

EFFECT OF TRASS, GRANULATED BLAST FURNACE SLAG  
AND FLY ASH ON DELAYED ETTRINGITE FORMATION

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AND FLY ASH ON DELAYED ETTRINGITE FORMATION**

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# **ABSTRACT**

## **EFFECT OF TRASS, GRANULATED BLAST FURNACE SLAG AND FLY ASH ON DELAYED ETTRINGITE FORMATION**

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Properly proportioned, placed and cured concrete can be durable under most conditions. However, deterioration of concrete does occur under certain environments. One of the problems that affect the durability of hardened concrete is delayed ettringite formation (DEF) which is an important problem encountered in precast concrete industry where high temperature curing is applied. Although there had been many researches on DEF, there are still many uncertainties about its chemistry and mechanism.

In this study, the effects of partial cement replacement by different mineral admixtures (trass, blast furnace slag and fly ash),  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio and specific surface area of cement on DEF were investigated. For this purpose, 9 groups of control cements were prepared with 3 different specific surface areas and 3 different  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratios. Different amounts of mineral admixtures were blended with the control cements. High temperature curing was applied to the cement pastes and the expansions of these pastes were measured periodically for 240 days.

The experimental results obtained were interpreted for a comparative analysis of the effects of the afore-mentioned parameters.

Keywords: delayed ettringite formation (DEF), expansion,  $\text{SO}_3/\text{Al}_2\text{O}_3$ , blaine fineness, trass, blast furnace slag, fly ash

# ÖZ

## TRAS, GRANÜLE YÜKSEK FIRIN CURUFU VE UÇUCU KÜLÜN GECİKMİŞ ETRENJİT OLUŞUMUNA ETKİSİ

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Uygun bir şekilde tasarlanan, yerleştirilen ve kürlenene beton çoğu koşulda sürdürülebilir bir dayanıklılık gösterebilir. Fakat, belirli koşullar altında beton bozulmaları gerçekleşebilir. Sertleşmiş beton durabilitesini etkileyen problemlerden birisi de gecikmiş etrenjit oluşumudur (GEO) ve betonu yüksek sıcaklıkta kürlenene prekast sektörünün en önemli problemi budur. GEO ile ilgili bir çok araştırma yapılmasına rağmen GEO kimyası ve mekanizması ile ilgili belirsizlikler halen sürmektedir.

Bu çalışmada, farklı mineral katkıların (tras, yüksek fırın curufu, ve uçucu kül) belirli oranlarda çimento ile ikamesinin,  $SO_3/Al_2O_3$  molar oranının ve özgül yüzey alanının gecikmiş etrenjit oluşumuna etkisi araştırılmıştır. Bu amaç doğrultusunda, 3 farklı özgül yüzey alanına ve 3 farklı  $SO_3/Al_2O_3$  oranına sahip toplam 9 adet kontrol çimento grubu hazırlanmıştır. Kontrol çimentolarına farklı oranlarda mineral katkıları eklenene numuneler hazırlanmıştır. Çimento pastaları yüksek sıcaklıkta kürlenmiş ve daha sonra 240 gün boyunca belirli periyotlarda genleşme ölçümleri alınmıştır.

Elde edilen deneysel sonuçlar daha önce belirtilen parametrelerin etkilerinin karşılaştırmalı analizi için yorumlanmıştır.

Anahtar Sözcükler: gecikmiş etrenjit oluşumu (GEO), genleşme,  $\text{SO}_3/\text{Al}_2\text{O}_3$ , özgül yüzey, tras, yüksek fırın curufu, uçucu kül

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## LIST OF ABBREVIATIONS

ASR	: Alkali-Silica Reaction
CH	: Monosulphate
C-S-H	: Calcium Silicate Hydrate
DEF	: Delayed Ettringite Formation
EEF	: Early Ettringite Formation
ESA	: External Sulphate Attack
FT	: Freezing and Thawing
GGBFS	: Ground Granulated Blast Furnace Slag
HLFA	: High Lime Fly Ash
ISA	: Internal Sulphate Attack
LLFA	: Low Lime Fly Ash
SEM	: Scanning Electron Microscope
WD	: Wetting and Drying

# CHAPTER 1

## INTRODUCTION

### 1.1 General

Concrete is the most commonly used construction material all over the world with an estimated annual consumption of 7.9 billion m<sup>3</sup> [U.S. Geological Survey, 2009]. It is used in the construction of buildings, dams, tunnels, roads, etc. Since it is used in such a high volume then its quality and durability obviously becomes very important. Although it has many advantages such as low cost, availability, ease of shaping and water resistance, concrete may have some drawbacks, also. Among these, the durability problems encountered have been investigated for a long time. One of the problems that affect the durability of hardened concrete is the delayed ettringite formation (DEF), which is a problem mostly observed in precast and prefabricated concrete elements to which high temperature curing is applied.

DEF is expansion and cracking of concrete associated with the delayed formation of the mineral ettringite (a hydrated calcium sulfoaluminate) which is otherwise a normal product of early cement hydration. DEF is a result of high early temperatures (above 70°C – 80°C) in the concrete caused either by application of accelerated (heat) curing or by the build-up of heat of hydration in mass concrete, which prevents the normal formation of ettringite. Cooling, followed by prolonged exposure to moist conditions can, in some circumstances, cause the slow formation of ettringite. Delayed formation of

ettringite in already hardened concrete leads to expansion and subsequent cracking and failure [BCA, 2006].

The first case of concrete deterioration related to DEF was observed in precast field concrete that had undergone high-temperature curing and subsequent exposure to moist conditions [Shimada et al., 2005]. After that, many failures of a number of precast concrete products manufactured at elevated temperatures have been reported, especially the railway ties. Cases of deterioration involving railway ties have been reported in several countries such as Finland, Germany, South Africa and United States of America [Sahu and Thaulow, 2004; Diamond, 2000; Ekolu et al., 2007b].

## **1.2 Objective and Scope**

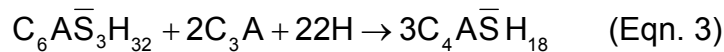
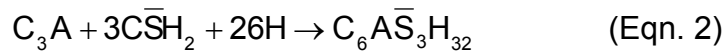
The objective of this study is to investigate the effect of different mineral admixtures on reducing DEF. For this purpose, 9 groups of control cements were prepared with three different specific surface areas and three different  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratios which are adjusted by adding natural gypsum. Different amounts of four different types of mineral admixtures (trass, granulated blast furnace slag, high lime fly ash and low lime fly ash) were blended with the control cements. High temperature curing was applied to the cement pastes and the expansions of these pastes were measured up to 240 days.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Delayed Ettringite Formation (DEF)

Tricalcium aluminate ( $C_3A$ ) is one of the four major clinker phases which reacts very rapidly with water and causes rapid setting (Eqn. 1). In order to retard this early setting of the paste, gypsum (major source of sulphates in cements) is added to clinker during grinding in the cement mill. With the presence of gypsum,  $(AlO_4)^-$  and  $(Ca)^{2+}$  ions released from  $C_3A$  and  $(SO_4)^{2-}$  ions released from gypsum react in an aqueous environment to form  $C_6\bar{A}\bar{S}_3H_{32}$  (ettringite) as the first hydrate (Eqn 2). After the total consumption of sulfate, further hydration makes the ettringite unstable and it may gradually convert into  $C_4\bar{A}\bar{S}H_{18}$  (monosulfate form) (Eqn 3). This kind of homogenous ettringite formation is called early ettringite formation (EEF) and it causes expansion but as concrete has not hardened, it can accommodate the expansion. Also, it is advantageously used for setting time retardation.



On the other hand, when ettringite forms heterogeneously at later ages (after months or years), in a rigid hardened concrete, it is called DEF and it can produce cracking, spalling and failure of concrete. In order to prevent this, the

sulphate content of the cement should be so adjusted that it is consumed totally by the reaction expressed as (Eqn. 2) and not later than in the first 24 hours after mixing with water. Excess sulphate may, likewise in accordance with reaction (Eqn. 2) cause expansion phenomena in hardened mortar or concrete [Labahn et al., 1983; Collepardi, 2003; Grattan-Bellew et al., 1998].

Even if the sulphate content in the concrete is just enough for the setting regulation process, there may be external sulphate sources which could penetrate into the hardened concrete and cause deterioration of the concrete. Thus, there are two kinds of sulphate attacks causing DEF related damages: External sulphate attack (ESA) and internal sulphate attack (ISA). ESA occurs when the environmental sulphate, from water or soil, penetrates into concrete and it is generally seen in permeable concretes. It also occurs in a moist environment favoring diffusion of sulphate through the aqueous phase of the capillary pores. On the other hand ISA occurs in a sulphate-free environment for the late sulphate release from gypsum-contaminated aggregates or thermal decomposition of ettringite. It is favored by preliminary microcracks where deposition of ettringite crystals can occur [Collepardi, 2003]. In Figure 2.1 classical sulphate attack and DEF (inside the dashed box) is grouped according to their sources [Tosun, 2007].

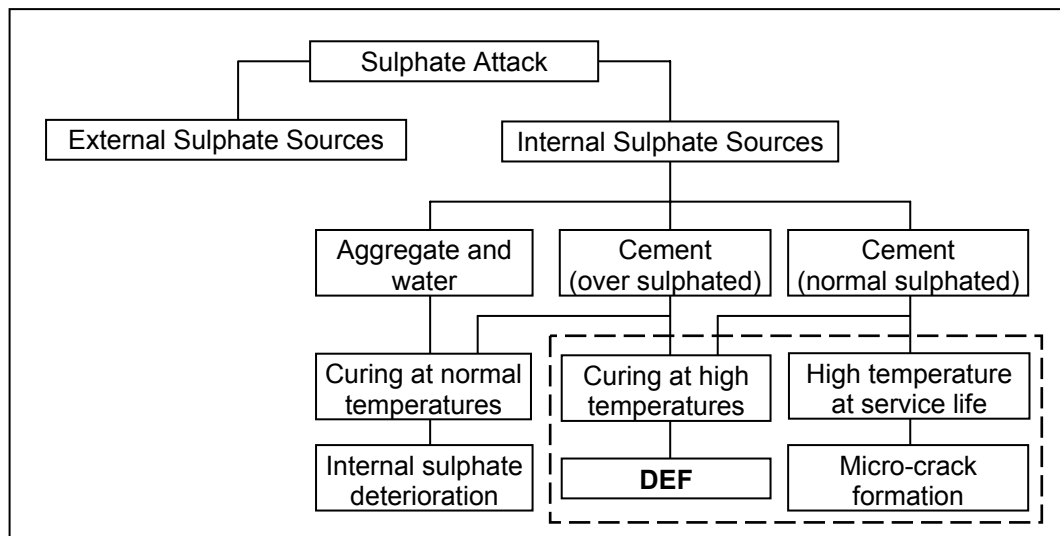


Figure 2.1 Grouping of classical sulphate attack and DEF according to sources [Tosun, 2007]

Scanning electron micrographs show that ettringite occurs in concrete in various forms, often as clusters of ettringite crystals, felt-like or parallel needles of differing sizes. If ettringite crystallizes out without spatial obstruction, as in the pores, then it has the typical needle-shaped crystal habit [Stark and Bollmann, 1999]. In Figure 2.2 SEM photographs of ettringite forms are given.

