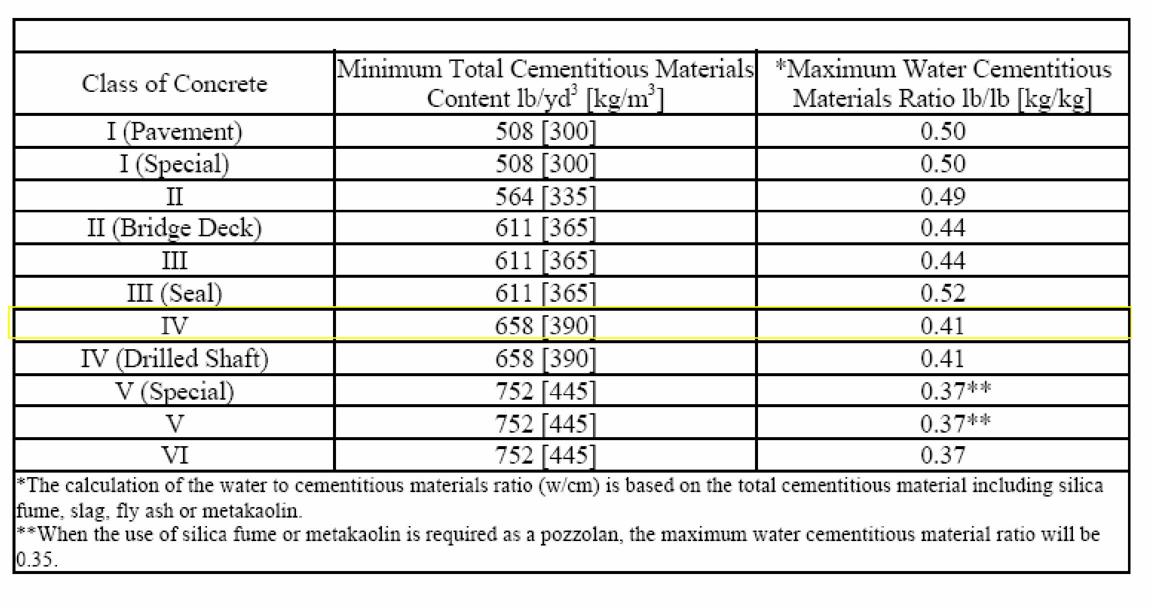
Material	Weights (lbs/4.5 cu.ft.)
Cement	109.667
Coarse Aggregate	279.107
Fine Aggregate	202.676
Water gal	39.657
WRDA 27 Type A (ASTM C494)	129.71 ml
w/c ratio	0.410
sand ratio	0.393

Table 10 FDOT Specifications for Concrete Mix Classes



Class of Concrete	Specified Minimum Strength (28-day) (psi) [(MPa)]	Target Slump (inches) [(mm)](c)	Air Content Range (%)
STRUCTURAL CONCRETE			
I (Pavement)	3,000 [21]	2 [50]	1 to 6
I (Special) (a)	3,000 [21]	3 [75] (b)	1 to 6
II (a)	3,400 [23]	3 [75] (b)	1 to 6
II (Bridge Deck)	4,500 [31]	3 [75] (b)	1 to 6
III	5,000 [35]	3 [75] (b)	1 to 6
III (Seal)	3,000 [21]	8 [200]	1 to 6
IV	5,500 [38]	3 [75] (b)	1 to 6
IV (Drilled Shaft)	4,000 [28]	8 [200]	0 to 6
V (Special)	6,000 [41]	3 [75] (b) (d)	1 to 5
V	6,500 [45]	3 [75] (b)	1 to 5
VI	8,500 [59]	3 [75] (b)	1 to 5

Table 11. FDOT Cementitious Content and w/c Ratio Requirements



Class of Concrete	Minimum Total Cementitious Materials Content lb/yd^3 [kg/m^3]	*Maximum Water Cementitious Materials Ratio lb/lb [kg/kg]
I (Pavement)	508 [300]	0.50
I (Special)	508 [300]	0.50
II	564 [335]	0.49
II (Bridge Deck)	611 [365]	0.44
III	611 [365]	0.44
III (Seal)	611 [365]	0.52
IV	658 [390]	0.41
IV (Drilled Shaft)	658 [390]	0.41
V (Special)	752 [445]	0.37**
V	752 [445]	0.37**
VI	752 [445]	0.37

*The calculation of the water to cementitious materials ratio (w/cm) is based on the total cementitious material including silica fume, slag, fly ash or metakaolin.

**When the use of silica fume or metakaolin is required as a pozzolan, the maximum water cementitious material ratio will be 0.35.

Mix proportioning adopted in this study was in accordance to ACI volumetric method, with a cement content of 658lbs and a w/c ratio of 0.41.The design compressive strength and slump were 5,500 psi and 3 inches respectively.

3.3.1.1 Coarse Aggregate Properties

The coarse aggregates used in concrete mixing were limestone. Before the commencement of the test the aggregates where washed and drained in order to remove any excess fine material that is created when the aggregates rubbed together. Then aggregates were sorted with a Gilson Testing Screen with hydraulic clamping into its individual grades. The grading curve adopted for coarse aggregates used here is depicted in Figure 37.

Table 12. Coarse Aggregate Gradation

Coarse Aggregate Size	Upper Limit	Lower Limit	Percentage Used
1-1/2"	100	100	100
1"	95	100	97.5
3/4"	60	85	72.5
1/2"	25	60	42.5
3/8"	8	30	19
#4	0	10	5
#8	0	5	2.5
PAN			0

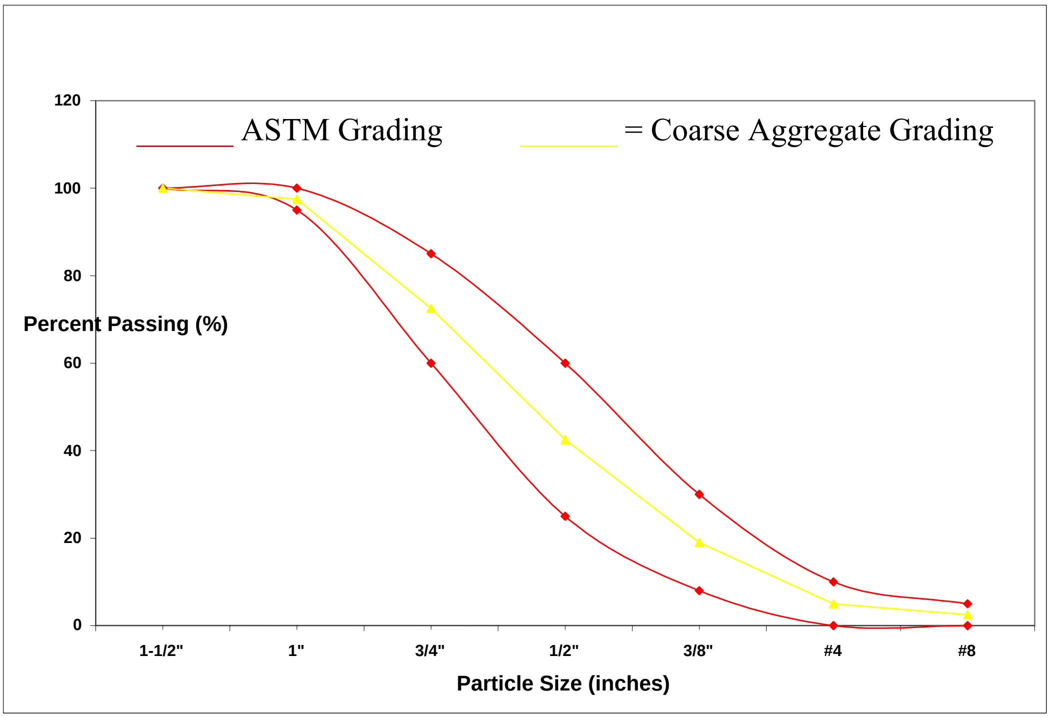


Figure 37. Grading curve for coarse aggregate

3.3.1.2 Fine Aggregates Properties

Fine aggregates used for the mix was silica sand. The sand was prepared by washing and drying in an oven. The sand was weighed OD (oven dry) condition. Then aggregates were sorted with a Gilson Testing Screen with Hydraulic Clamping into its individual grades. The aggregate grading curve adopted in this study is shown in Figure 38.

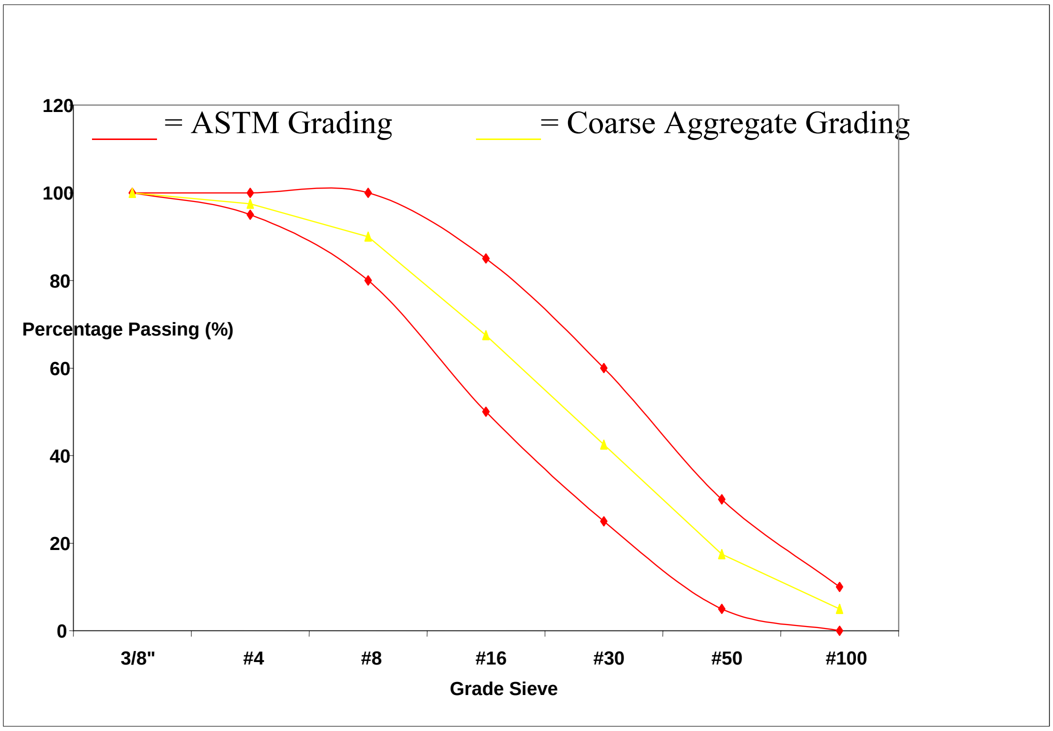


Figure 38. Grading curve for fine aggregates

3.3.2 Compressive Strength

Results of compressive strength variation with exposure time to lime and sulfate solutions are depicted in Figures 39 through Figure 62.