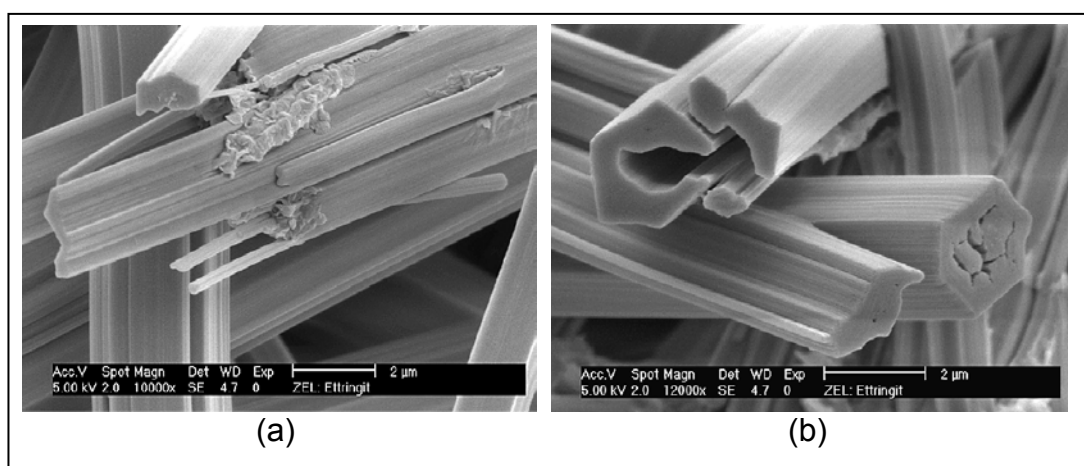


Figure 2.2 SEM Micrographs of ettringite forms (a) thick needle-like appearing (b) needle-shaped with hexagonal cross-section [Stark and Bollmann, 1999]

## **2.2 Factors Influencing DEF-Related Expansion**

The first investigation about DEF-related expansion was published by Lerch in 1945. After that, different hypotheses were developed by many authors about the formation of ettringite and accordingly many parameters which affect DEF were defined. Despite extensive investigations in connection with DEF, the direct cause is still controversial and remains unclear [Stark and Bollmann, 1999; Shimada et al., 2005]. The most common parameter that almost all the authors agree is the high curing temperature of the concrete or the high temperatures that the mass concrete reaches because of the heat of hydration. Some of the other factors are the cement composition, specific surface area, aggregate properties and the additives.

### **2.2.1 Curing Conditions**

Exposure to elevated temperatures (above 70°C) during curing for a sufficient period and subsequent exposure to moisture promotes DEF expansion mechanism. With rising temperature there is a drop in the thermodynamic stability of ettringite in favor of monosulphate. Depending on the thermodynamic data the theoretical transformation from ettringite into monosulphate ranges between 70 and 90 °C [Stark and Bollmann, 1999]. There is a general agreement in the literature that 70°C is the threshold temperature, below which expansion does not occur. According to a research done by Ramlochan et al. [2003], there was a systematic increase of the ultimate expansion of mortars with increasing curing temperatures. Similar results were also obtained by Kelham [2004] and by Taylor et al. [2001] in different studies. Figure 2.3 shows the results of the studies of Ramlochan et al. [2003] and Kelham [2004], respectively.

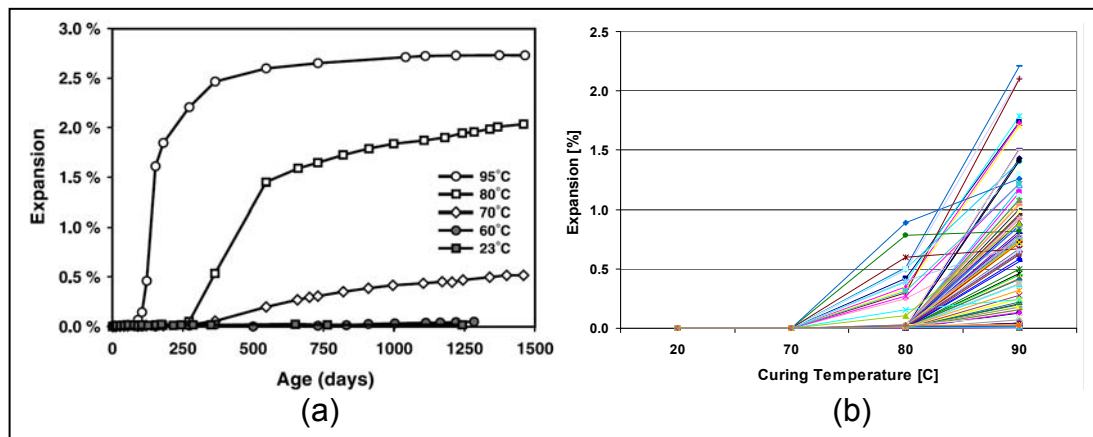


Figure 2.3 Expansion of mortars cured at different temperatures (a) according to Ramlochan, (b) according to Kelham [Ramlochan, 2003; Kelham, 2004]

The large amount of ettringite detected in concrete is also affected by different failure mechanisms during curing like alkali - silica reaction (ASR), freezing and thawing (FT), and wetting and drying (WD). Batic et al. [2000], in their study, concluded that the amount of delayed ettringite crystallized in concretes will largely depend on the environment surrounding the specimens. The amount of delayed ettringite crystals is minimum under permanent saturation conditions, it is somewhat larger in concretes subjected to FT, and it is substantially increased due to the action of WD cycles. Deterioration mechanisms operating in concretes affected by ASR seem to be linked only to the formation of siliceous gels of an amorphous nature.

### 2.2.2 Chemical Composition of Cement

There have been a number of laboratory studies in order to relate expansion from DEF to cement composition. Up to now no reliable correlation which can be applicable to all cement types and compositions was obtained. However, it has been suggested that the risk of damage may be reduced to some extent by using cements that are low in  $\text{SO}_3$ ,  $\text{C}_3\text{A}$ , alkalis,  $\text{MgO}$  and  $\text{C}_3\text{S}$  [Ramlochan et al., 2003].



In the literature,  $\text{SO}_3$  amount and the  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio are often considered to be the dominating factors and it is obvious that high  $\text{SO}_3$  content in cement is a significant factor in DEF [Escadeillas et al., 2007; Zhang et al, 2002a]. If there is no  $\text{SO}_3$ , there can be no ettringite. If there is too much, ettringite but not monosulphate will be present at the end of the heat treatment. If there is no  $\text{Al}_2\text{O}_3$ , there can again be no ettringite, and if there is too much, monosulphate but not ettringite will be present. The pessimum  $\text{SO}_3$  is likely to increase with the content of  $\text{Al}_2\text{O}_3$ ; this produces a pessimum in the  $\text{SO}_3/\text{Al}_2\text{O}_3$  ratio [Taylor et al., 2001]. In their study Zhang et al. [2002b], recorded expansions for the mortars made from cements with  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratios falling between about 0.85 and about 1.40. Maximum expansion was recorded about molar ratio of about 1.00 and no expansion was recorded below molar ratio of 0.80. The results are plotted in Figure 2.4. In their paper, they also defined a DEF Index (Eqn. 4).

$$\text{DEF Index} = \left( \frac{\text{SO}_3}{\text{Al}_2\text{O}_3} \right)_m \times \left[ \frac{(\text{SO}_3 + \text{C}_3\text{A})_w}{10} \right] \times \sqrt{\text{Na}_2\text{O}_{\text{eq}}} \quad (\text{Eqn. 4})$$

where;  $(\text{SO}_3 / \text{Al}_2\text{O}_3)_m$  is the molar ratio of  $\text{SO}_3$  to  $\text{Al}_2\text{O}_3$  of the cement,  $(\text{SO}_3 + \text{C}_3\text{A})_w$  is the combined weight percentage of  $\text{SO}_3$  and  $\text{C}_3\text{A}$  in the cement and  $\sqrt{\text{Na}_2\text{O}_{\text{eq}}}$  is the square root of the weight percentage of  $\text{Na}_2\text{O}_{\text{eq}}$  in the cement.

Zhang et.al. [2002b] concluded that there is no expansion for an index below 1.1 and there is always expansion above this value. Figure 2.5 shows this relationship.