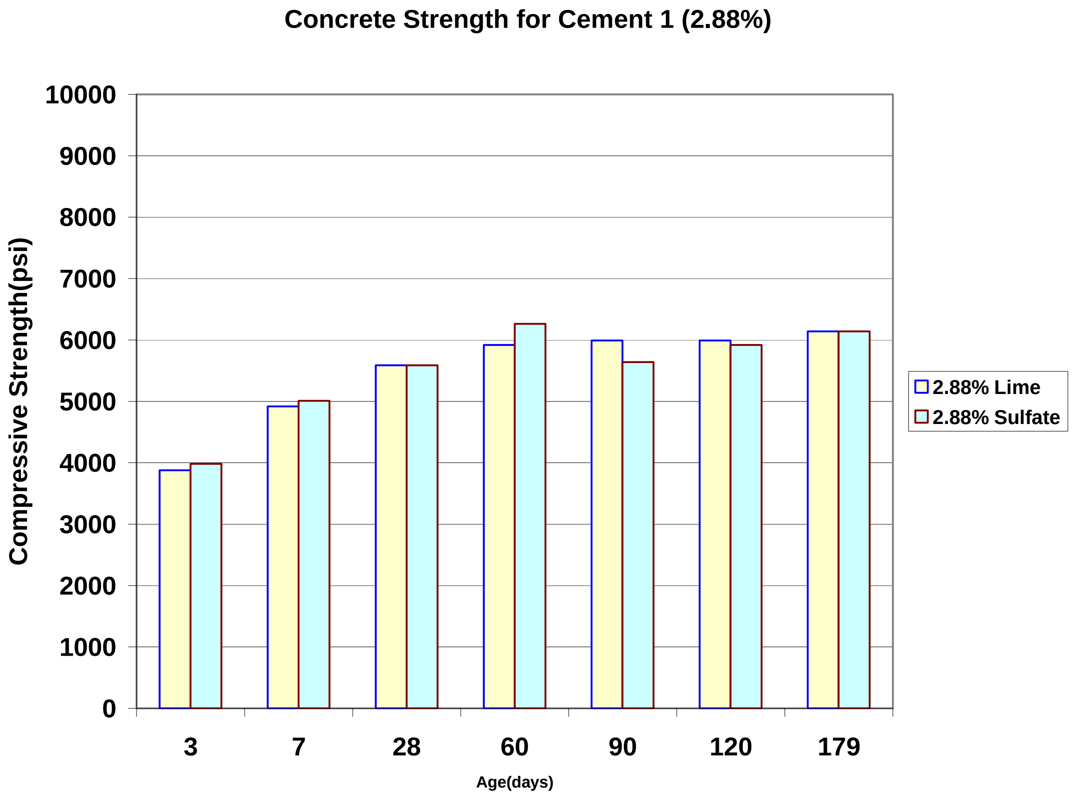


Figure 39. Concrete compressive strength in lime and sulfate

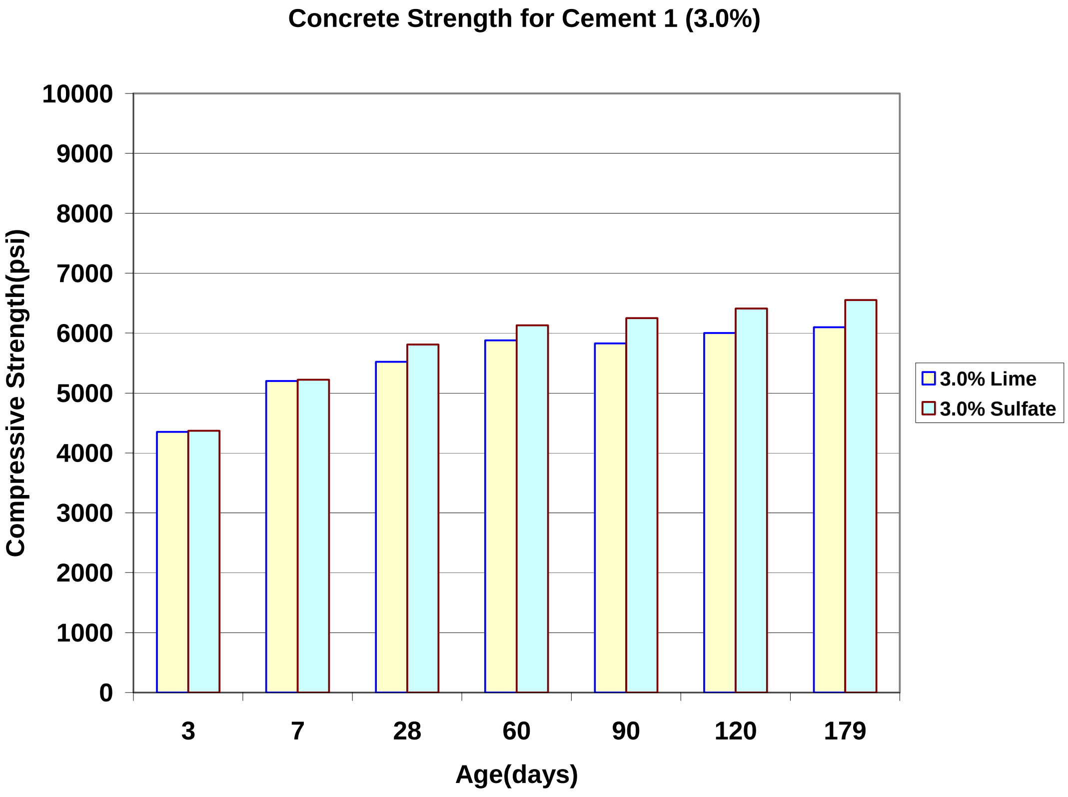


Figure 40. Concrete compressive strength in lime and sulfate

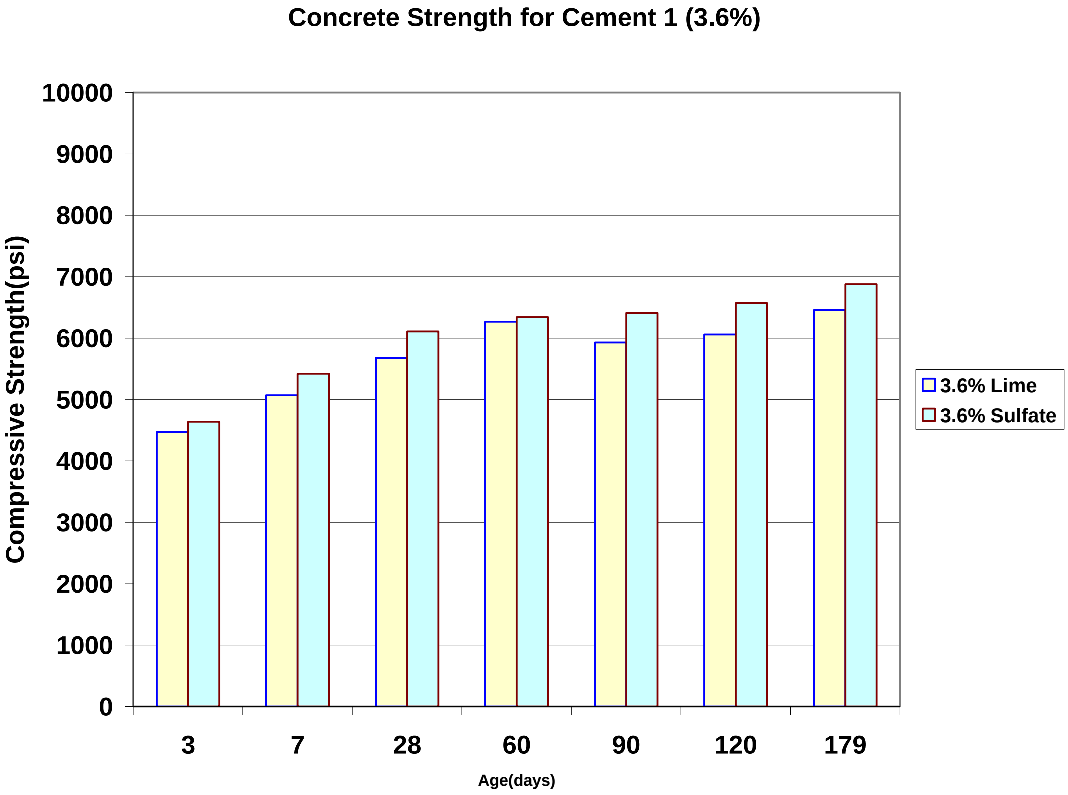


Figure 41. Variation of concrete compressive strength for cement 1

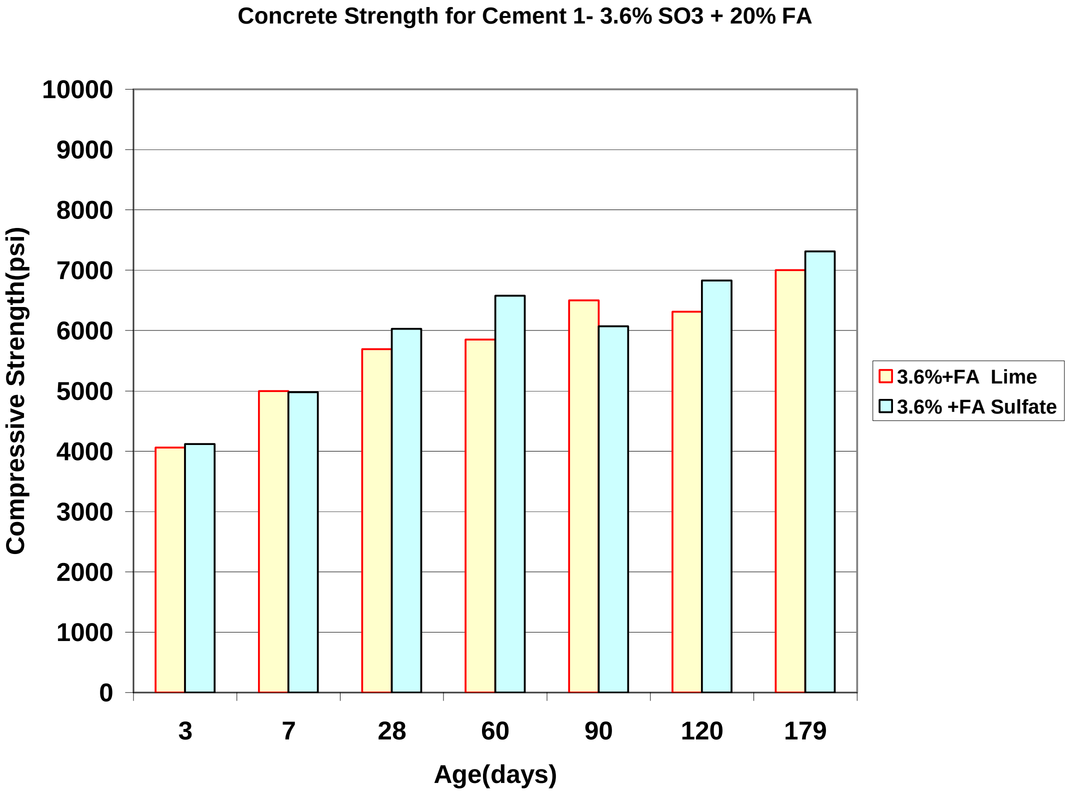


Figure 42. Variation of concrete compressive strength for cement 1

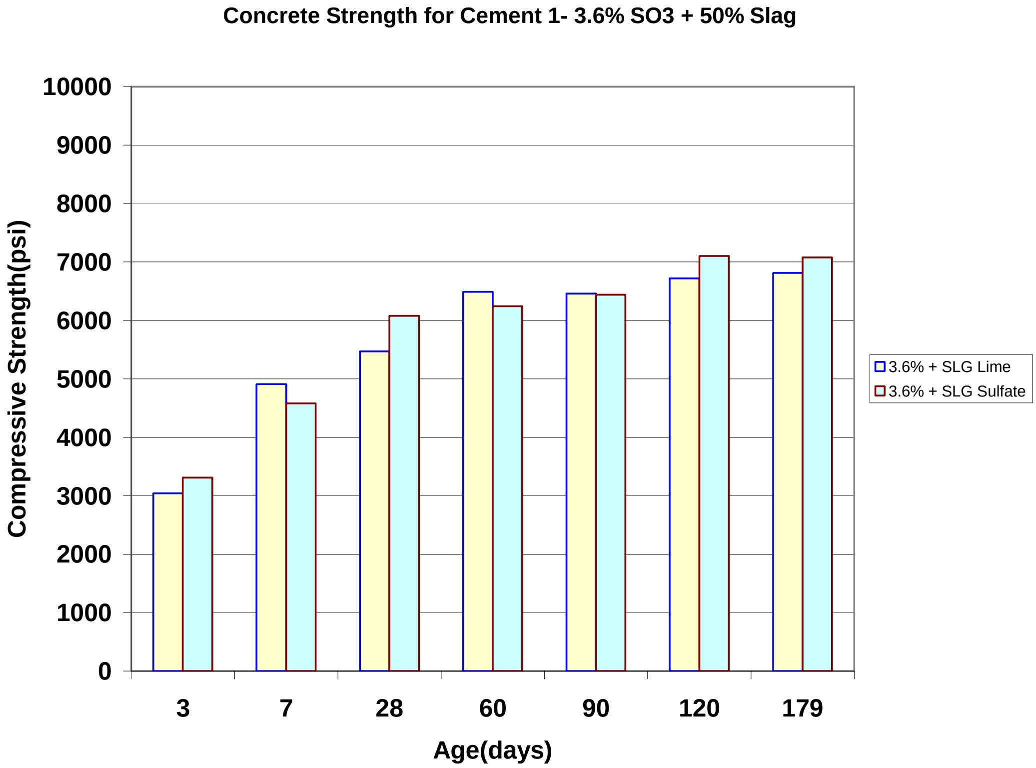


Figure 43. Variation of concrete compressive strength for cement 1

For cement 1, it can be seen from Figures 3.3 through 3.7 that increasing the SO_3 content above 3.0% increases the strength of concrete up to 180 days for both lime and sulfate exposure. In addition, increasing the SO_3 content to 3.6%, the compressive strength of concrete exposed to sulfate solution appears to be higher than that attained by concrete exposed to lime. Incorporation of pozzolanic materials appears to increase the strength at a later age for both exposure conditions compared to the unblended mixes. For the period of exposure reported in this study increasing the SO_3 content of cement to 3.6% did not seem to affect the durability of concrete in lime or sulfate environment.

For cement 2, Figures 3.8 and 3.12 show that increasing SO_3 content from the as-received content to 3.0%, did not affect the compressive strength of concrete exposed to lime or sulfate. Further increase of the SO_3 content to 3.6% increases the strength in lime and sulfate up to 180 days of exposure. Similar to cement 1, incorporation of fly ash or slag decreases concrete early strength but increases the later strength.

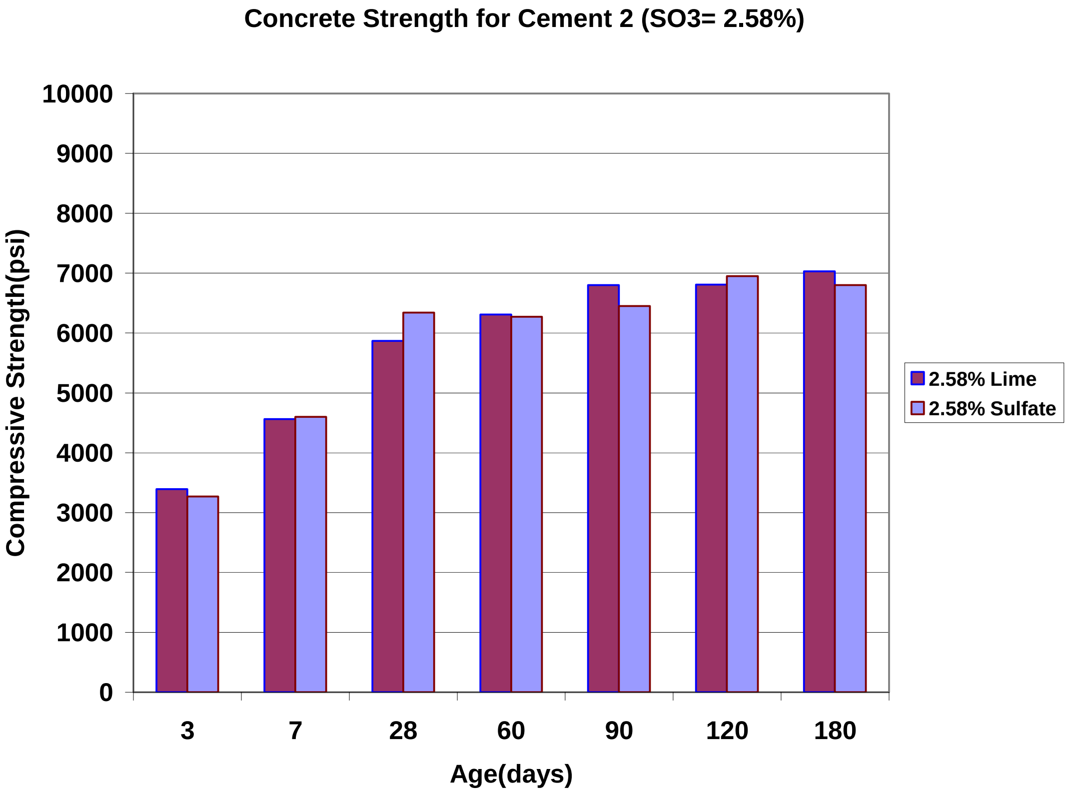


Figure 44. Variation of concrete compressive strength for cement 2

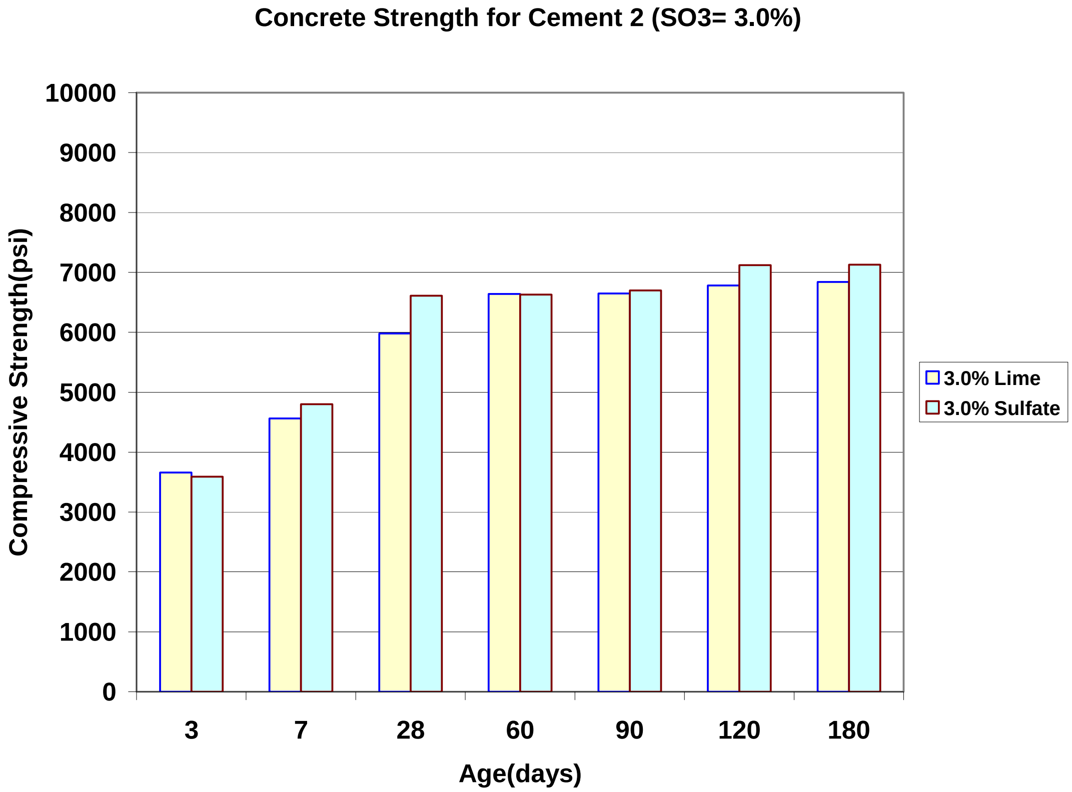


Figure 45. Variation of concrete compressive strength for cement 2

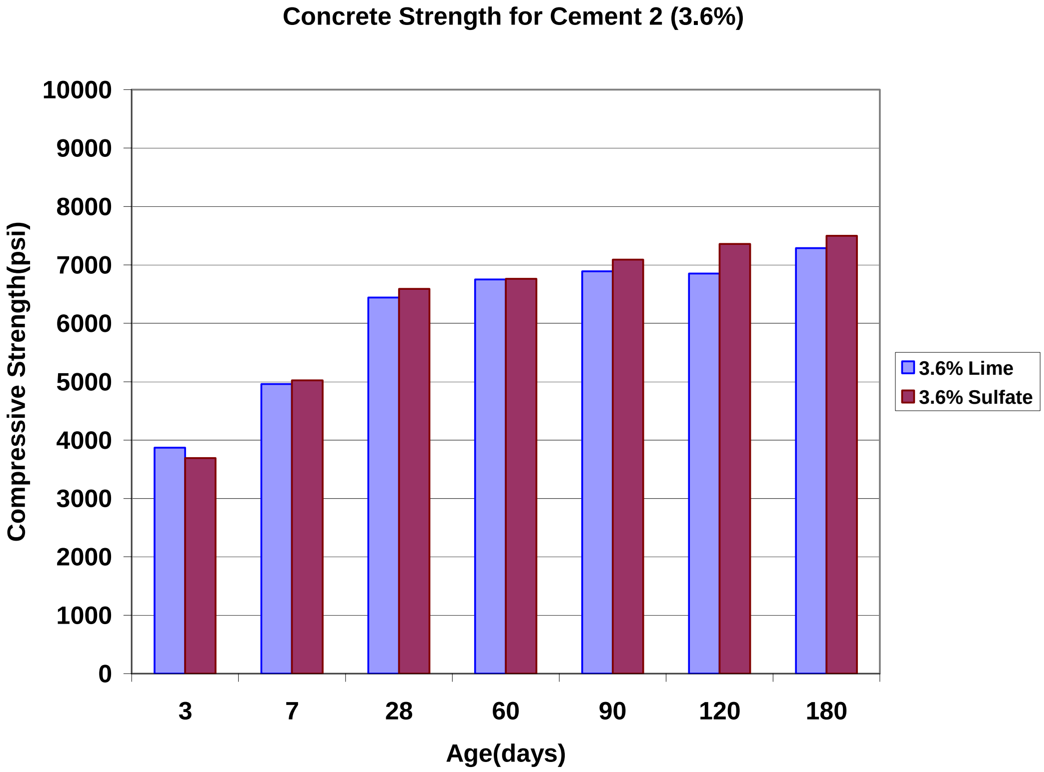


Figure 46. Variation of concrete compressive strength for cement 2

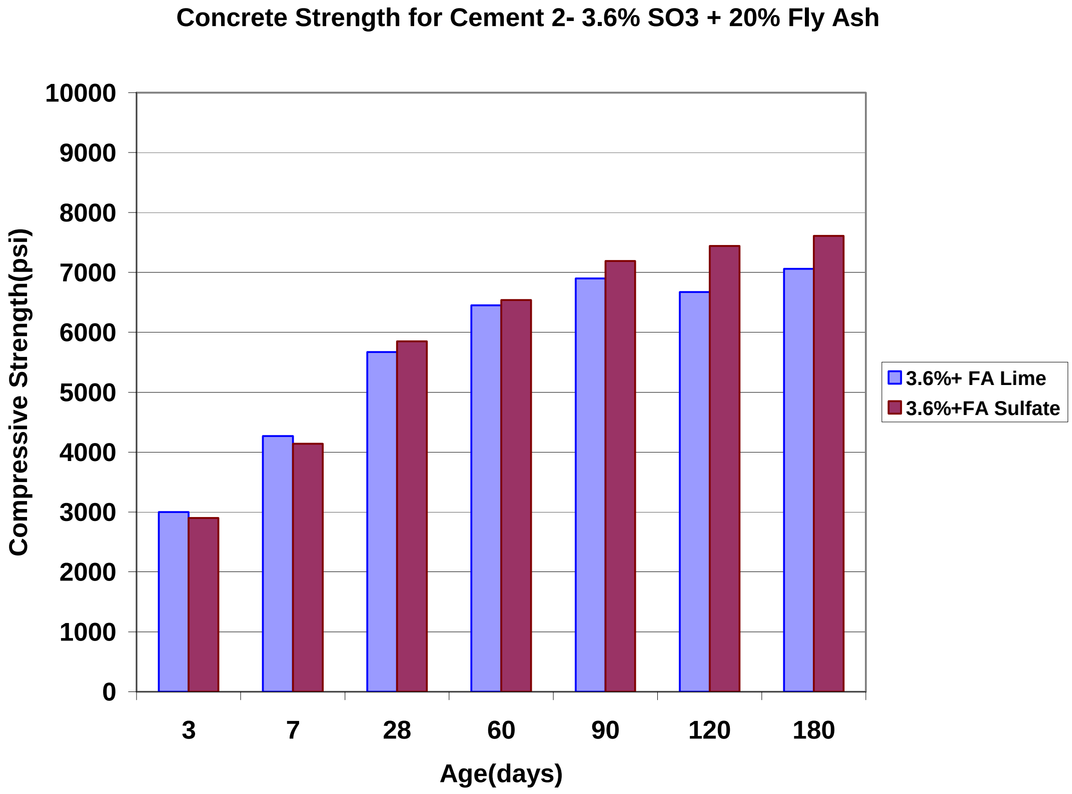


Figure 47. Variation of concrete compressive strength for cement 2

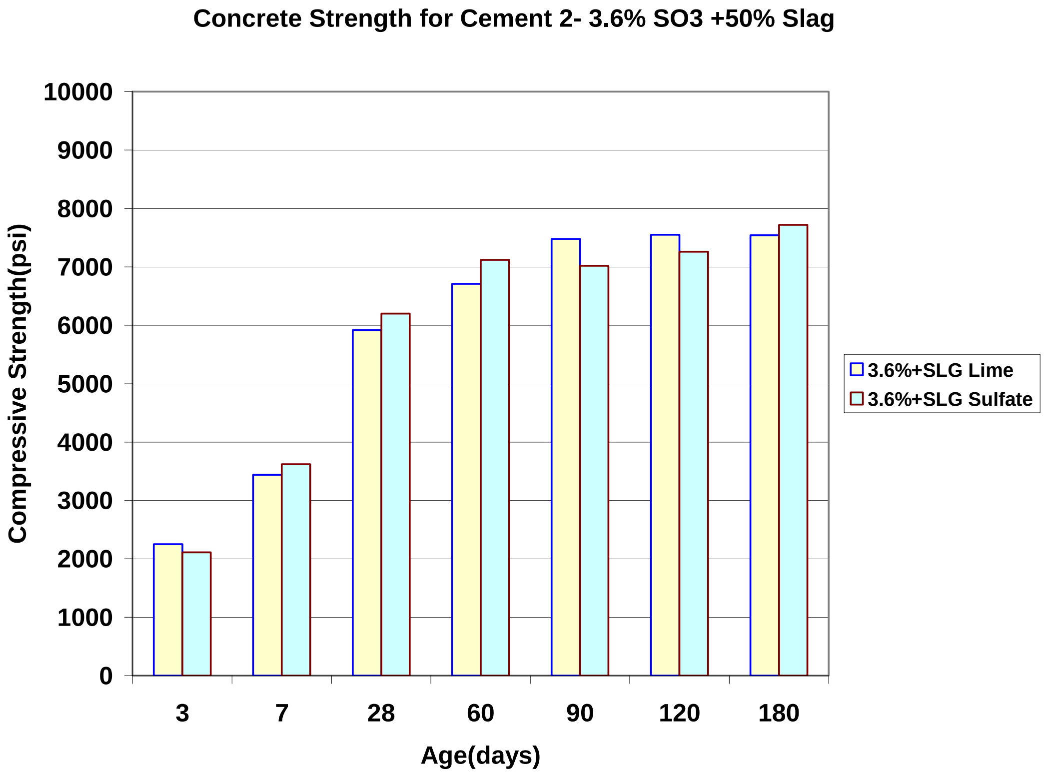


Figure 48. Variation of concrete compressive strength for cement 2

The results for cement 3 are depicted in Figures 3.13 through 3.17. Similar to the previous cements, increasing the SO_3 content to 3.0% did not seem to change the compressive strength behavior in lime or sulfate exposure. Increasing the SO_3 content to 3.6% appears to level off the strength at 180 days of exposure to sulfate. This is different from the other cements as there was an observed increase in strength up till the age of 180 days in sulfate solution. Incorporation of mineral admixture improved the strength gain significantly in both exposure conditions.

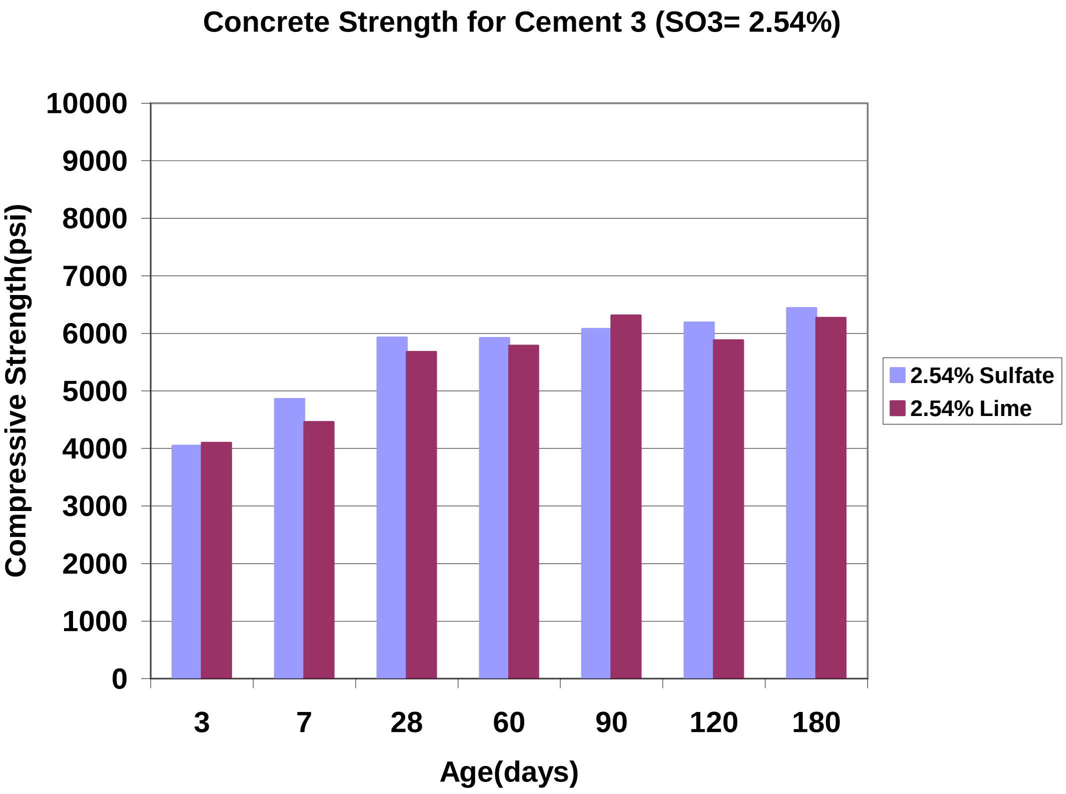


Figure 49. Variation of concrete compressive strength for cement 3

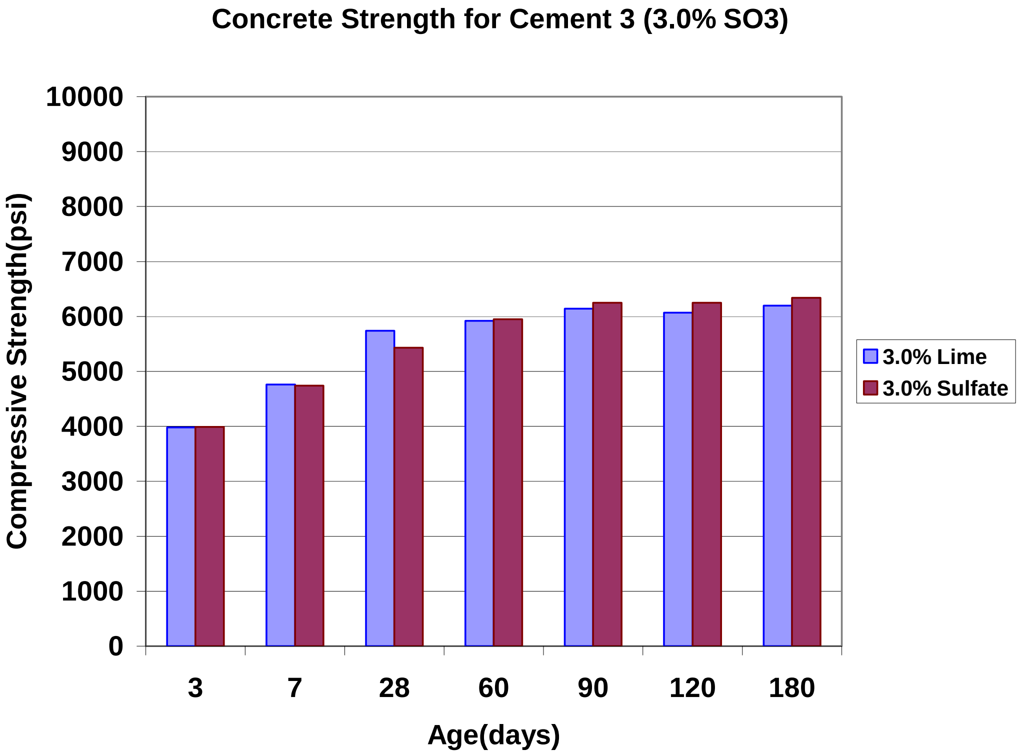


Figure 50. Variation of concrete compressive strength for cement 3

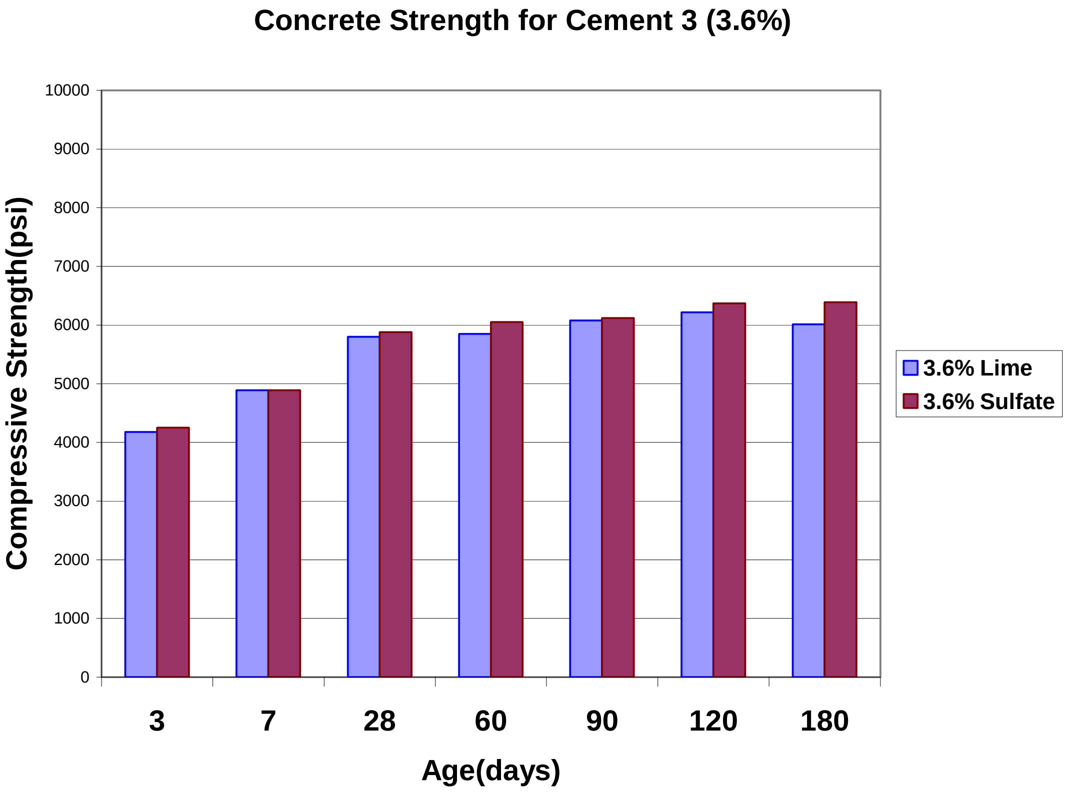


Figure 51. Variation of concrete compressive strength for Cement 3

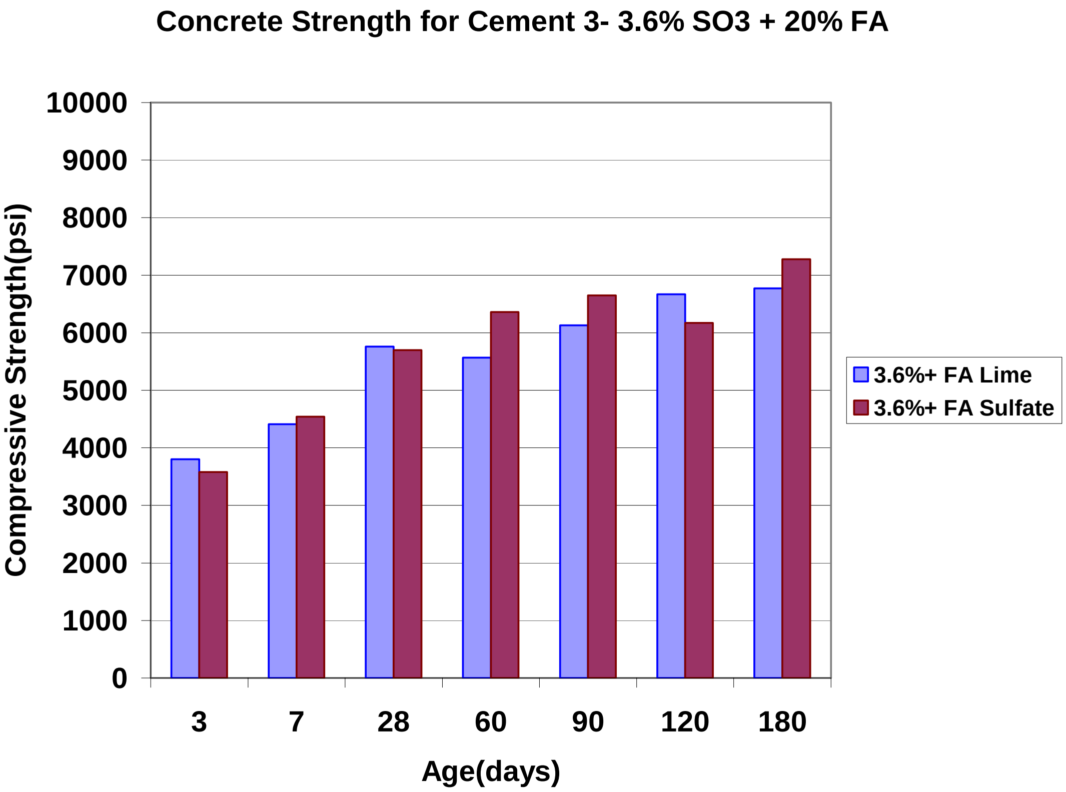


Figure 52. Variation of concrete compressive strength for cement 3

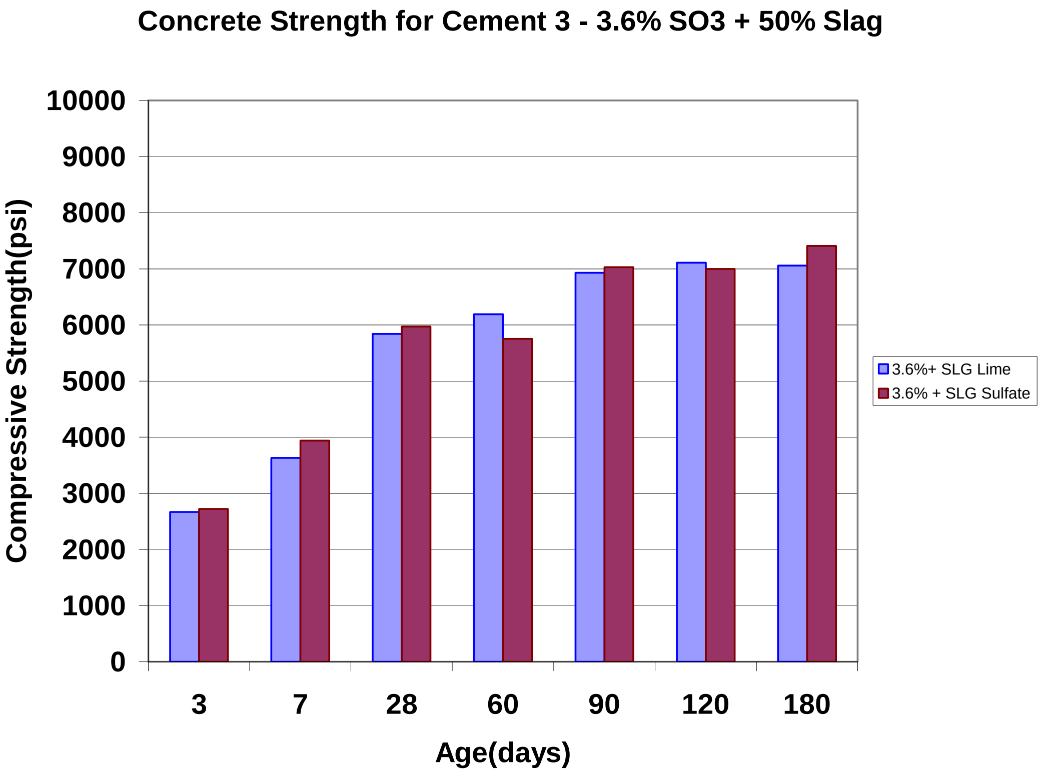


Figure 53. Variation of concrete compressive strength for cement 3

The strength behavior for cement 4 is depicted in Figures 3.18 through 3. 22 were it can be seen that increasing the SO_3 content to 3.0% increased the early strength in lime. However, at later age there was no significant variation. On increasing the SO_3 content to 3.6 %, the strength in lime and sulfate seems to experience a clear drop from those reported for the as-received cement. Again, as for all the cements studied here, incorporation of mineral admixtures improved the strength at later ages for both exposure conditions. It is to be remembered that cement 4 has the highest tricalcium silicate content among all cements here. The effect of increasing the SO_3 content on the morphology and porosity of calcium silicate hydrate gel is expected to be of more significance in cement 4 than the other cements.