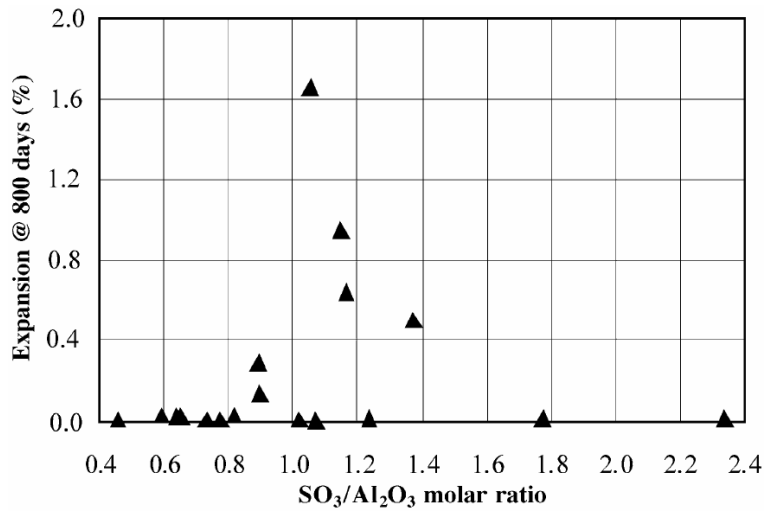


Figure 2.4 Expansion of mortar bars treated at 85 °C after 800 days vs. SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of the cement used [Zhang et al., 2002b]

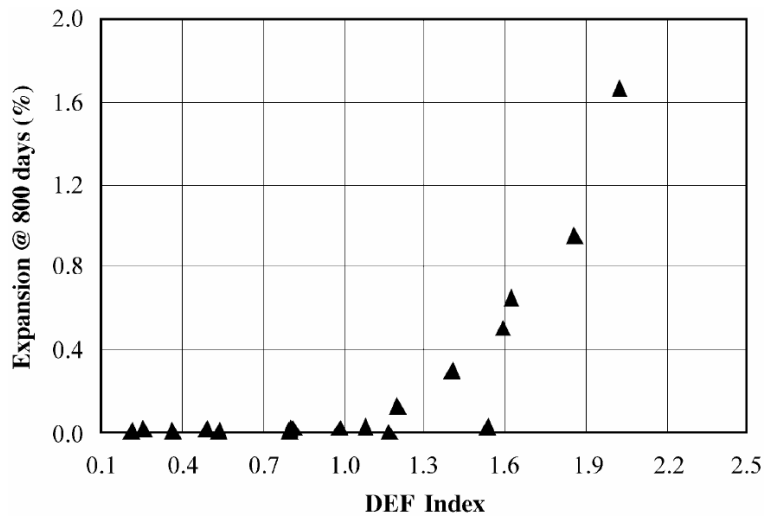


Figure 2.5 DEF index of cement vs. expansion of mortar bars at 800 days [Zhang et al., 2002b]

Kelham [1996] proposed a more complex equation taking into account the fineness and chemical composition of the cement as follows:

$$\begin{aligned} \text{Expansion at } 90^\circ\text{C} = & (0.00474 \times \text{SSA}) + (0.0768 \times \text{MgO}) + (0.217 \times \text{C}_3\text{A}) + (0.0942 \times \text{C}_3\text{S}) + (1.267 \times \text{Na}_2\text{O}_{\text{eq}}) - \\ & (0.737 \times | \text{SO}_3 - 3.7 - [1.02 \times (\text{Na}_2\text{O})_{\text{eq}}] |) - 10.1 \end{aligned} \quad (\text{Eqn. 5})$$

The cement alkali content was found to have a significant effect on DEF-induced expansion. It is known to affect the solubility of ettringite [Zhang et al., 2002b; Pavoine, 2006]. For cements with high  $\text{SO}_3$  content, expansion is favored by high alkali contents, but in the case where the cement has low  $\text{SO}_3$  content than alkali has no significant effect. It is because of the fact that increased alkali content, especially if combined with high  $\text{SO}_3$  content, tends to increase the rate of alite ( $\text{C}_3\text{S}$ ) hydration at early ages, which could increase the expansion produced by the formation of a given amount of ettringite during storage [Taylor et al., 2001].

High  $\text{C}_3\text{A}$  content is required for DEF to be developed [Zhang et al., 2002a].

In their study, Gonzáles et al. [1997], worked with four low- $\text{C}_3\text{A}$  Portland cements with different  $\text{C}_3\text{S}$  content (40 to 74%). The greatest expansion was measured for high  $\text{C}_3\text{S}$  content cement. The increase of  $\text{C}_3\text{S}$  content implies an increase of the CH liberated during the hydration of Portland cement and modifies the development of strength, heat and porosity of the hardened paste. In sulphate environment, CH can convert to gypsum leading to surface damage. But, it is not well established that gypsum formation leads to expansion.

### **2.2.3 Specific Surface Area**

In order to increase the early strength of cement, the producers generally choose to grind the clinker to high fineness values in order to increase the reactivity of the cement. However, when the fineness of cement increases, the heat of hydration of cement and DEF susceptibility increases accordingly.

In his study, Kelham [1996] prepared cements with the same compositions but different fineness values. The expansions of the mortars with these cements are recorded after curing at 90 °C for 12 hours followed by 5 years

of storage. The results are given in Figure 2.6. It is obvious that expansion potential is increased with increasing specific surface area.

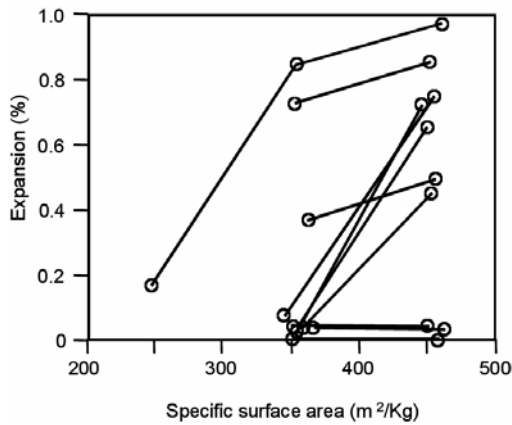


Figure 2.6 Effect of cement fineness on expansion [Kelham, 1996]

As in the study of Kelham, Tosun [2006] ground the same clinker with different grinding times in order to obtain 3 different blaine fineness values of 3000, 4000 and 5000 cm<sup>2</sup>/g. After preparing mortars with these cements, DEF potential was investigated. Tosun concluded that, in the short term, the effect of specific surface area is not significant. However, in the long term, the rate of expansion of mortars prepared with finer cements exceeded those of the coarser ones.

## 2.2.4 Aggregate Properties

Aggregate properties have major effects on the expansive behavior associated with DEF. In their investigation Grattan-Bellew et al. [1998], used 6 different types of aggregate, namely basalt, dolostone, granite, limestone, siliceous limestone, and pure crystalline quartz, in order to evaluate the effect of aggregate composition and particle size on the expansion of mortar bars, due to DEF. Only mortar bars made with quartz aggregate showed significant expansion. Expansion was found to be inversely proportional to the particle size of the quartz aggregate. The rate of expansion is related to the surface

area of the aggregate. Similar results were obtained by Fu et al. [1997] where mortar bars made with finer sand high in quartz expanded more than those made with coarser sand high in limestone.

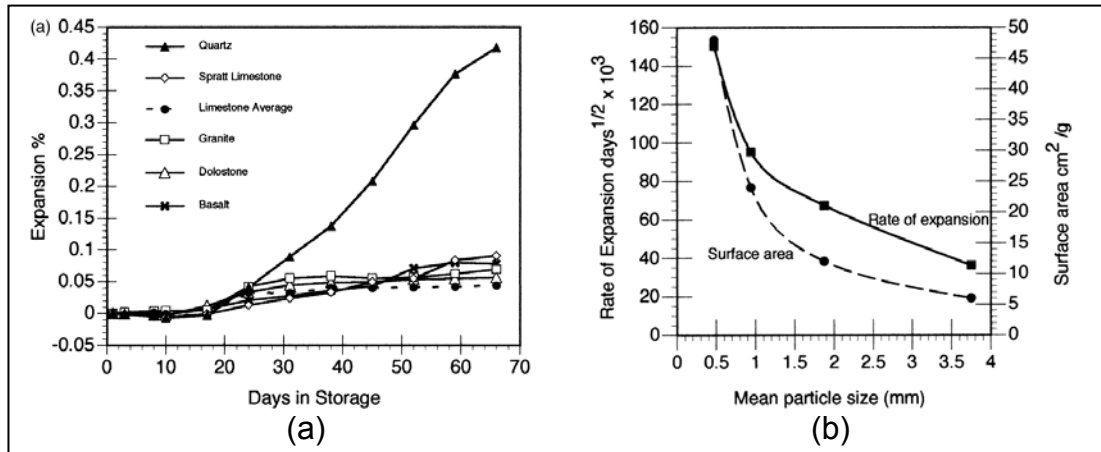


Figure 2.7 Effect of (a) aggregate composition, and (b) specific surface area on DEF

### 2.2.5 Pore Solution

The pore solution is the major store for sulphate in the heated material other than monosulphate, but calculations based on the probable amounts and compositions of the pore solution and the C-S-H show that it is much less important in respect than the C-S-H [Taylor et al., 2001].

The expansion was significantly suppressed when the specimens are stored in saturated air rather than in water. Furthermore, it is shown that storage in alkali solution reduces or even eliminates the expansion as the alkali concentration increases. In both cases, the reduced expansion was the result of preventing leaching of alkalis in the system into the environment. This is an important observation, clearly indicating that the alkali leaching drastically alters pore solution chemistry, and greatly influences the DEF-related expansion. Therefore, as DEF is receptive to changes in pore solution

chemistry, increased connectivity and diffusivity of the system may facilitate ettringite reformation and possibly enhance the DEF susceptibility [Shimada et al., 2005].

### **2.2.6 Microcracks**

There have been claims that ettringite growth in microcracks is fully or partly responsible for DEF-related expansion, as ettringite nuclei preferentially form in crack tips rather than on plane solid surfaces, and that existing cracks are the critical sites of expansion [Shimada et al., 2005]. In their study, Ekolu et al. [2007b], concluded that the presence of microcracking in DEF expansive cementitious systems promotes both an earlier onset of delayed ettringite formation and a greater related ultimate damage.

### **2.2.7 Mineral Admixtures**

Mineral admixtures which modify the characteristics that influence the durability of concrete seem to reduce the potential risk of concrete expansion. Instead of using high early strength Portland cements in concrete elements, blended cements like pozzolanic or blast furnace slag cements should be preferred [Pavoine et al., 2006; Lawrence, 1993]. In most cases, the long-term expansion is reduced, rate of expansion is slowed down, and the onset of expansion is delayed by the addition of any amount of admixtures. Since in the literature  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio is considered to be a very important factor for expansion and the potential of expansion is increased with the increasing molar ratio, than the efficacy of a particular admixture on controlling the expansion must be related to its  $\text{Al}_2\text{O}_3$  content. For example, in their study, Ramlochan et al. [2003] concluded that Metakaolin, which contains a high amount of reactive  $\text{Al}_2\text{O}_3$ , was the most effective in controlling expansion at relatively low cement replacement levels.

Slag and fly ash, which are also sources of  $\text{Al}_2\text{O}_3$ , were also effective in suppressing expansion at higher replacement levels. Silica fume was less effective in controlling expansion at conventional replacement levels, and only at higher replacement levels expansion may be delayed.

In order to control expansion, higher replacement levels of slag or fly ash is needed. However, at higher levels of replacement the early strength of cement decreases, which may make them unsuitable for precast concrete. In order to overcome this problem a small amount of silica fume or metakaolin, which increases the early strength, should be added to the mixture. Moreover, ternary-blended cementitious systems have other benefits for the long-term durability of concrete [Ramlochan et al., 2003].

## CHAPTER 3

### EXPERIMENTAL STUDY

#### 3.1 General

This study was intended to determine the effect of different admixtures on DEF-related expansion. In order to achieve this objective, first of all, 9 different types of control cement were prepared with 3 different specific surface areas and 3 different  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratios by adding natural gypsum. Different amounts of trass, GGBFS, low-lime fly ash, and high-lime fly ash were mixed with these control cements. Totally 117 cement samples were prepared.

Before preparing the cement pastes for high temperature curing, the normal consistency water requirements of all the cement samples were determined according to TS EN 196-1 and all the specimens were prepared accordingly. Finally, the pastes were heat-cured similar to the temperature cycle that Escadeillas et al.[2007] applied in their studies, which is representative of the treatments generally used in precast concrete industry. The expansion measurements were performed according to a prescribed schedule.

All the tests were performed in the Quality Control Laboratory of Bolu Cement Plant.



### 3.2 Materials

The Portland cement clinker, gypsum and trass were obtained from Bolu Cement Factory and the origin of gypsum and trass were Bala/Ankara mines and Tekke/Bolu mines respectively. Granulated blast furnace slag, high lime fly ash and low lime fly ash were obtained from Erdemir Steel Plant, Çayırhan and Tunçbilek Thermal Power Plants, respectively.

The clinker was interground with gypsum and 5% (by weight) limestone (as a minor additional constituent) to three different blaine fineness values as 4000, 4750 and 5500 cm<sup>2</sup>/g, to obtain the control cements.

Additional gypsum was separately ground to 5000 cm<sup>2</sup>/g blaine fineness, and was added to the control cements in order to obtain cements with SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of 0.8, 1.0, and 1.2.

Trass and granulated blast furnace slag were ground to 4925 and 5341 cm<sup>2</sup>/g blaine fineness, respectively, and blended with the Portland cements prepared beforehand in 3 different proportions.

Fly ashes were similarly blended with the Portland cements. However, they were not ground as they were already in finely divided form. Also high lime fly ash from Çayırhan Thermal Power Plant was Class C, and low lime fly ash from Tunçbilek Thermal Power Plant was Class F, according to their CaO contents.

The chemical compositions of the gypsum and the mineral admixtures used are given in Table 3.1.

Table 3.1: Chemical and physical analysis of gypsum and the mineral admixtures

	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	SO <sub>3</sub> (%)	K <sub>2</sub> O (%)	Na <sub>2</sub> O (%)	Blaine (cm <sup>2</sup> /g)
Gypsum	-	-	-	-	-	45.38	-	-	-
Trass	58.31	15.75	4.95	4.44	1.69	-	1.62	6.41	4925
GGBFS	35.69	13.50	3.11	31.81	7.54	-	0.70	3.61	5341
Low Lime Fly Ash	60.99	16.73	11.45	3.98	5.96	0.43	1.80	0.12	2829
High Lime Fly Ash	46.17	11.58	9.10	14.64	6.45	0.39	2.75	0.14	2120

### 3.3 Sample Preparation

In this study, 117 different cement samples were prepared. Nine of them were control samples without any mineral admixture. The mineral admixture incorporated cements were prepared by replacing 10, 30 and 50% (by weight) of the control cements by the admixtures.

Each cement, thus prepared, was designated by appropriate letters and numbers that indicate the type and amount of admixture used, blaine fineness and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio. The letters and numbers used in the designations and their explanations are given in Table 3.2.

Table 3.2: Abbreviations used in cement designations

Abbreviation	Explanation
NA	No admixture
T10	10% trass
T30	30% trass
T50	50% trass
S10	10% slag
S30	30% slag
S50	50% slag
LF10	10% low lime fly ash
LF30	30% low lime fly ash
LF50	50% low lime fly ash
HF10	10% high lime fly ash
HF30	30% high lime fly ash
HF50	50% high lime fly ash
SS40	Specific surface area of 4000 cm <sup>2</sup> /g
SS47	Specific surface area of 4750 cm <sup>2</sup> /g
SS55	Specific surface area of 5500 cm <sup>2</sup> /g
SA08	SO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio of 0.8
SA10	SO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio of 1.0
SA12	SO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio of 1.2

Thus, for example,

LF30-SS47-SA12

designates the cement containing 30% low-lime fly ash; with specific surface area of 4750 cm<sup>2</sup>/g and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.2 and

NA-SS55-SA08

designates a control cement without any admixture; with specific surface area of 5500 cm<sup>2</sup>/g and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 0.8.

The chemical analysis of the control cements are given in Table 3.3.

Table 3.3: Chemical analysis of the control samples

	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	SO <sub>3</sub> (%)	K <sub>2</sub> O (%)	Na <sub>2</sub> O (%)
SS40-SA08	21.47	6.06	2.75	58.80	1.69	3.89	0.56	0.17
SS40-SA10	21.23	5.99	2.81	59.13	1.81	4.72	0.55	0.17
SS40-SA12	20.61	5.87	2.87	59.47	1.75	5.72	0.54	0.15
SS47-SA08	20.69	5.85	2.88	60.82	1.63	3.64	0.57	0.16
SS47-SA10	20.44	5.70	2.81	60.06	1.69	4.20	0.57	0.16
SS47-SA12	20.37	5.54	2.75	59.30	1.81	5.32	0.56	0.15
SS55-SA08	20.09	5.47	2.75	61.24	1.57	3.54	0.59	0.17
SS55-SA10	19.75	5.43	2.81	60.90	1.51	4.18	0.59	0.17
SS55-SA12	19.62	5.31	2.75	60.57	1.51	5.10	0.59	0.17

### 3.4 Test of Samples

#### 3.4.1 Normal Consistency (Water Demand)

In spite of preparing the pastes for expansion measurements with the same water/cement ratio of 0.5, normal consistency test was applied to all samples. The tests were performed in accordance with TS-EN 196-3.

#### 3.4.2 Setting Time

After the determination of water demand of the pastes, they were placed to the automatic vicat machine. The initial and final setting times of the samples were determined by this machine, in accordance with TS-EN 196-3.

### 3.4.3 Expansion

For the expansion tests, cement pastes were prepared instead of mortars, in order to eliminate the effect of aggregates on expansion. The pastes were prepared according to the water demands, which were determined beforehand. ToniMix model mortar mixer, manufactured by ToniTechik, was used to prepare the pastes according to TS EN 196-3. After mixing, the pastes were cast in 25×25×285 mm molds made of plexiglass. 3 paste bars were cast for each cement type.

After casting, the specimens were cured at room temperature (20°C) and 100% relative humidity for 1 hour. Next, they were heat cured in their plexiglass molds, covered with aluminum folio to prevent the evaporation of water during the heat treatment. The specimens were placed in a drying oven, with a temperature controller, manufactured by Heraus. The temperature cycle applied to the specimens is given in Figure 3.1.

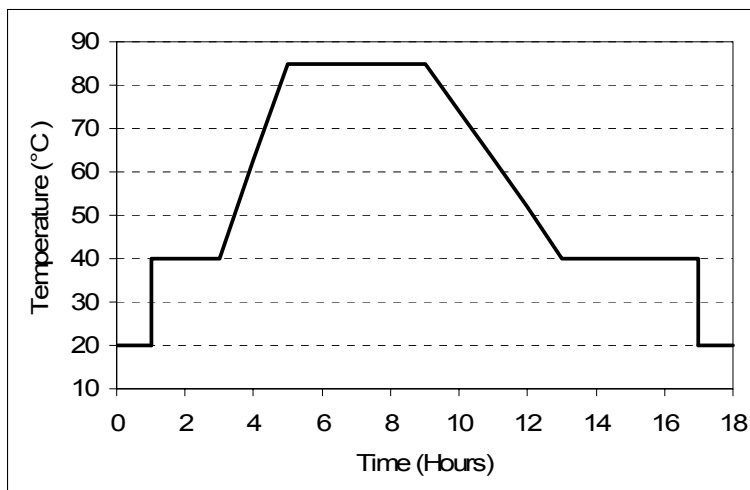


Figure 3.1 Temperature cycle imposed on specimens

The oven was operated at 40°C for 2 hours. Then, the temperature was increased to 85°C (maximum temperature) within 2 hours. The specimens were held at 85°C for 4 hours and then ramped down to 40°C over 4 hours.

They were stored at this temperature for 4 hours and finally the molds were taken away from the oven and kept at room temperature for 1 hour. After that, the bars were removed from plexiglass molds and the initial lengths of the bars were measured by caliper, manufactured by Mitotoyo. Then, the bars were placed in water at 20°C.

After 3 days of curing under water, the paste bars were subjected to 3 wetting-drying cycles, 1 day in a drying oven at 85°C followed by 1 day in water, which was similar to Duggan Method. The reason for this cycle is to increase the rate of formation of ettringite, so that the effect of DEF on expansion potential can be observed in shorter time periods. The length measurements were performed after water curing periods of wetting-drying cycles as shown in Figure 3.2. The length change at the end of wetting-drying cycle was accepted as initial expansion of the specimen.