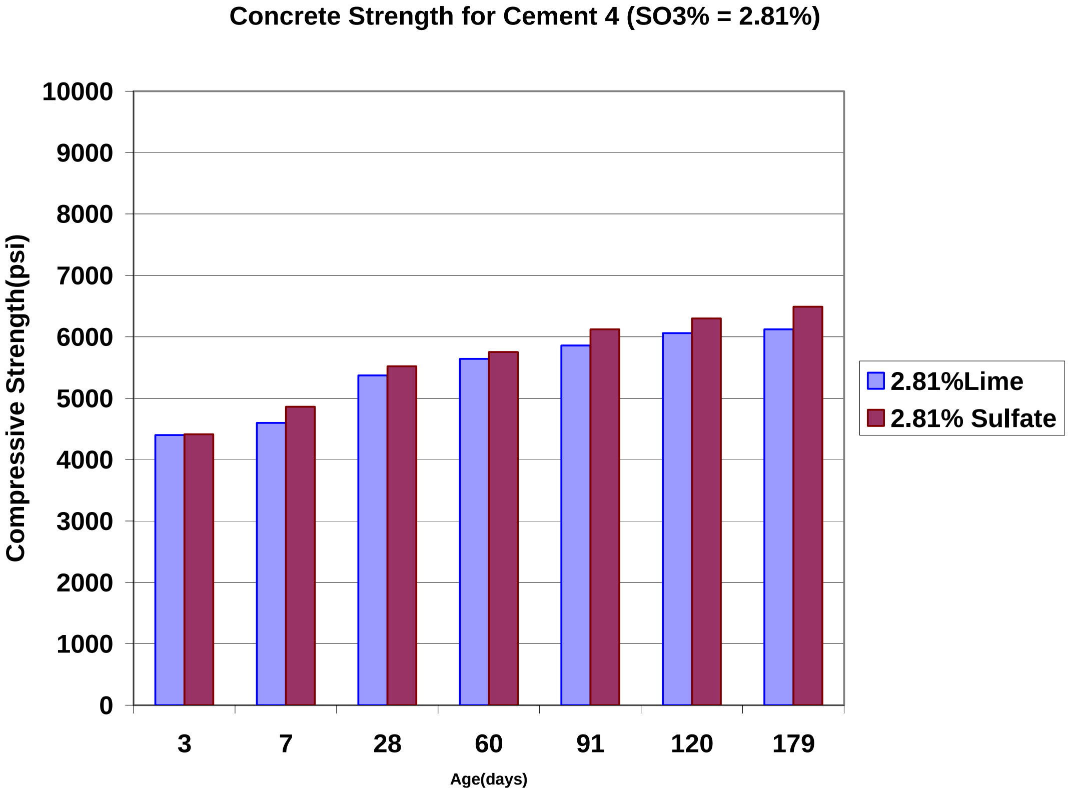


Figure 54. Variation of concrete compressive strength for cement 4

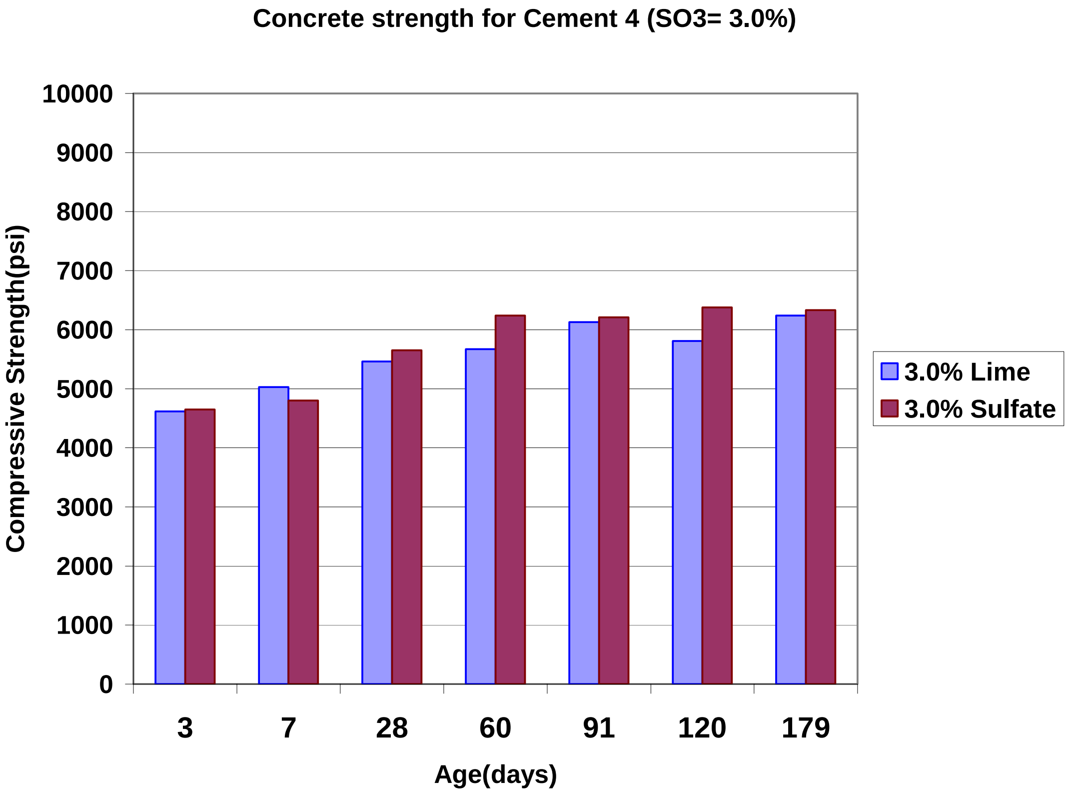


Figure 55. Variation of concrete compressive strength for cement 4

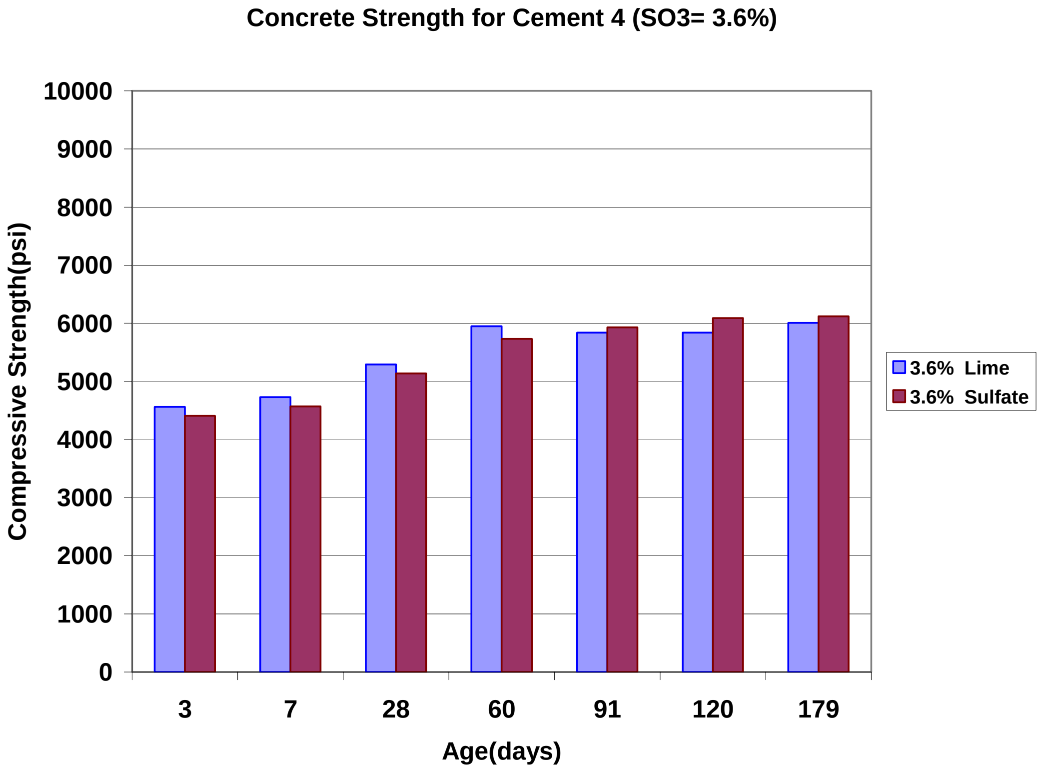


Figure 56. Variation of concrete compressive strength for cement 4

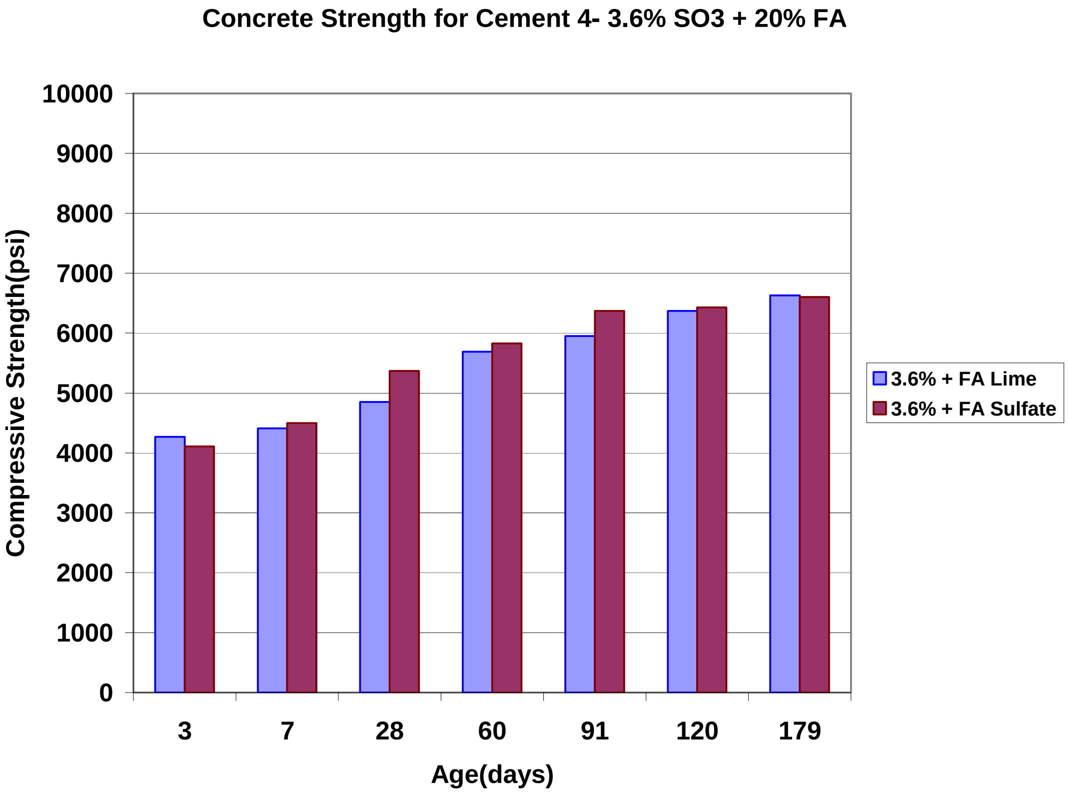


Figure 57. Variation of concrete compressive strength for cement 4

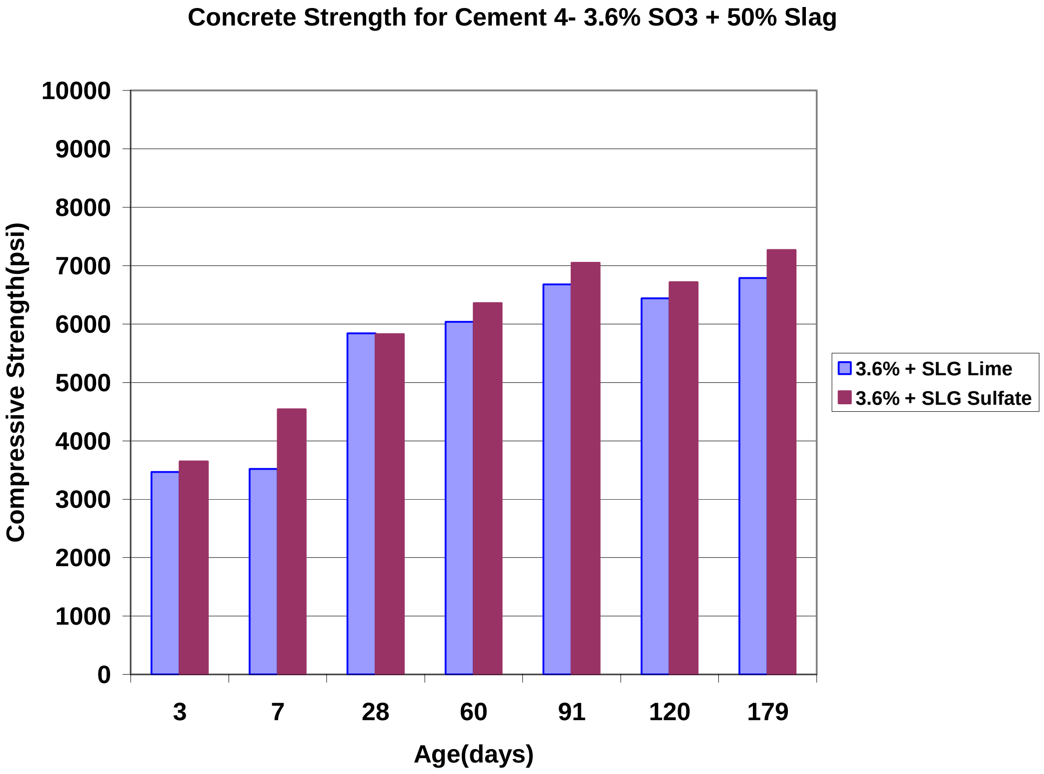


Figure 58. Variation of concrete compressive strength for cement 4

In conclusion, for the period reported here of 180 days, it appears that increasing the SO_3 content did not have significant effect on concrete strength. However, for cements 3 and 4 of higher tricalcium silicate content, there appears to be signs of deterioration at 180 days of exposure to sulfates with increasing the SO_3 content as can be seen from the data depicted in Figures 59 through 62. Longer exposure times of up to two years would have revealed additional significant information.

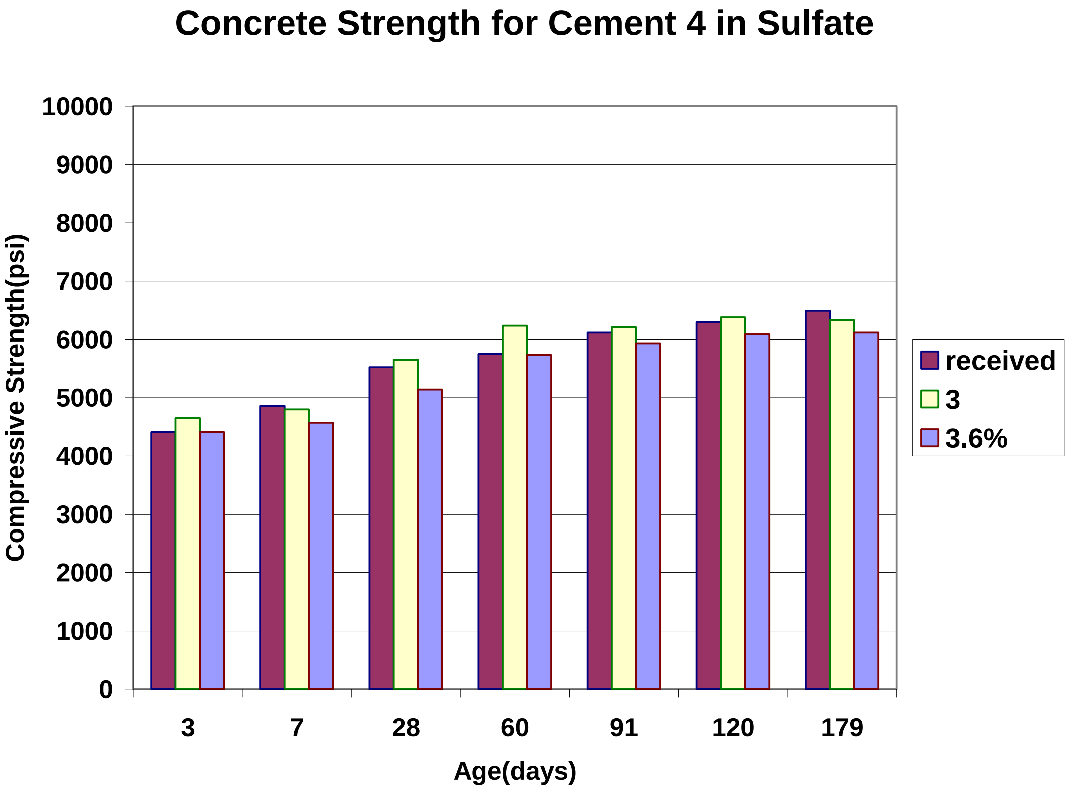


Figure 59. Variation of concrete compressive strength for cement 4

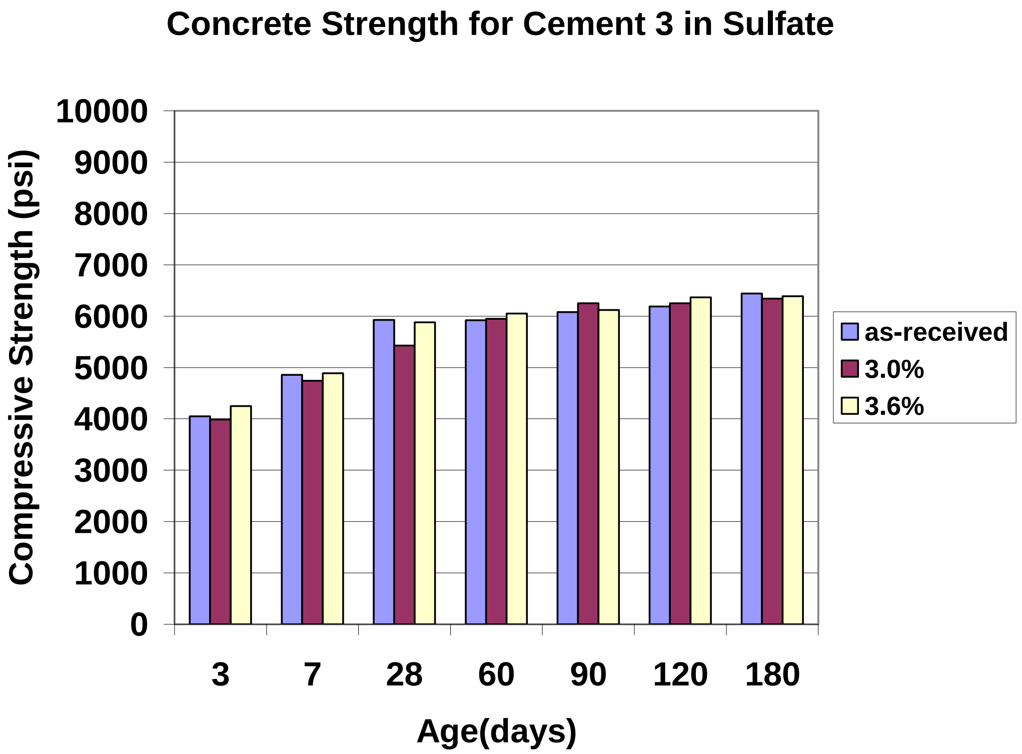


Figure 60. Variation of concrete compressive strength for cement 3

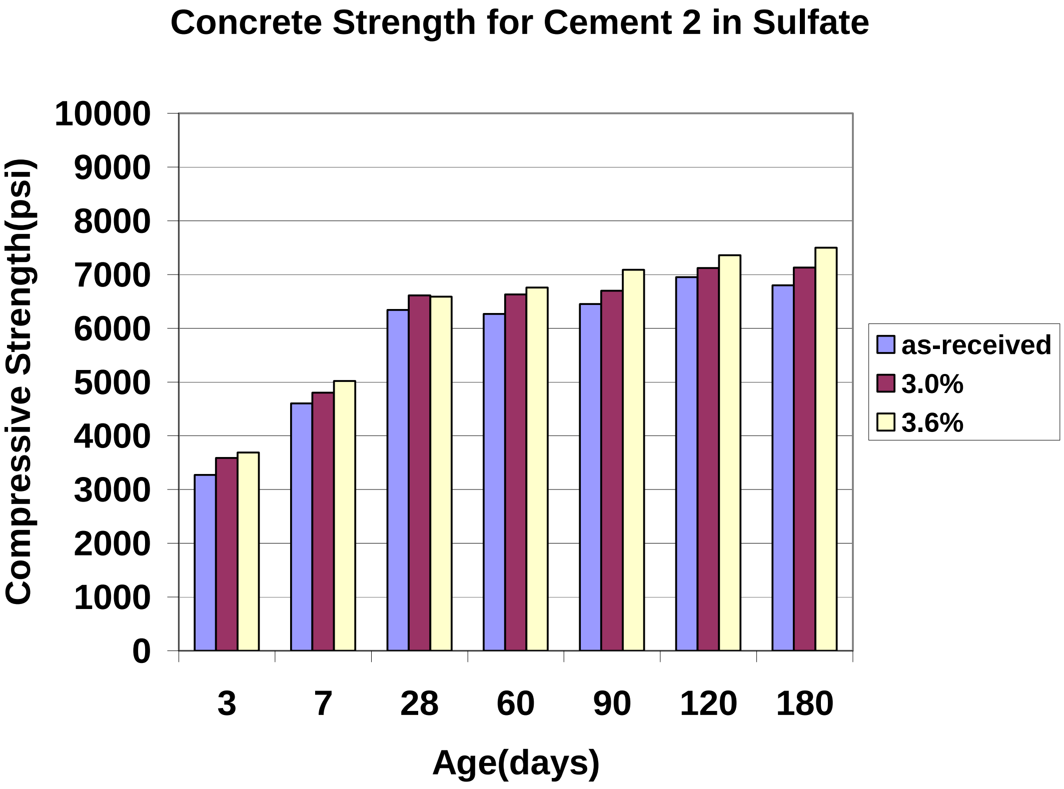


Figure 61. Variation of concrete compressive strength for cement 2

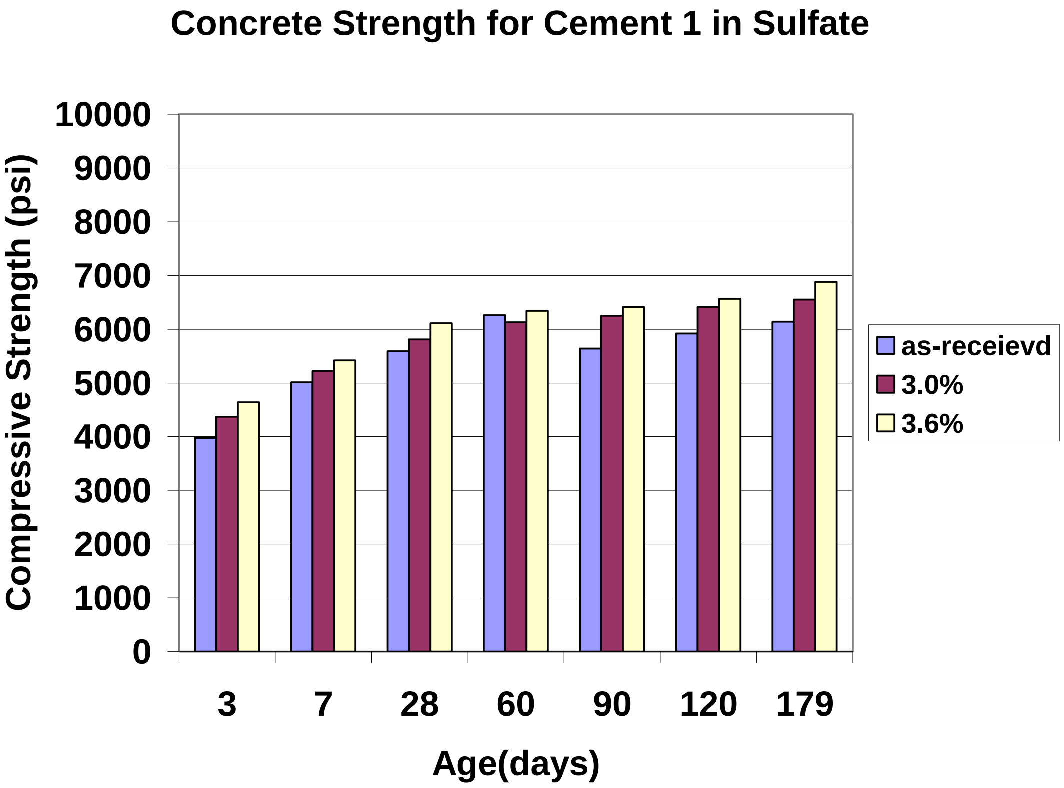


Figure 62. Variation of concrete compressive strength for cement 1

3.3.3 Concrete Setting Time

Concrete setting time was assessed in accordance to ASTM-C403. The effect of increasing the SO_3 content of Portland cement on the setting behavior of cements is shown in Figures 63 through Figure 70. Increasing the SO_3 content for cement 1 did not seem to affect the initial set significantly; however, the final setting time shows a decrease with increasing SO_3 content. Incorporation of fly ash increased the initial and final set while slag decreased the setting time when compared to 3.6% SO_3 mix.

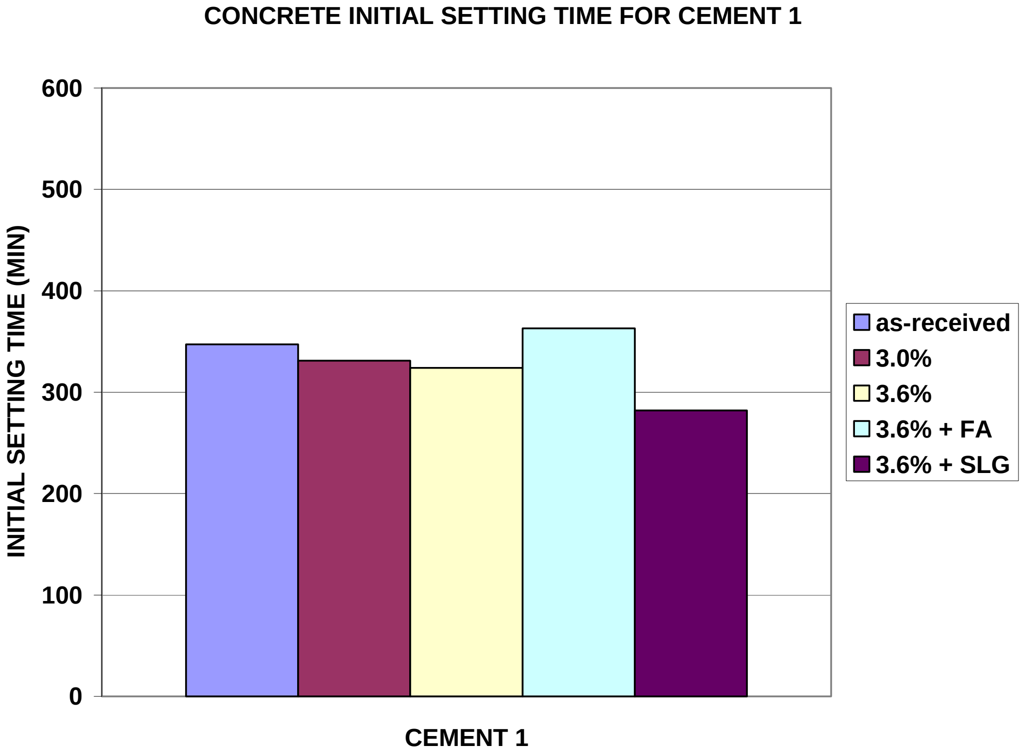


Figure 63. Initial setting behavior for cement 1

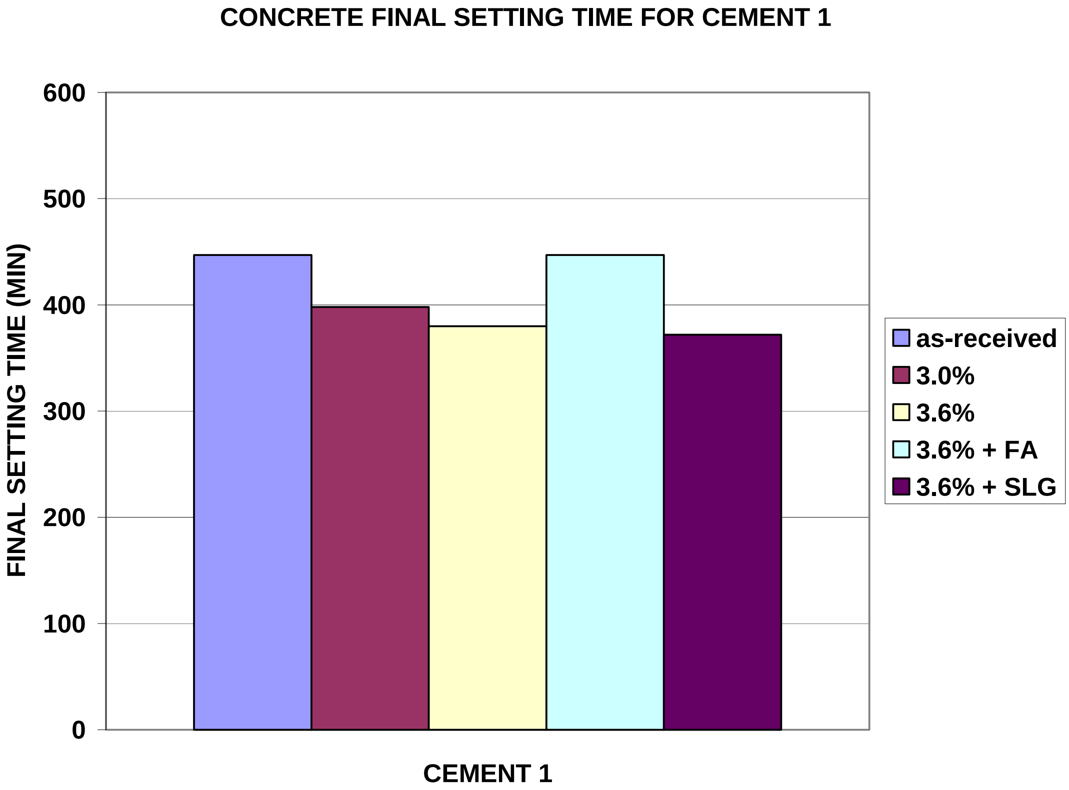


Figure 64. Final setting for cement 1

For cement 2, the setting time showed insignificant variation with increasing the SO_3 content to 3.6%. Again as in the case of cement 1, incorporation of fly ash increases the setting time while slag decreased the setting time below that attained by the as-received cement.

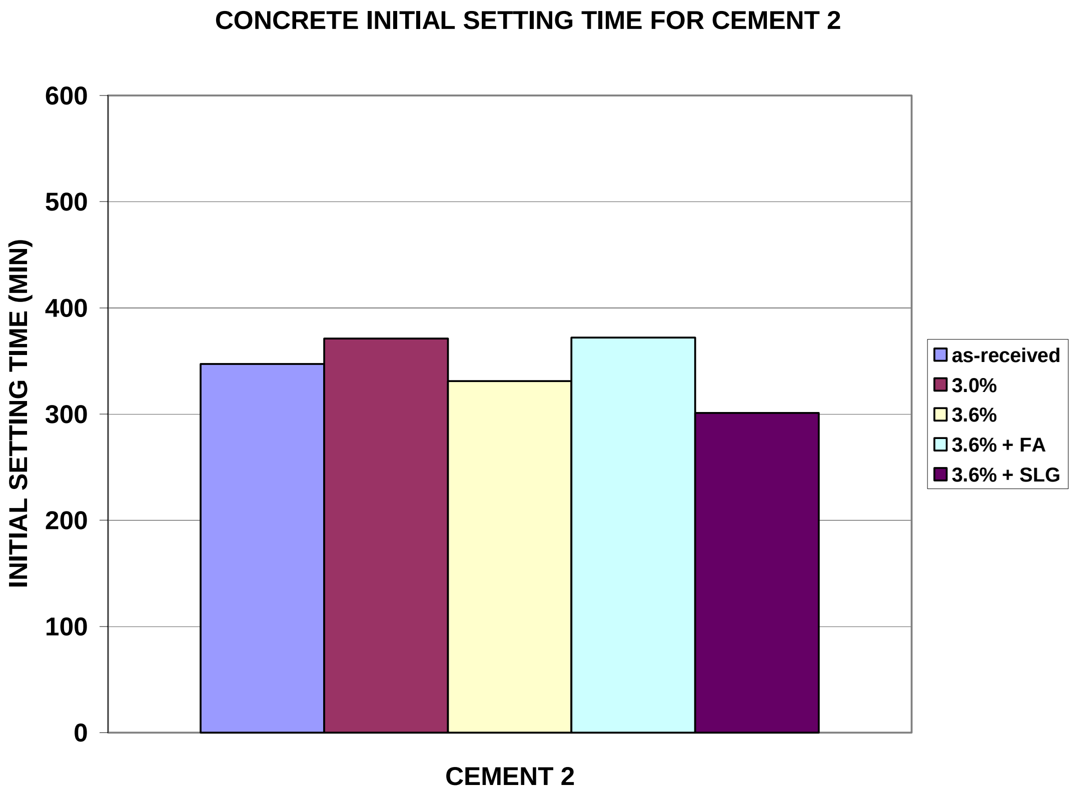


Figure 65. Initial setting behavior for cement 2

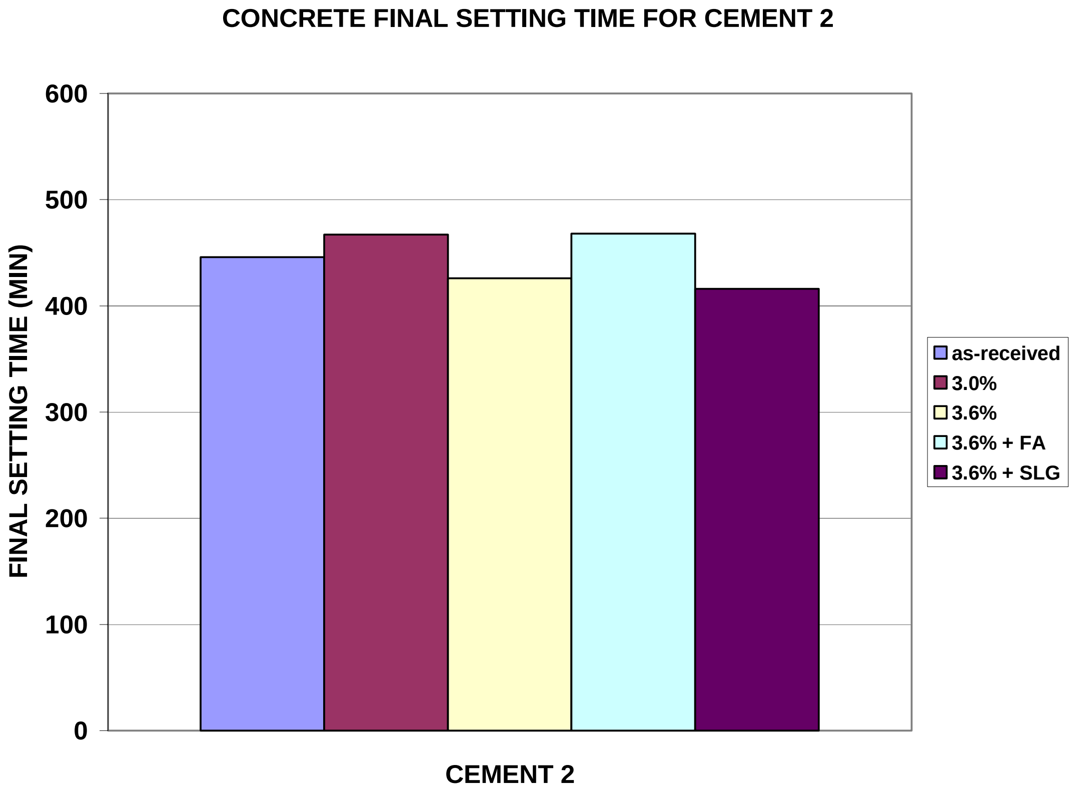


Figure 66. Final setting behavior for cement 2

For cement 3, the setting times did not show significant variation with increasing SO_3 content. Increasing the SO_3 content to 3.6% with additions of slag reduced the setting time. Similar setting behavior was observed for cement 4, where increasing the SO_3 content to 3.6% did not result in significant changes in the setting behavior However, incorporation of slag decreased the setting times while fly ash did not introduce any changes on the setting behavior.

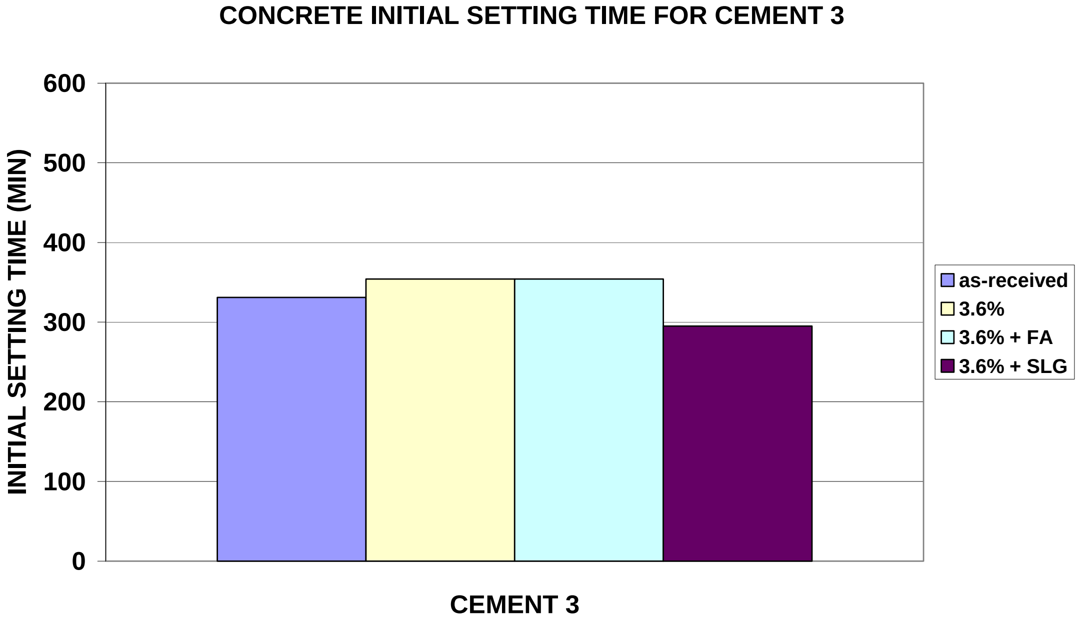


Figure 67. Initial setting behavior for cement 3

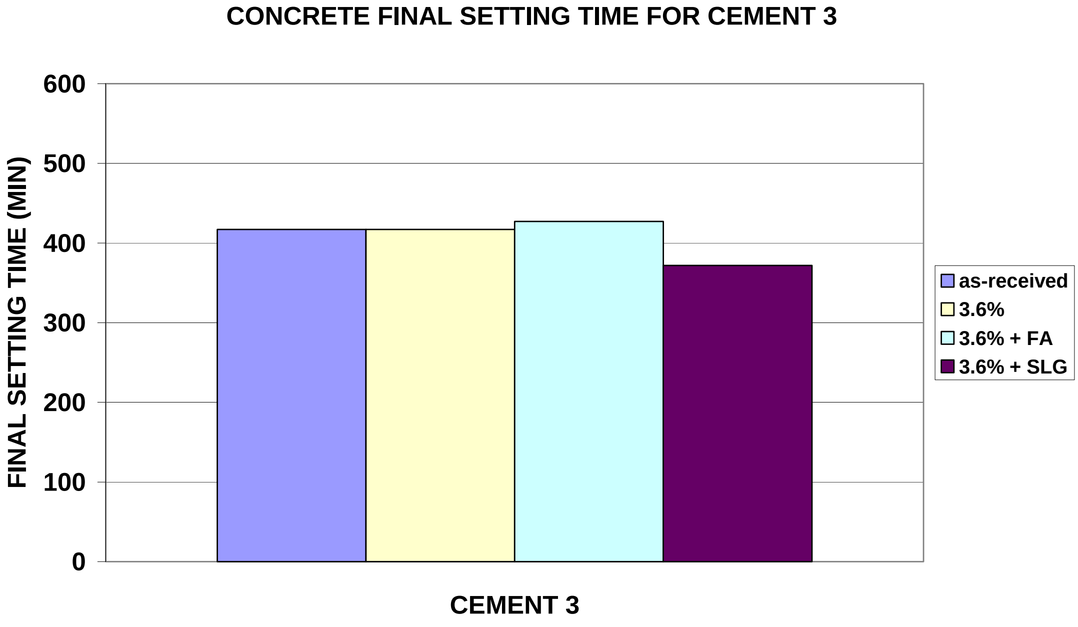


Figure 68. Final setting behavior for cement 3

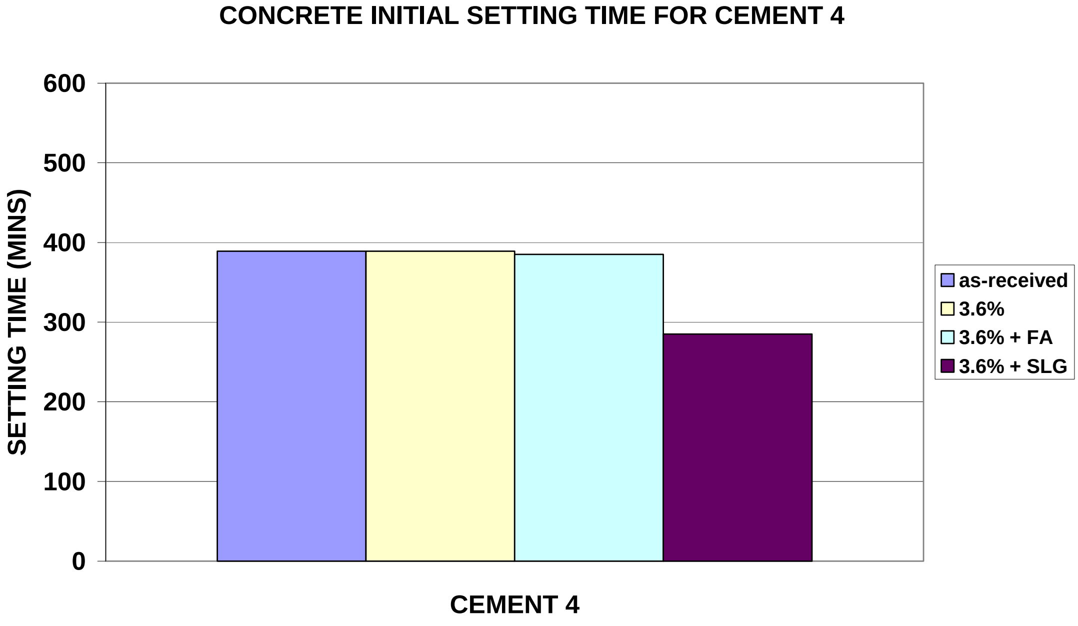


Figure 69. Initial setting behavior for cement 4

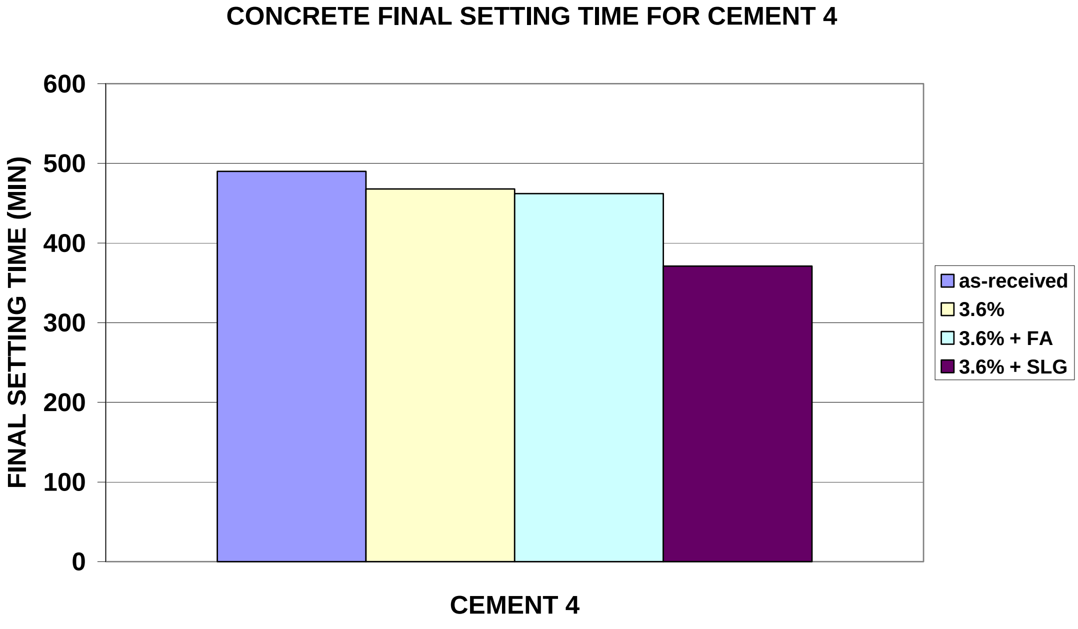


Figure 70. Final setting behavior for cement 4

In general, it can be concluded that incorporation of slag in concrete mixes has significant effect on the setting behavior of concrete. Independent of the chemical composition of the cement, incorporation of slag has the effect of reducing both the initial and final set of concrete. Incorporating fly ash in concrete mixes has more significance on concrete mixes with lower tricalcium silicate content. For cement 1 and 2 with lower tricalcium silicate content, fly ash concrete doped with SO_3 content of 3.6% showed longer initial and final setting times than similar plain concrete mixes doped to the same SO3 content. This does not appear to be the case for higher tricalcium silicate cements, that is, cements 3 and 4. In this case, inclusion of fly ash in concrete mixes had no significance on the setting behavior.