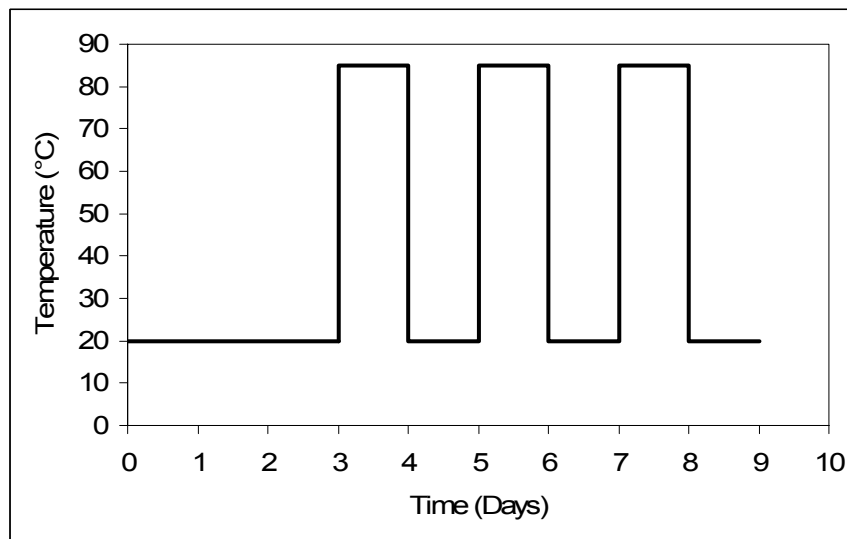


Figure 3.2 Wetting-drying cycle imposed on specimens

After recording the initial expansions, the lengths of the paste bars were measured weekly for 12 weeks. Then, the measurement period was increased to 1 month for 3 more records. The final measurement was performed after 240 days from the initial expansion measurement.

## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

#### **4.1 General**

In this section the results of the experiments and measurements are presented. Also they are discussed and compared with the results of previous works.

#### **4.2 Normal Consistency (Water Demand) and Setting Time**

Water demand and setting time of control samples are given in Appendix B.1. From these results, it can be concluded that fineness is an important factor affecting the water demand. As the blaine fineness increases, the specific surface, and accordingly the reaction surface of the sample increases too, which means more water is needed for the reactions. The effect of fineness on water demand is shown in Figure 4.1.

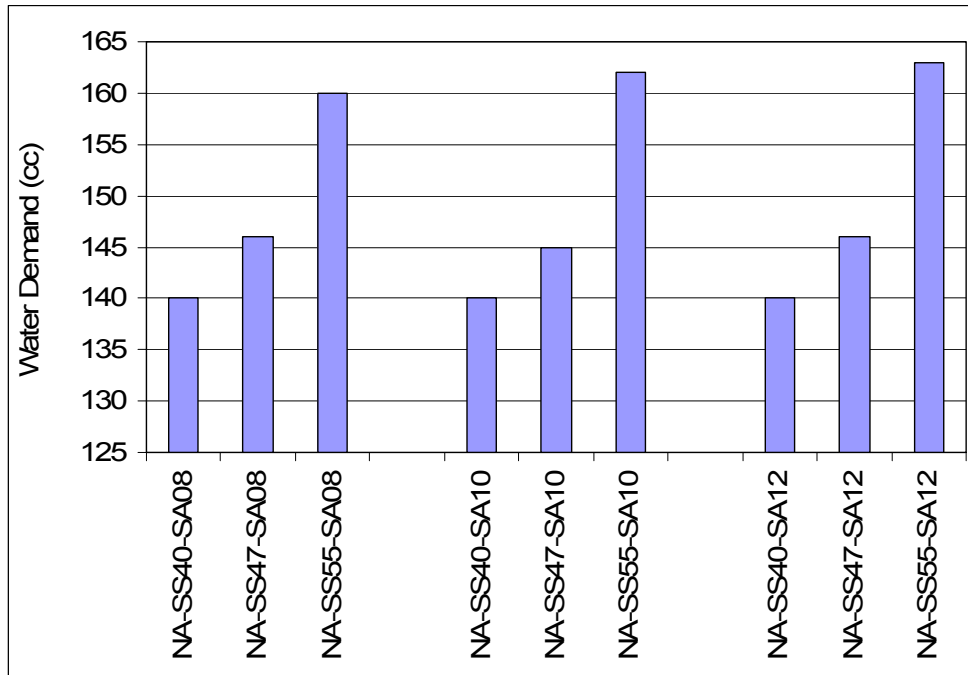


Figure 4.1 Effect of fineness on water demand

SO<sub>3</sub> content, namely the gypsum content, is the key factor affecting the setting time. As the gypsum content increased the initial setting times of the samples increased accordingly. On the other hand the final setting times were decreased unexpectedly with increasing SO<sub>3</sub> content. The use of gypsum in cement production was also defined as setting time regulator in TS-EN 197-1. The effect of SO<sub>3</sub> content on setting time is given in Figure 4.2 and Figure 4.3.



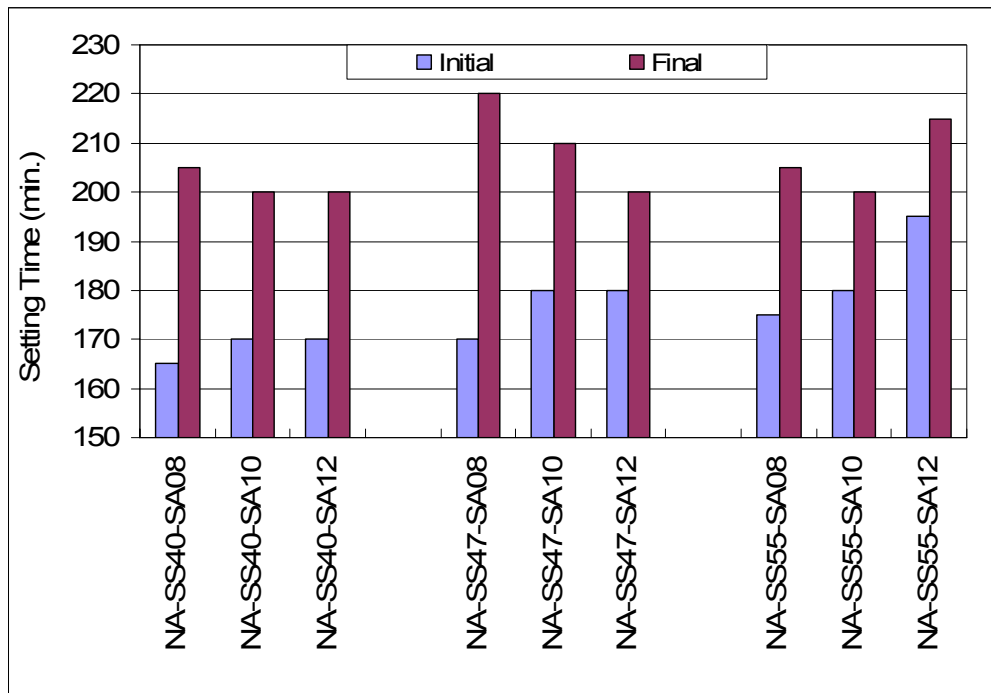


Figure 4.2 Effect of  $\text{SO}_3$  content on setting time

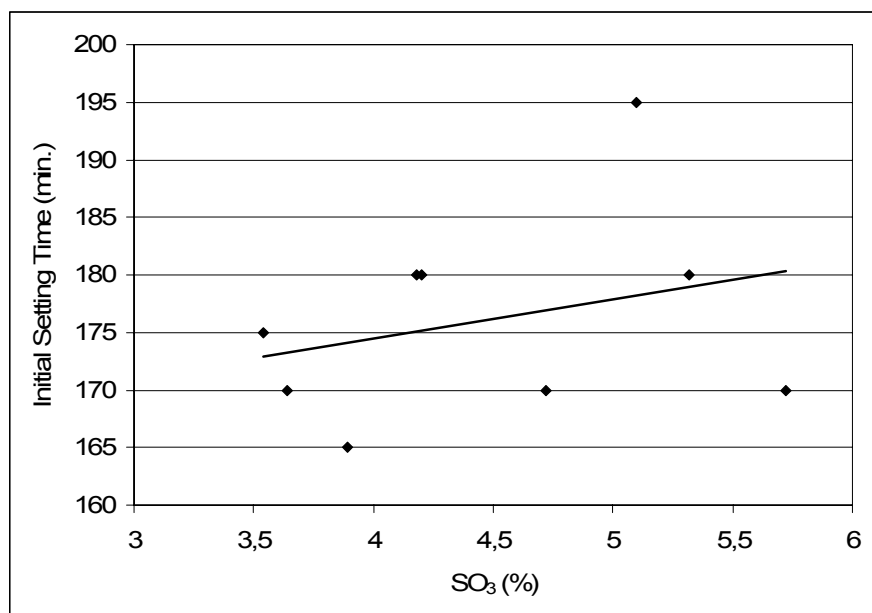


Figure 4.3 Effect of  $\text{SO}_3$  content on initial setting time

Water demand and setting time of samples containing trass additive are given in Appendix B.2 and given in Figure 4.4. As the blaine fineness increases, water demand increases accordingly. In addition to that, as the

amount of trass additive increases the water demand of the samples also increases, except the samples with 5500  $\text{cm}^2/\text{g}$  blaine fineness and containing 50% trass additive. Since the blaine fineness of trass is 4925  $\text{cm}^2/\text{g}$ , blending it with control samples having 5500  $\text{cm}^2/\text{g}$  decreases the overall blaine fineness of the mixture.

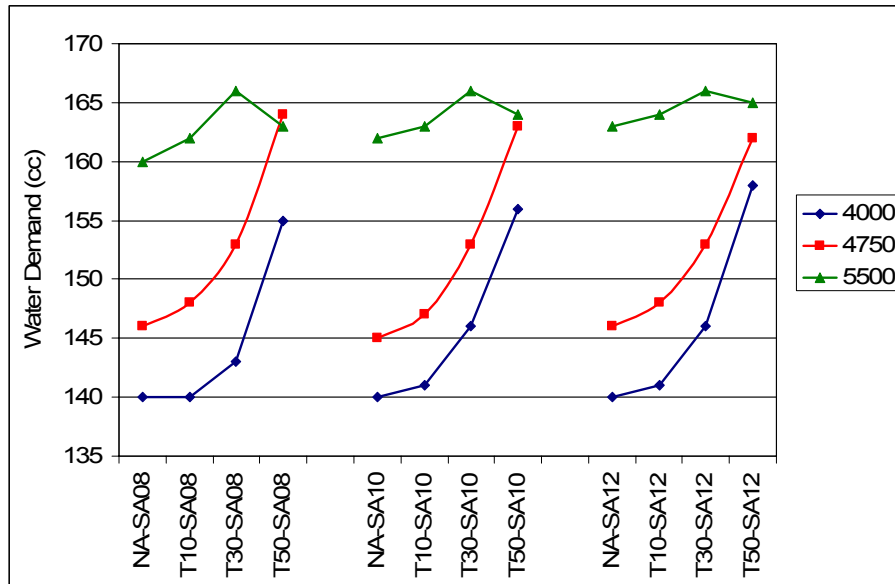


Figure 4.4 Water demands of samples containing trass additive

Initial and final setting times of the samples containing trass additive are given in Figure 4.5 and 4.6 respectively. Initial setting time seems to increase with increasing blaine fineness. Also it increases with increasing  $\text{SO}_3$  content up to  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0. After that it has no significant effect on initial setting time. However, there is no relationship with final setting times.