It can be concluded that increasing the SO_3 content of cements did not seem to affect the setting behavior of concrete except for cement 1. In addition, incorporation of fly ash in mixes doped to higher SO_3 content seems to result in affecting the setting behavior of cements with lower tricalcium silicate content. Incorporation of slag in concrete mixes reduced the setting time, independent of the mineralogical composition of cements. This might be due to the high alumina content in slag.

3.3.4 Surface Resistivity

Surface resistivity measurements were conducted on concrete mixes to assess permeability or pore connectivity and microstructure integrity. The results for all concrete mixes are depicted in Figures 71 through 74. For the period reported here of 180 days, it can be seen that incorporation of mineral admixtures increases significantly concrete surface resistivity. Though the incorporation of slag increased resistivity more than incorporation of fly ash, it is noticed that resistivity values are reaching a plateau for slag mixes at 120 days. However, fly ash mixes appear to continue to increase their resistivity up to 180 days. Additionally, fly ash mix for cement 2 has the highest resistivity values for both slag and fly ash mixes up to an age of 180 days.

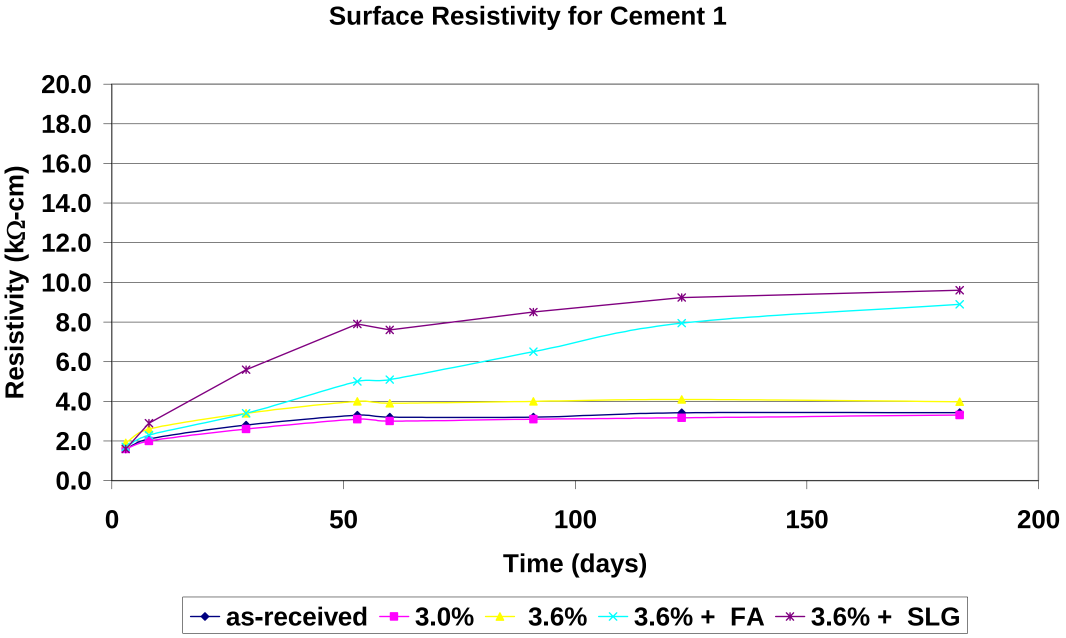


Figure 71. Surface resistivity for cement 1 concrete

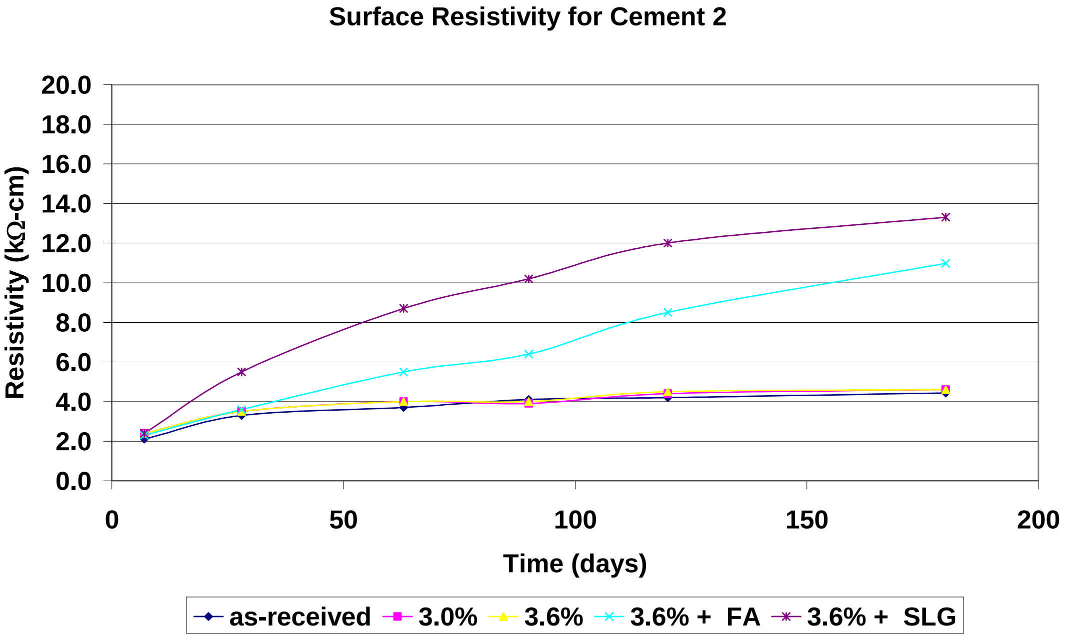


Figure 72. Surface resistivity for cement 2 concrete

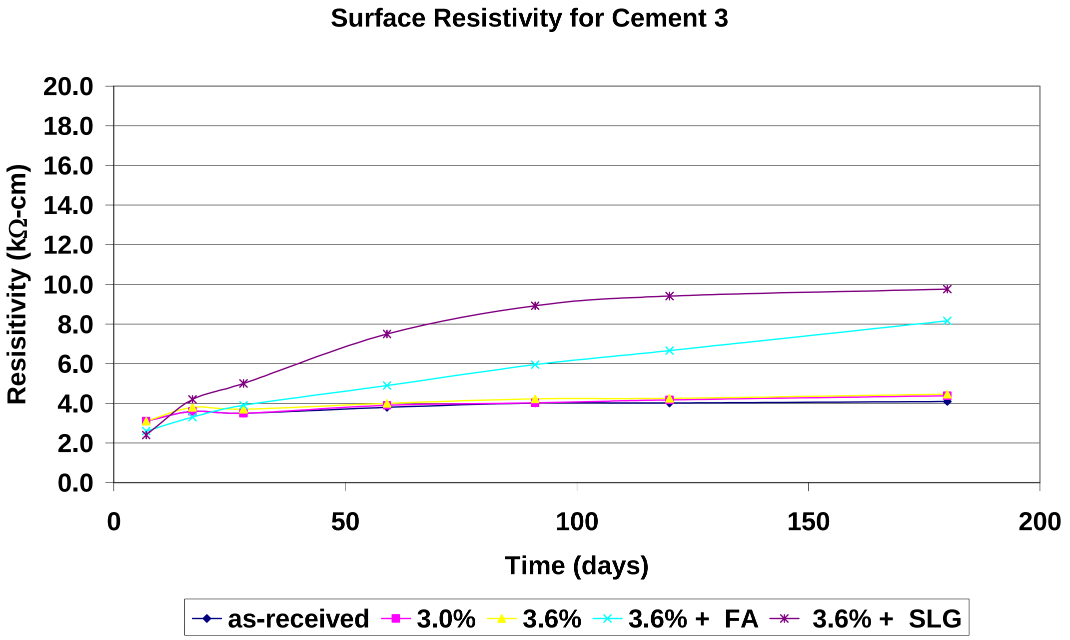


Figure 73. Surface resistivity for cement 3 concrete

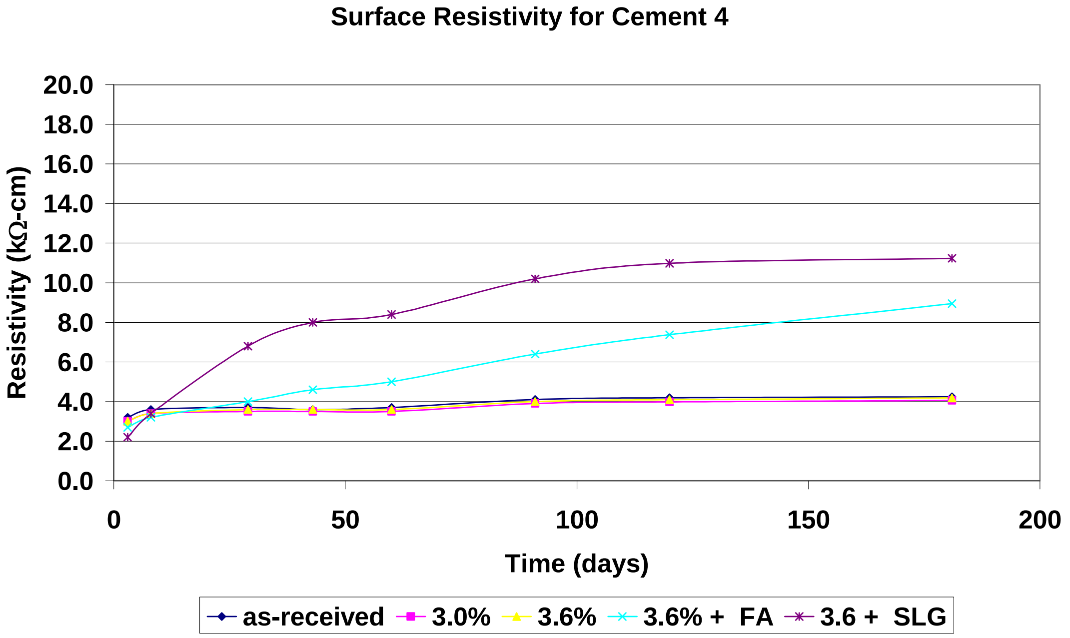


Figure 74. Surface resisitivity for cement 4 concrete

As for the plain mixes with variable SO_3 content, there is a slight increase in resistivity with curing time. In general, initial increase of resistivity is accounted for through pore size refinement that occurs due to continuous hydration. On the other hand, a decrease in surface resistivity is expected to occur with phase formation that can lead to microcracking and therefore more opened structure for the ionic movement within the concrete matrix. This effect did not initiate for the period reported here of 180 days.

In conclusion, for the period of exposure reported here of 180 days, surface resistivity measurements indicate the beneficial effect of incorporating mineral admixtures in concrete mixes with higher SO_3 content. As for the effect of increasing the SO3 content, longer periods would be indicated to assess microstructural changes through resistivity measurements.

3.3.5 Open-Circuit Potential Measurements

Open-circuit potential measurements for concrete are presented in Figures 3-75 through 3-93. For cement 1, and for variable SO_3 content, it appears that all specimens experienced potential drop with the exception of one. Incorporation of mineral admixtures rendered no drop in potential. For mixes incorporating mineral admixtures, the potential was more positive than -0.2V indicating a good probability that no active corrosion is occurring at the time of measurement. Cement 2 showed no drop in potential for the as-received condition. Increasing the SO_3 content to 3.0 showed possible corrosion activity but the potential drop was less than -0.35V. Further increase in SO_3 did not show any corrosion activity for this cement.

For cement 3, increasing the SO_3 content to 3.6 initiated a drop in potential but less than the -0.35V. Concrete blended with mineral admixtures sustained passive behavior for the period reported here. Cement 4, shows an increase in the number of specimens to experience potential drop with increasing the SO_3 content from the as-received condition. However, similar to the other cements addressed in this investigation, doping cement with sulfates in the presence of mineral admixtures appear to render concrete passive over the period of exposure reported here.

In conclusion, most of the cements studied here did not show significant modification in their corrosion behavior with increasing the SO_3 content, except for cement 4, where there was an increase in the number of specimens experiencing a potential drop with increasing the SO_3 content of cement. However, longer periods of exposure are required in order to properly assess durability of concrete. Higher levels of sulfates can generate expansive phase transformation that can lead to microcrack formation. This in turn would render the microstructure more permeable to the ingress of chloride ions. The results also indicate the beneficial effect of incorporating mineral admixtures on the corrosion behavior.