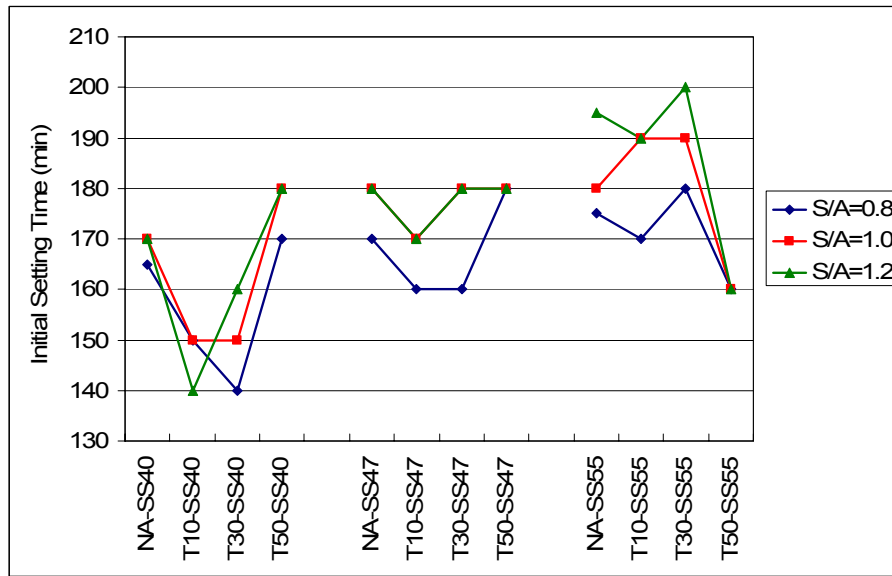


Figure 4.5 Initial setting times of the samples containing trass additive

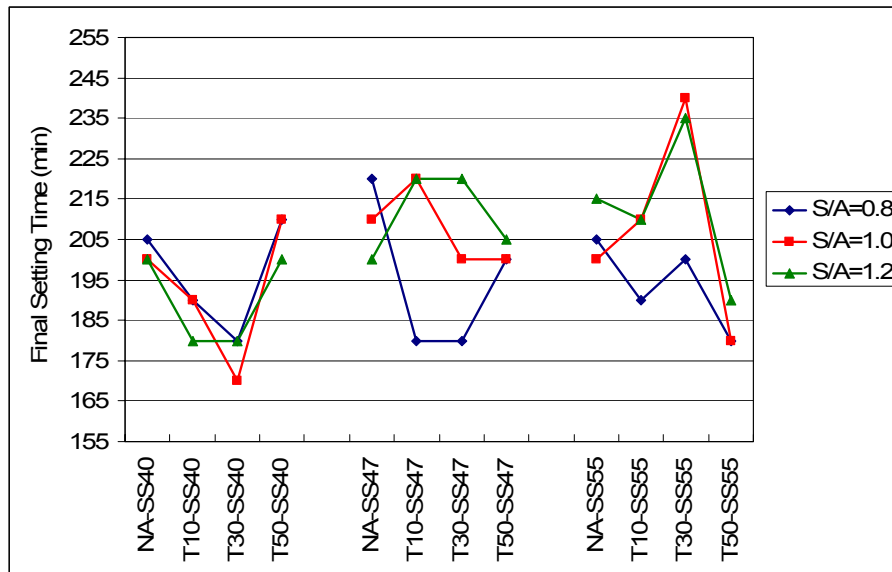


Figure 4.6 Final setting times of the samples containing trass additive

Water demand and setting time of samples containing GGBFS additive are given in Appendix B.3 and given in Figure 4.7. As the blaine fineness increases, water demand increases accordingly. In addition to that, as the amount of GGBFS additive increases the water demand of the samples with 4000 and 4750  $\text{cm}^2/\text{g}$  blaine fineness also increases upto 30% replacement level. After that threshold point, water demand decreases. For the samples

with 5500 cm<sup>2</sup>/g the threshold point is 10%. The increase in gypsum content seems not so effective on water demand.

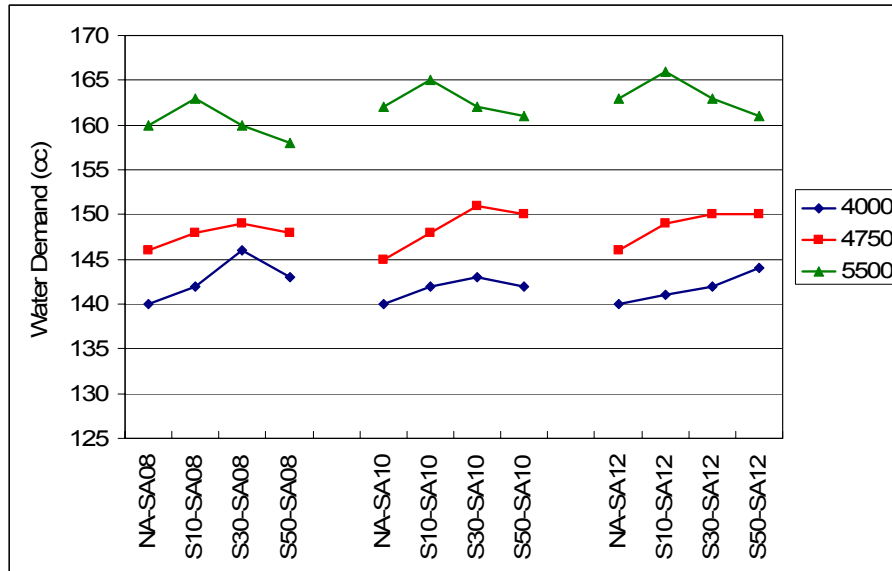


Figure 4.7 Water demand of samples containing GGBFS additive

Initial and final setting times of the samples containing GGBFS additive are given in Figure 4.8 and 4.9 respectively. Initial and final setting times seem to increase with increasing blaine fineness. However, there is no relationship between the SO<sub>3</sub> content and setting times.

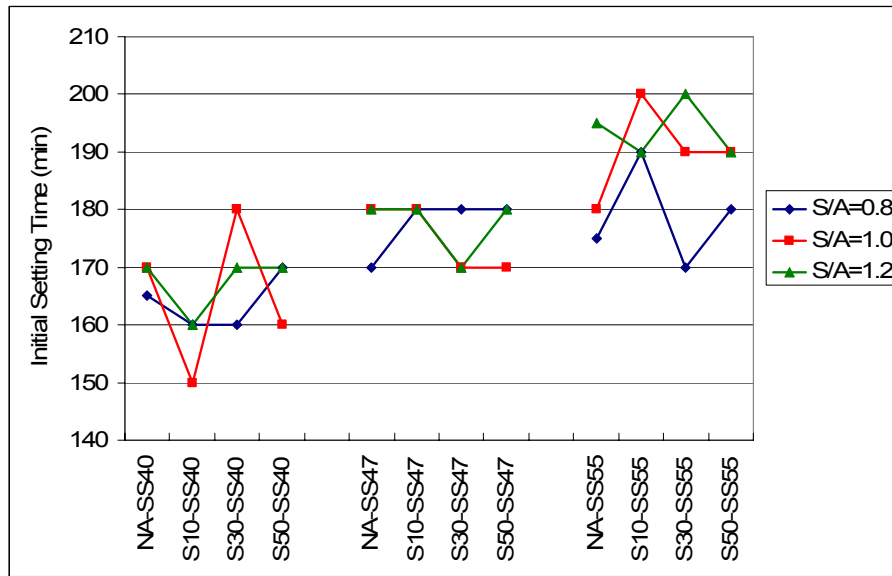


Figure 4.8 Initial setting times of the samples containing GGBFS additive

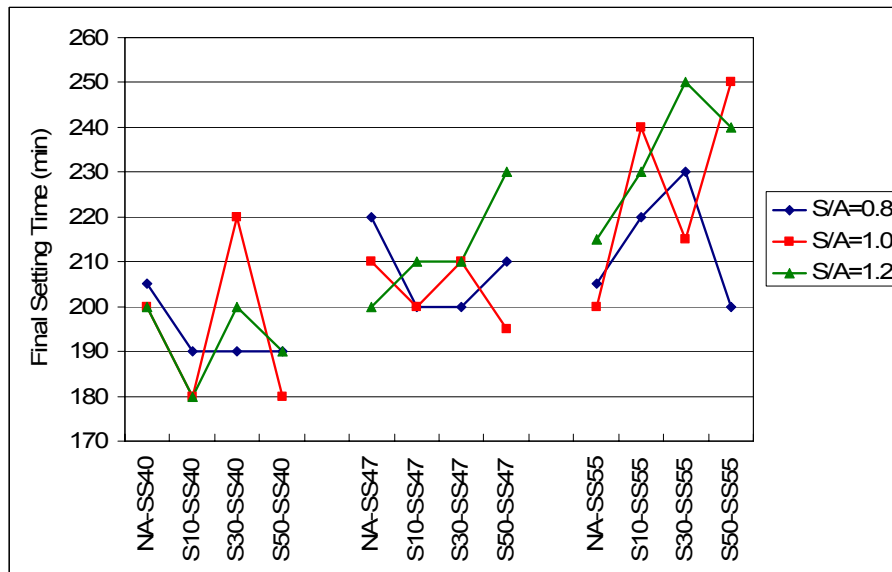


Figure 4.9 Final setting times of the samples containing GGBFS additive

Water demand and setting time of samples containing LLFA additive are given in Appendix B.4 and given in Figure 4.10. As the blaine fineness increases, water demand increases accordingly. In addition to that, as the amount of LLFA additive increases, whose specific surface is  $2829 \text{ cm}^2/\text{g}$ , the specific surface of the sample decreases and as a result the water demand decreases. However, water demands of the samples with 5500

cm<sup>2</sup>/g blaine fineness were unexpectedly higher than the other samples. The increase in gypsum content seems not so effective on water demand.

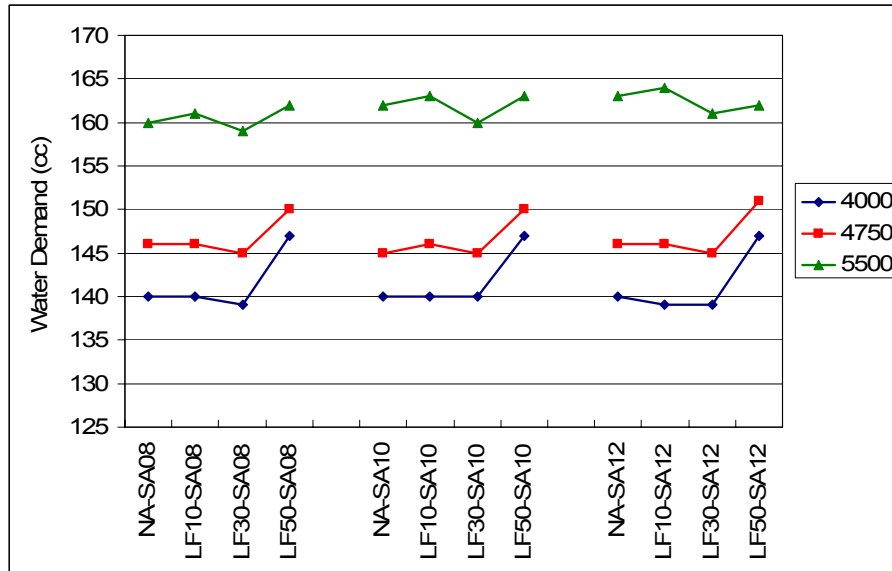


Figure 4.10 Water demand of samples containing LLFA additive

Initial and final setting times of the samples containing LLFA additive are given in Figure 4.11 and 4.12 respectively. Initial and final setting times seem to increase with increasing blaine fineness. Also, initial and final setting times increases as SO<sub>3</sub> content increases upto SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 1.0. After that threshold point the effect of SO<sub>3</sub> content reverses and decreases the initial and final setting times.

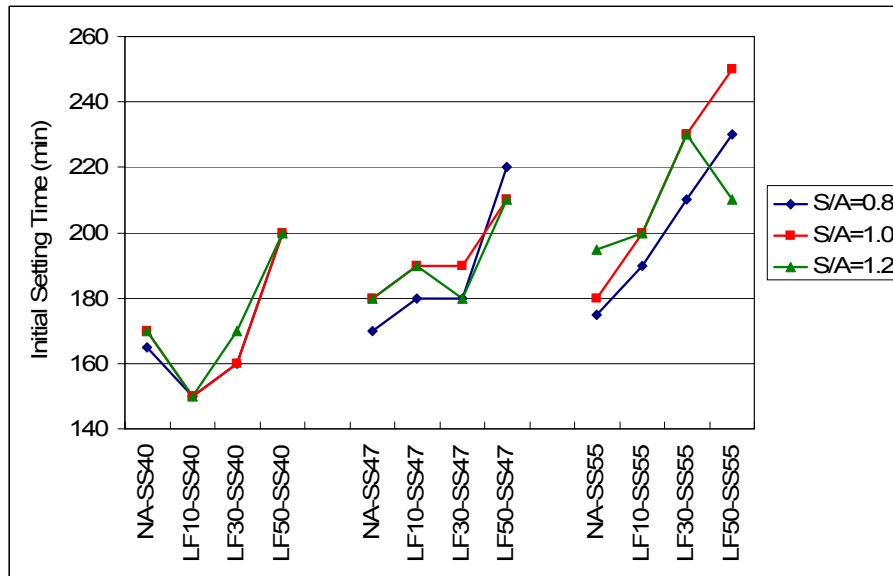


Figure 4.11 Initial setting times of the samples containing LLFA additive

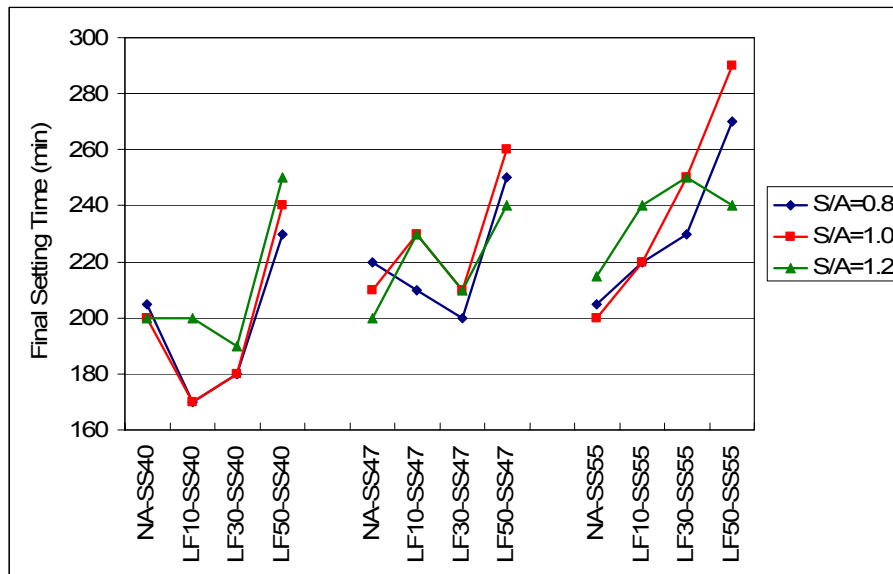


Figure 4.12 Final setting times of the samples containing LLFA additive

Water demand and setting time of samples containing HLFA additive are given in Appendix B.5 and given in Figure 4.13. As the blaine fineness increases, water demand increases accordingly. In addition to that, as the amount of HLFA additive increases, whose specific surface is  $2120 \text{ cm}^2/\text{g}$ , the specific surface of the sample decreases and as a result the water

demand decreases. The increase in gypsum content seems not so effective on water demand.

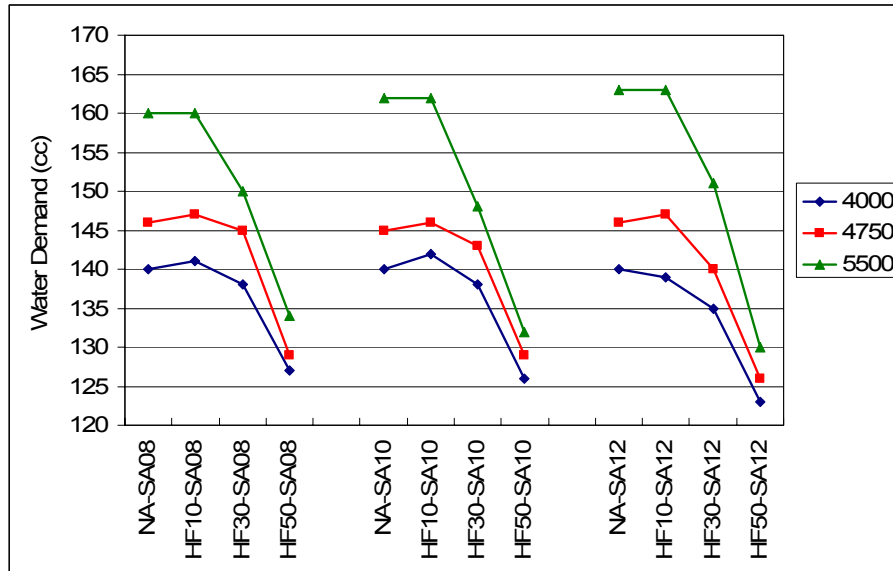


Figure 4.13 Water demand of samples containing HLFA additive

Initial and final setting times of the samples containing HLFA additive are given in Figure 4.14 and 4.15 respectively. There is no relationship about initial and final setting times.