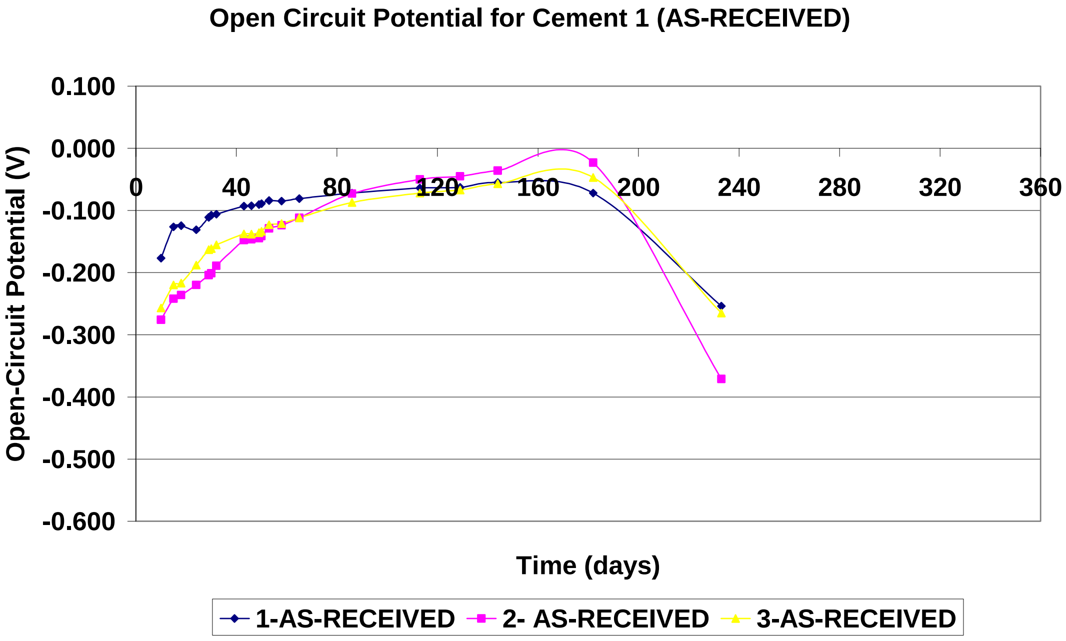


Figure 75. Open circuit potential for cement 1 concrete

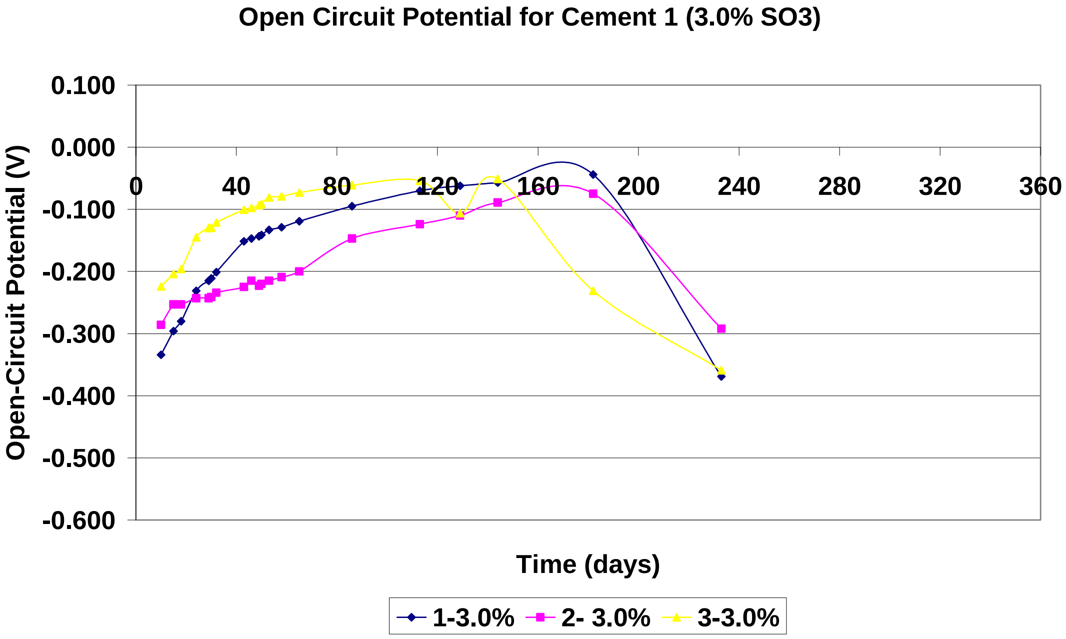


Figure 76. Open circuit potential for cement 1 concrete

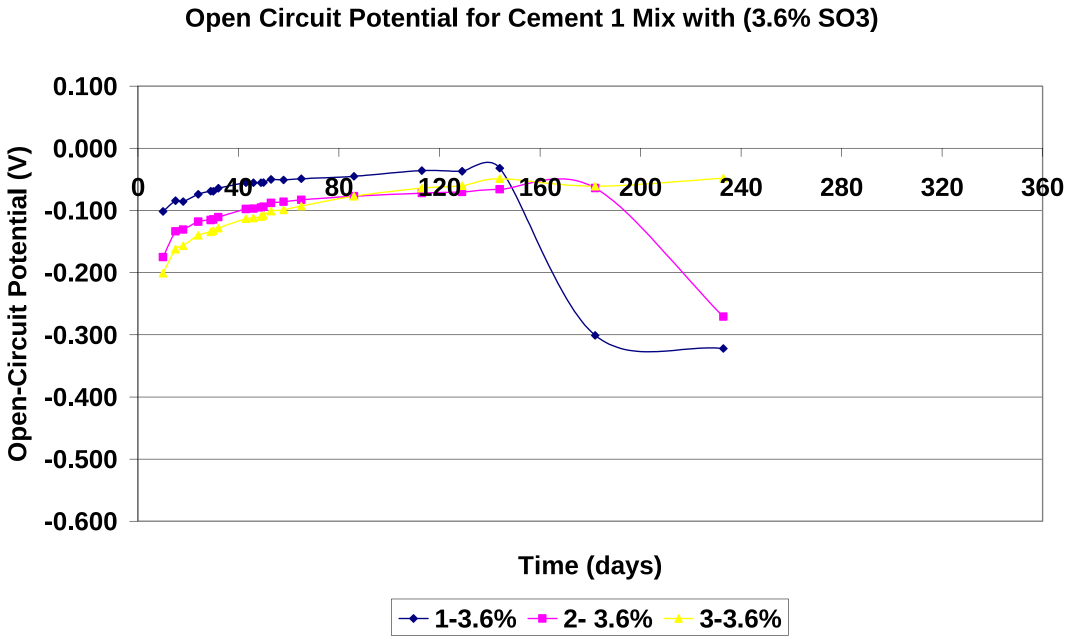


Figure 77. Open circuit potential for cement 1 concrete

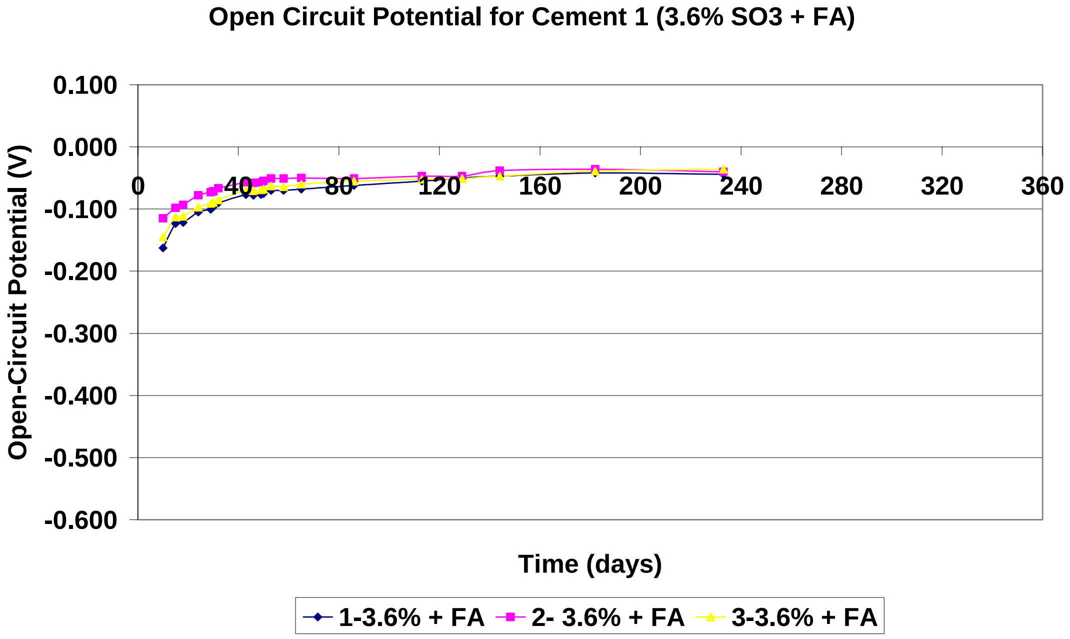


Figure 78. Open circuit potential for cement 1 concrete

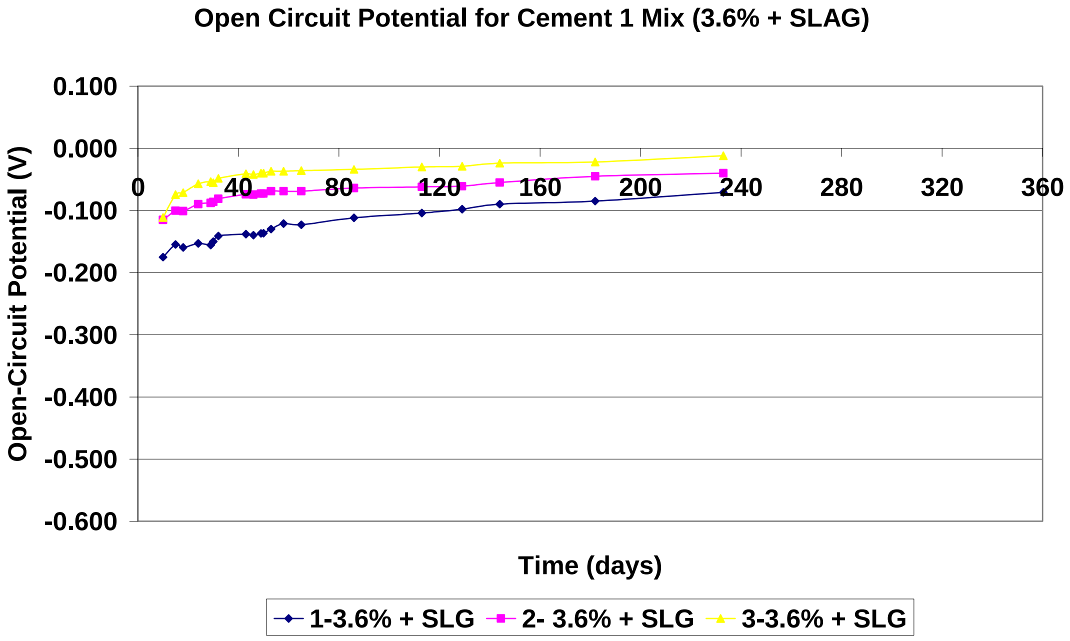


Figure 79. Open circuit potential for cement 1 concrete

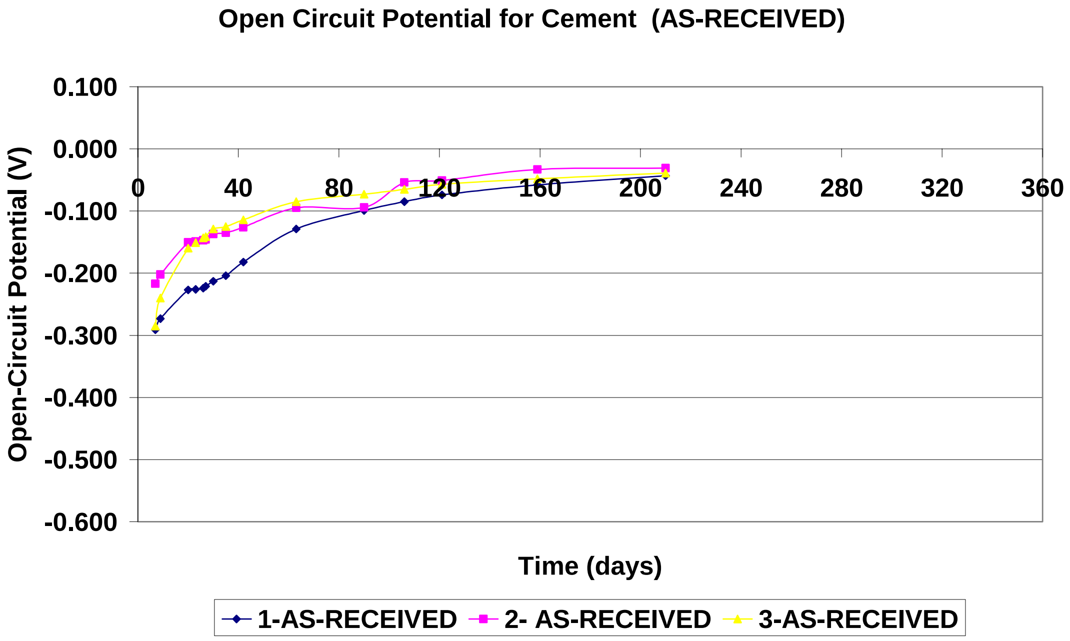


Figure 80. Open circuit potential for cement 2 concrete

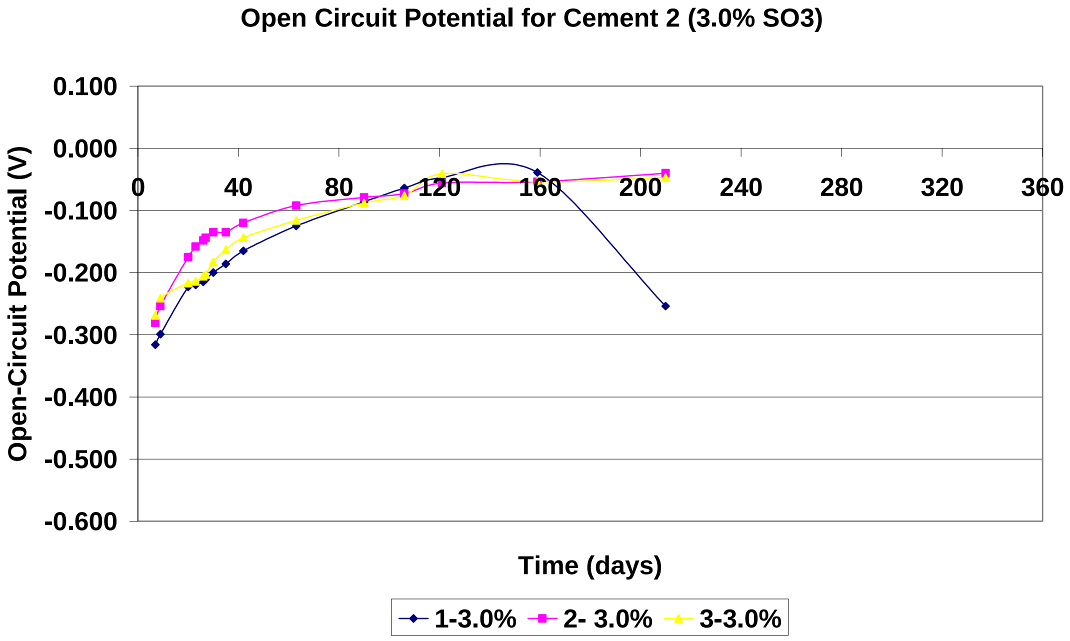


Figure 81 Open circuit potential for cement 2 concrete

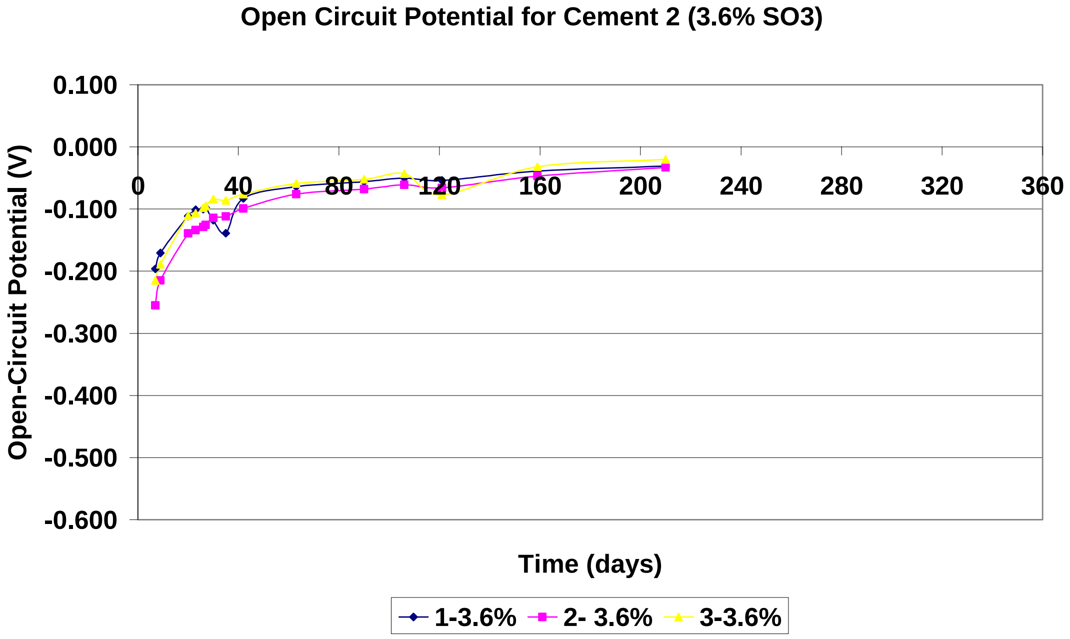


Figure 82. Open circuit potential for cement 2 concrete

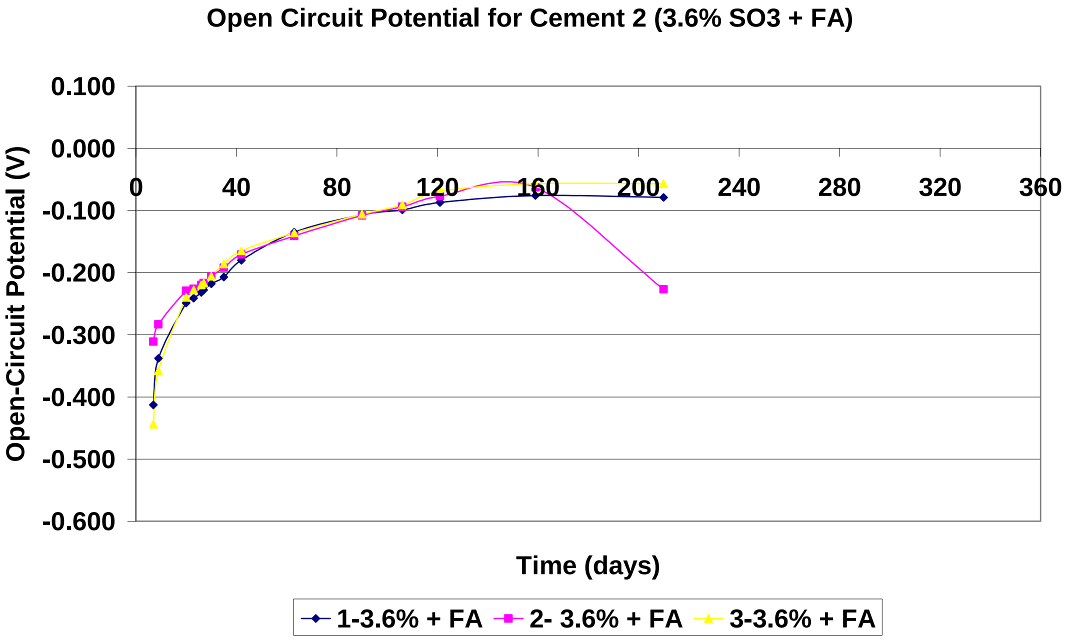


Figure 83. Open circuit potential for cement 2 concrete

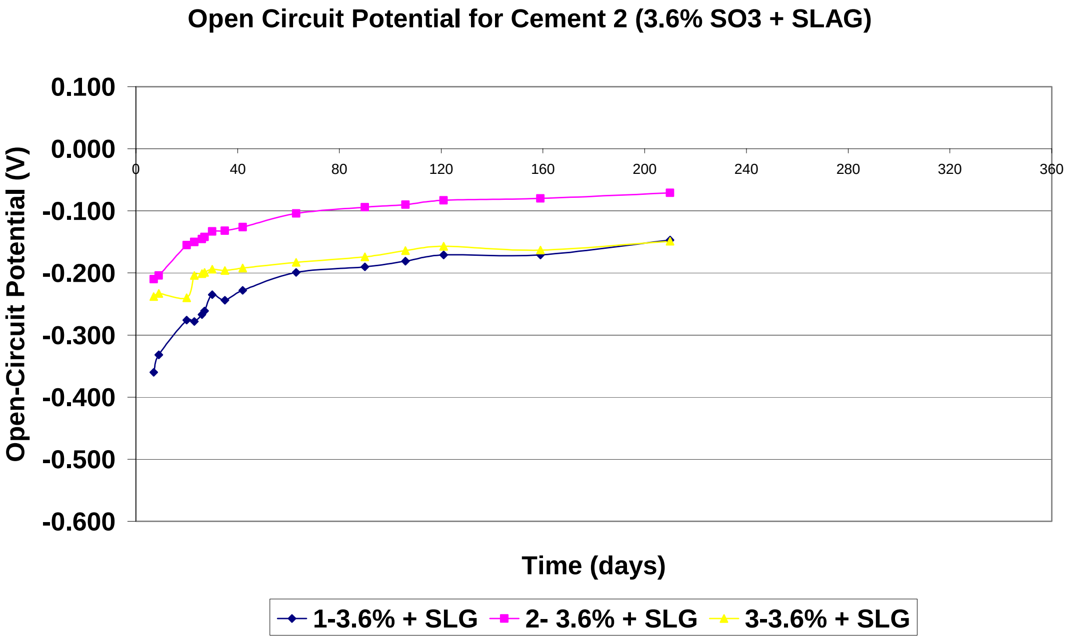


Figure 84. Open circuit potential for cement 2 concrete

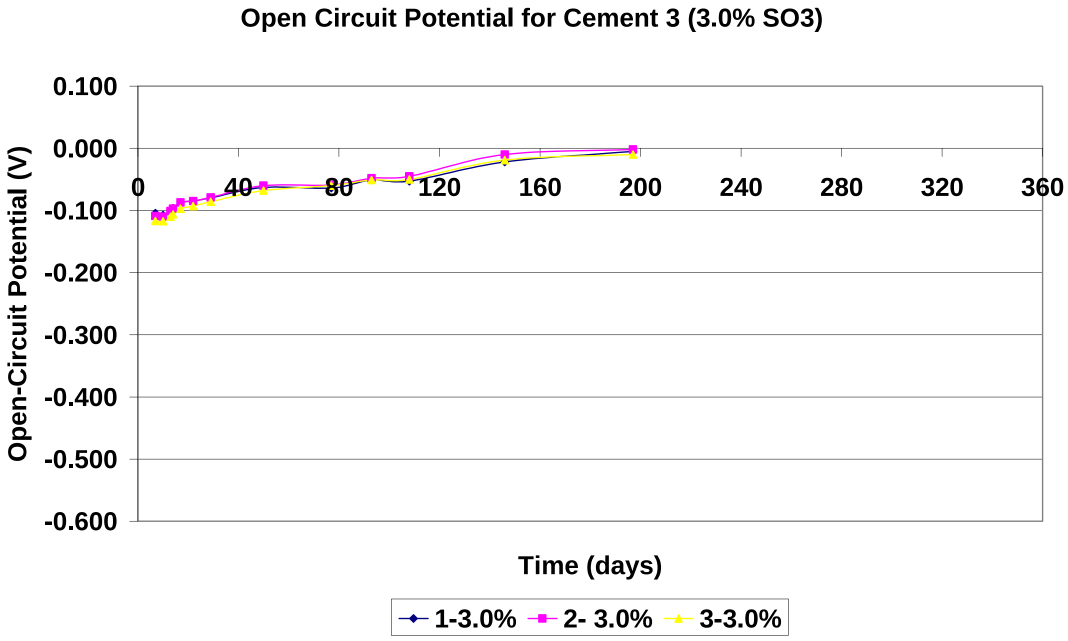


Figure 85. Open circuit potential for cement 3 concrete

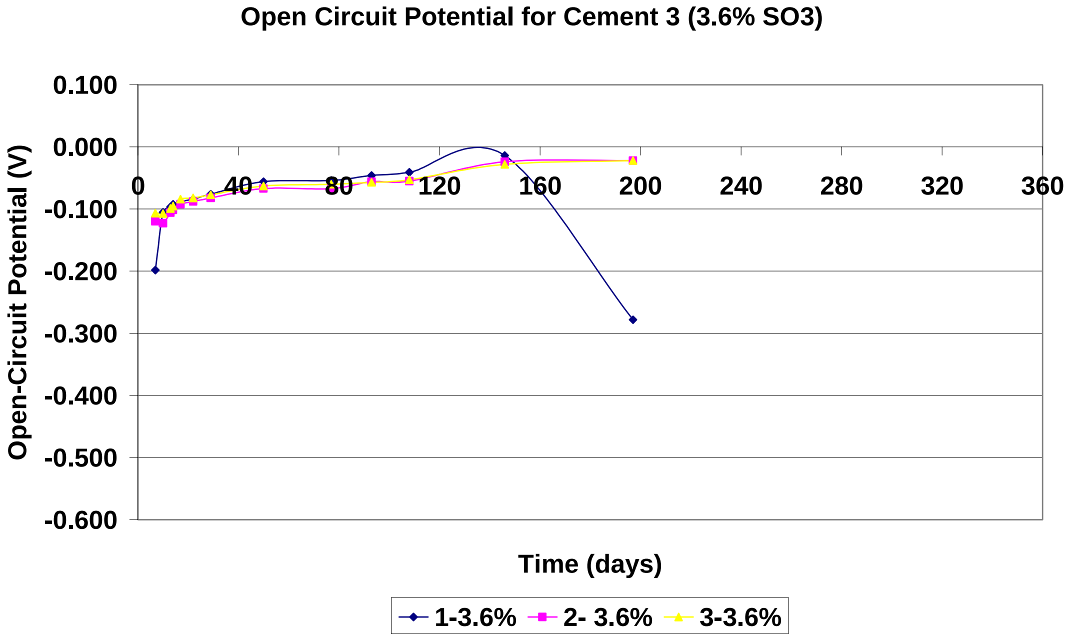


Figure 86. Open circuit potential for cement 3 concrete

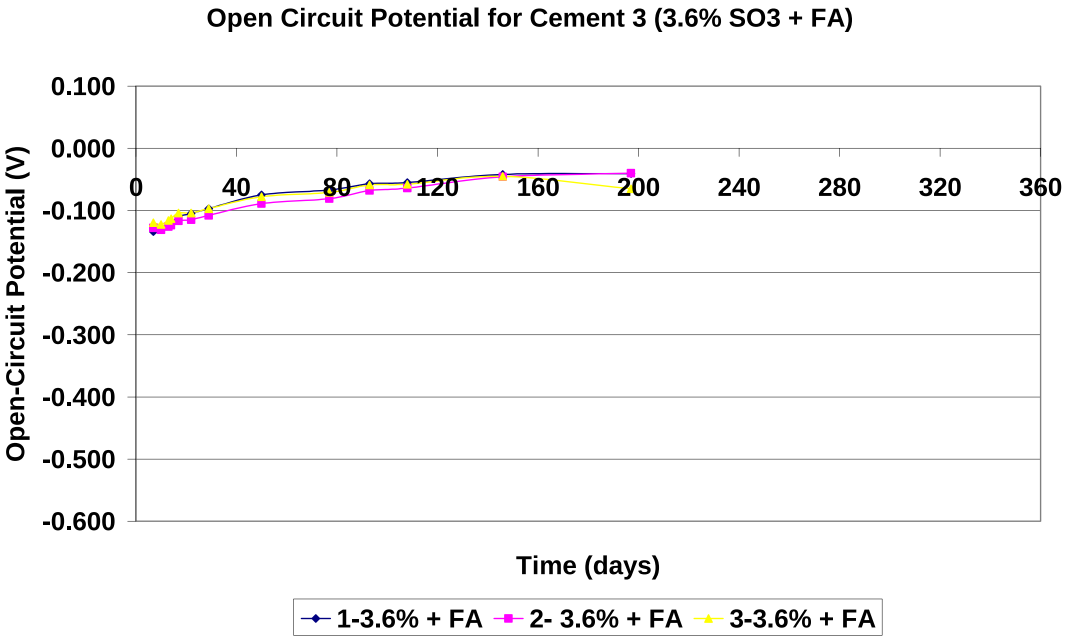


Figure 87. Open circuit potential for cement 3 concrete

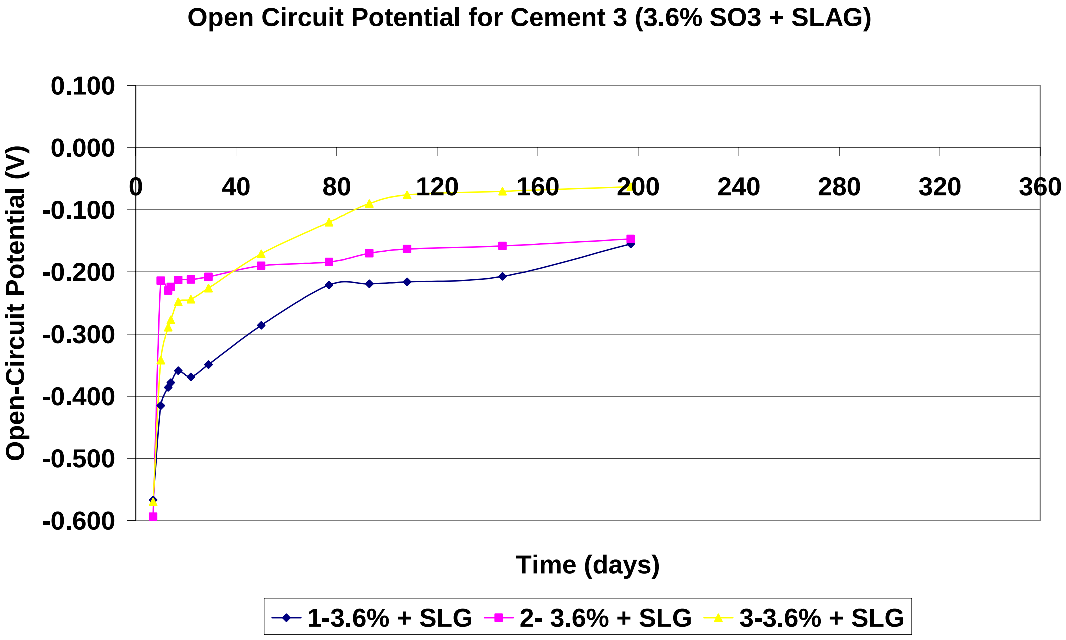


Figure 88. Open circuit potential for cement 3 concrete

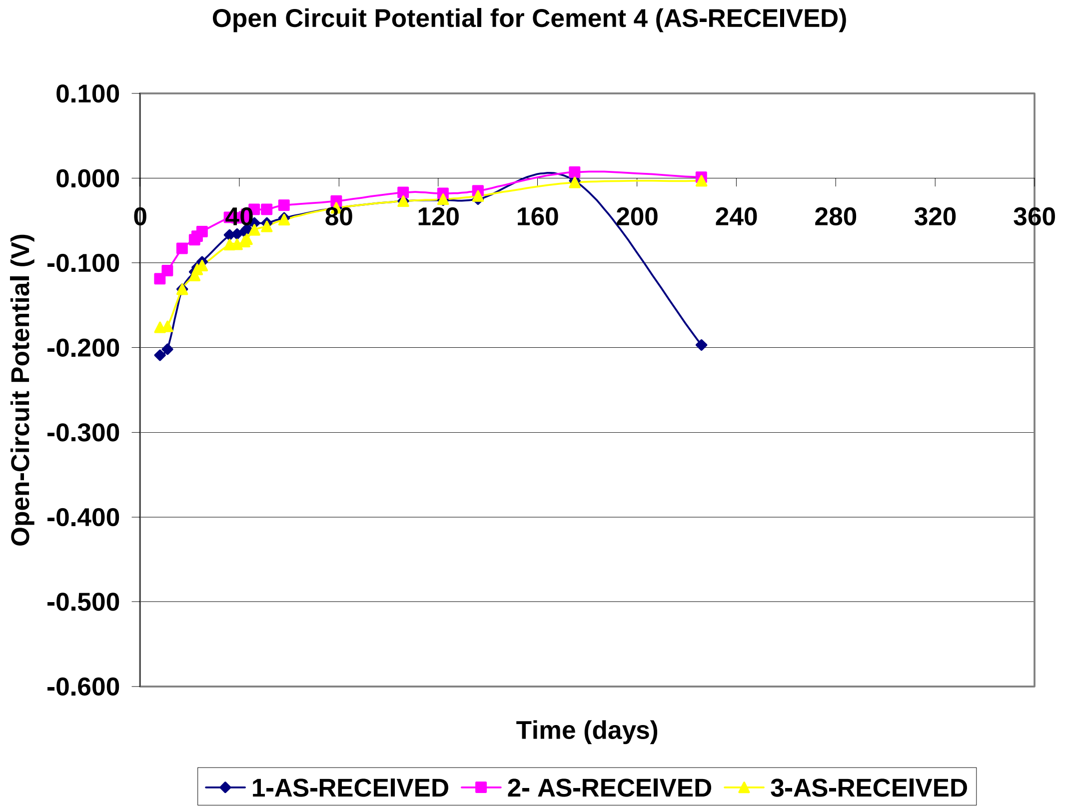


Figure 89. Open circuit potential for cement 4 concrete

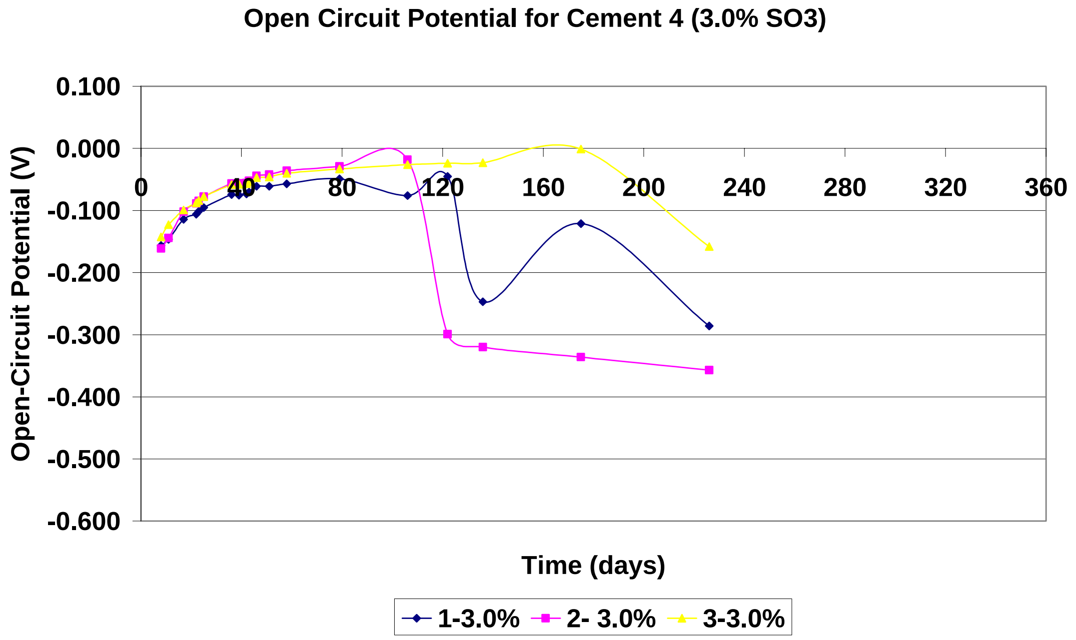


Figure 90. Open circuit potential for cement 4 concrete

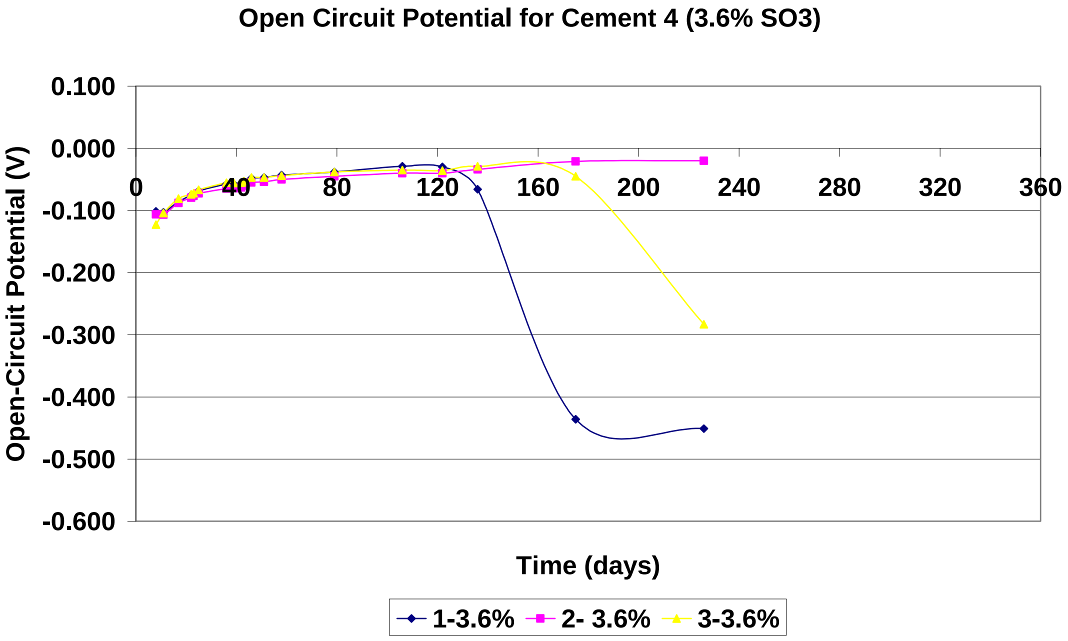


Figure 91. Open circuit potential for cement 4 concrete

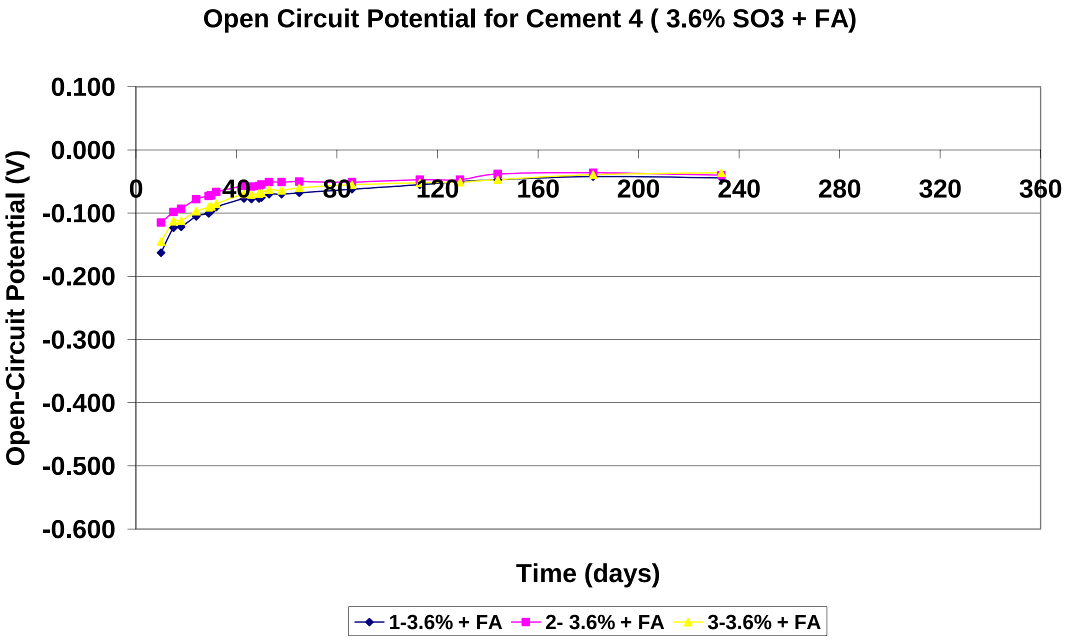


Figure 92. Open circuit potential for cement 4 concrete

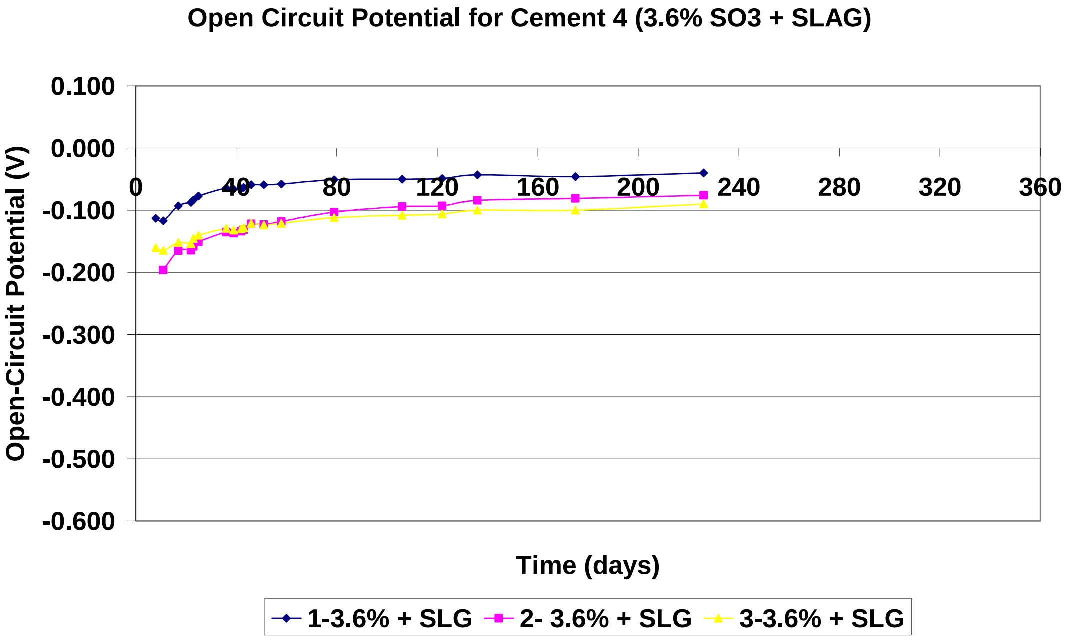


Figure 93. Open circuit potential for cement 4 concrete

CHAPTER IV
CONCLUSIONS AND RECOMMENDATIONS

The following is a summary of the findings of this investigation on the effect of increasing sulfur trioxide content in Portland cement on durability of concrete:

1. Increasing sulfur trioxide content of cements up to 4.2% did not generate failure in accordance with ASTM-C1038 criterion independent of the cement mineralogical composition.
2. Expansion behavior in lime was found to depend on the mineralogy and alkali content of cements. For the same sulfur trioxide content, cements with higher tricalcium aluminate and alkali oxides experienced less expansion than those of low tricalcium aluminate and alkali oxides.
3. Expansion behavior in sulfate environment was found to depend on alkali oxides and mineralogical composition of the cement.
4. For cements with low alkali and tricalcium aluminate content, the effect of increasing SO_3 content to 3.0% did not generate adverse expansion in sulfate solution except for high tricalcium silicate cement (67%). However, increasing the SO_3 content for these cements to 3.6% increased the expansion experienced by the mortar at an age of 180 days for all cements.
5. For moderate tricalcium aluminate and alkali content cement, increasing sulfur trioxide content to 3.6% did not have adverse effects on its expansion behavior in sulfate environment.
6. Sulfur trioxide content of cement was found to affect the rate and amount of strength loss in sulfate exposure. The strength performance of the mortars with varying SO_3 content of the cement was found to depend on cement composition. For cements of low alkali and tricalcium aluminate content, increasing SO_3 content to 3.6% was found to increase the magnitude of strength loss. For those cements, strength loss was found to be dependent on the tricalcium silicate content of the cement. A drop of 3,000 psi at 360 days was reported for mortars that contained cements with an SO_3 content of 3.6% and tricalcium silicate content of 67%.

7. Drying shrinkage results indicate that increasing the SO_3 content beyond 3.0% increased shrinkage for all cements.
8. Concrete strength data reported here for a period of 180 days indicate that for cements of low alkali and aluminate content but high tricalcium silicate, increasing the SO_3 content to 3.6% increases the drop in strength at 180 days.
9. For the period reported here of 180 days, the effect of increasing sulfur trioxide content on surface resistivity and open-circuit potential measurements did not reveal significant effects on the role of the increasing the SO_3 content on those properties. However, incorporation of mineral admixtures did improve the resistivity and maintained the steel rebar potential at high passive values.

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

1. In order to maintain durability of structural concrete, limiting SO_3 content of Portland cement to 3.0% should be maintained.

2. Initiate a study to address the effects of higher alkali and tricalcium aluminate content on concrete long term durability at ambient and elevated temperatures.

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