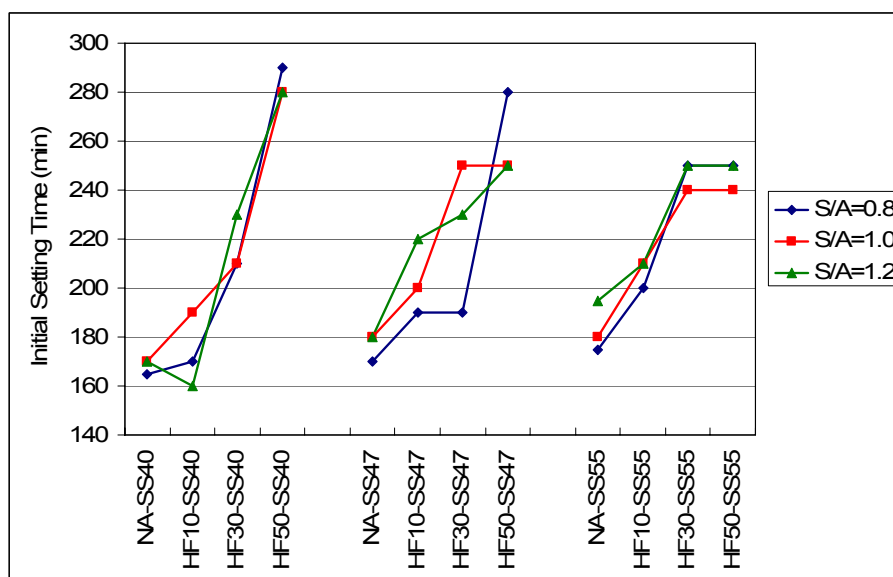


Figure 4.14 Initial setting times of the samples containing HLFA additive



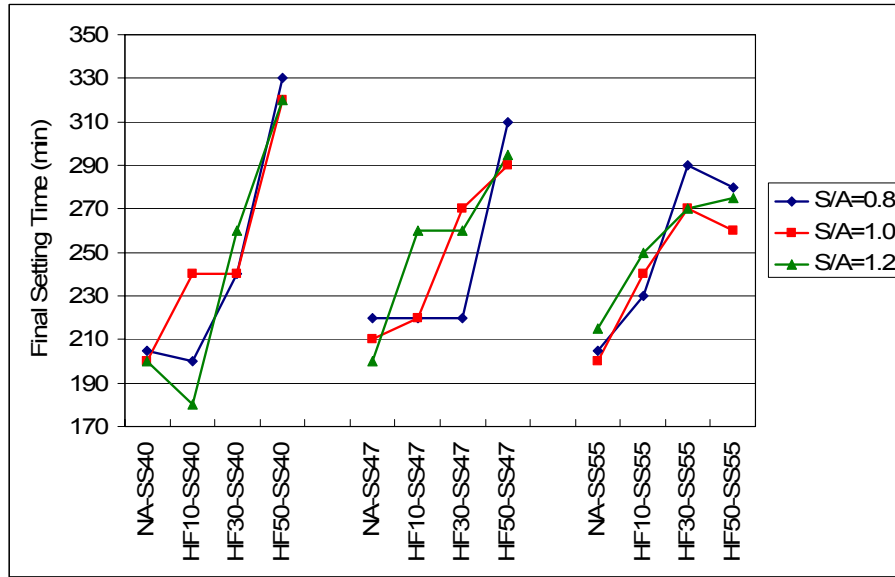


Figure 4.15 Final setting times of the samples containing HLFA additive

### 4.3 Expansion

#### 4.3.1 Control Samples

Expansion measurements were performed up to 240 days. First of all, the effect of  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio on expansion for cements having different blaine finenesses namely 4000, 4750, and 5500  $\text{cm}^2/\text{g}$  are given in Figure 4.16, 4.17, and 4.18, respectively. As  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio increased, the expansion of the samples increased accordingly, consistent with the study of Zhang et al.[2002b]. This phenomena was also considered to be the predominating factor for DEF in the literature. However, the expansion of the sample with 5500 blaine and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8 was unexpectedly higher than the others with the same blaine. Since the water demand of that sample found less than the others, the paste was prepared with lower water content. So that, after the formation of ettringite according to (Eqn. 2), it can not be converted to monosulphate with further hydration because of the lack of water. This resulted with higher expansion values.

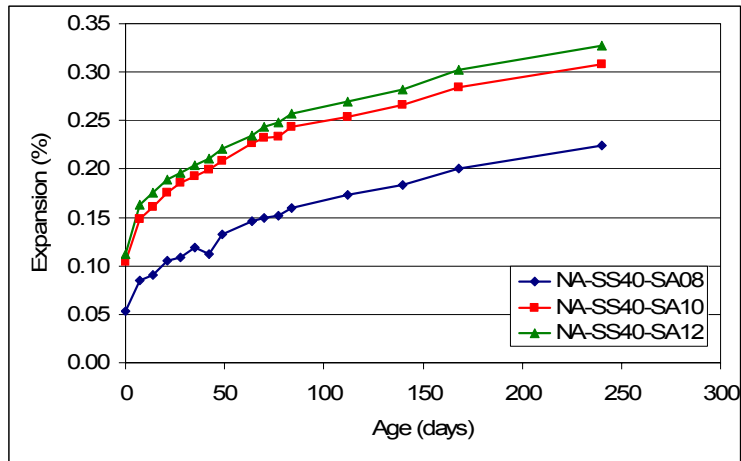


Figure 4.16 Expansion of control cements with blaine fineness of 4000 cm<sup>2</sup>/g

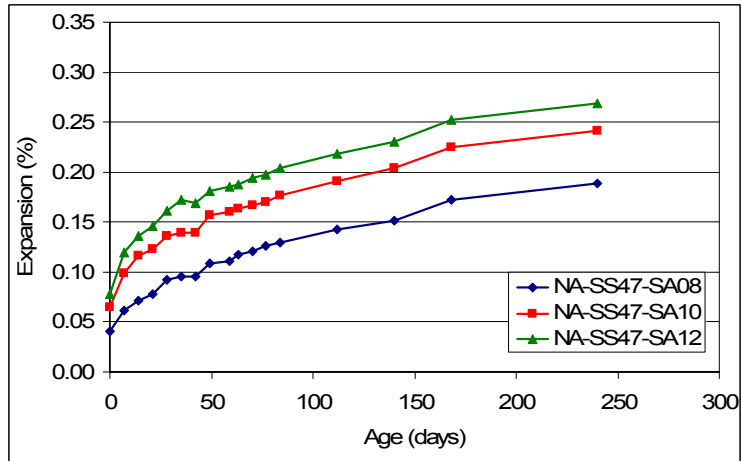


Figure 4.17 Expansion of control cements with blaine fineness of 4750 cm<sup>2</sup>/g

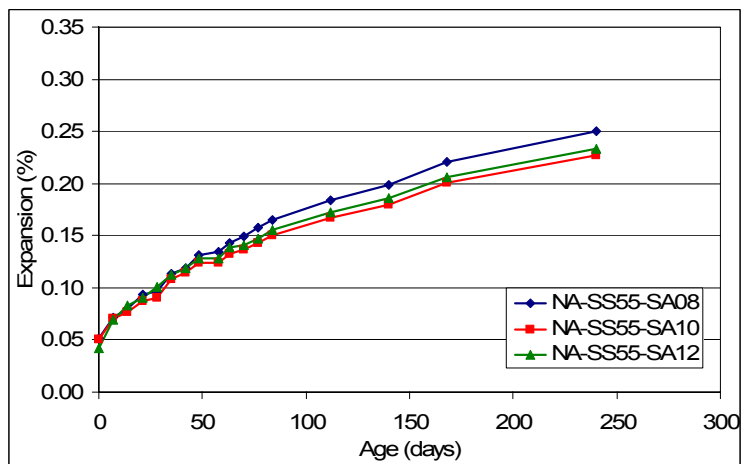


Figure 4.18 Expansion of control cements with blaine fineness of 5500 cm<sup>2</sup>/g

Next, the effect of blaine fineness on expansion for cements having different  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio namely 0.8, 1.0, 1.2 are given in Figure 4.19, 4.20, and 4.21 respectively. It was observed that expansion is inversely proportional with fineness. As the blaine fineness increased, the expansion of the samples decreased. However, the expansion of the sample with 5500 blaine and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8 was unexpectedly higher than the others with the same blaine. It could be resulted because of the experimental errors.

Similar results were obtained by Tosun [2006] for the initial stages of testing (2-3 months), that expansion rates of finer cements were less than coarser ones. However, in the long term, the rate of expansion of finer cements exceeded the coarser ones, which could be due to different hydration characteristics and pore structure of mortars including cements with different fineness values. In this study, expansion rates were measured up to 240 days, so that it is difficult to comment on long term expansion rates.

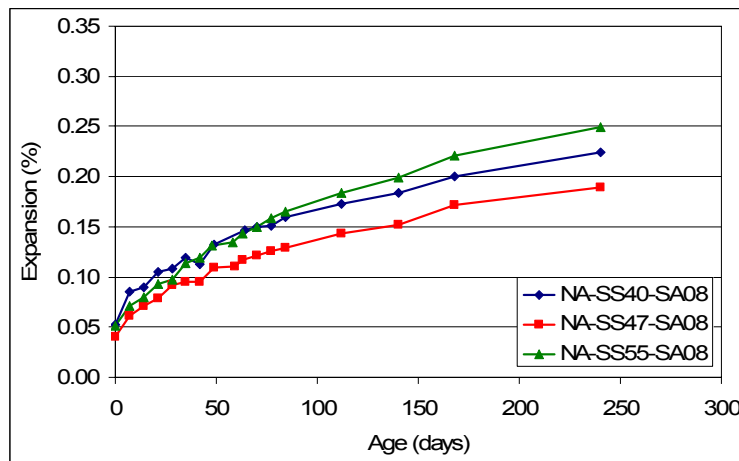


Figure 4.19 Expansion of control cements with  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

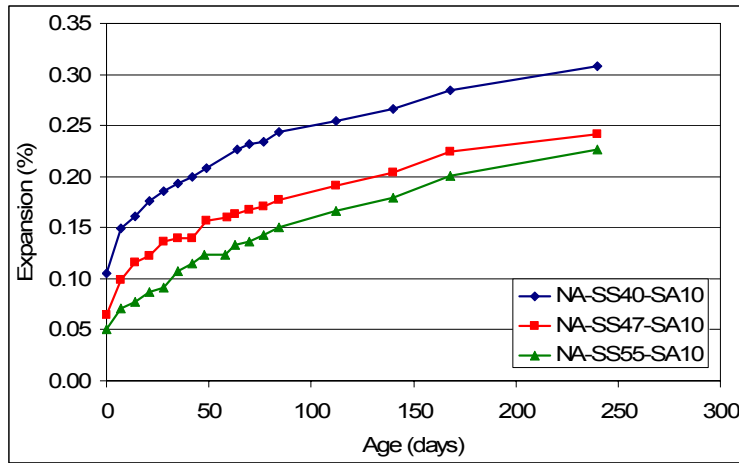


Figure 4.20 Expansion of control cements with SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.0

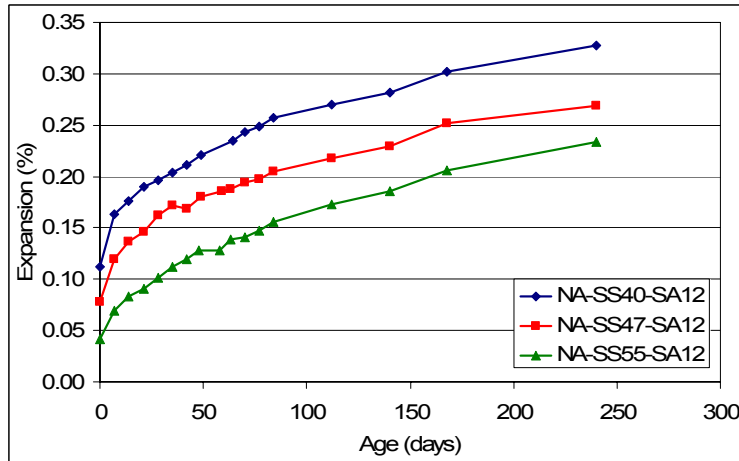


Figure 4.21 Expansion of control cements with SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.2

In Figures 4.22 and 4.23, the relationship between expansion and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio and blaine fineness is given for short term and long term, respectively. From these figures it can be said that as SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio increases, expansion increases. On the other hand, as specific surface area increases the expansion decreases for short term periods, but on the long term, the expansion of finer cements seems to expand more.

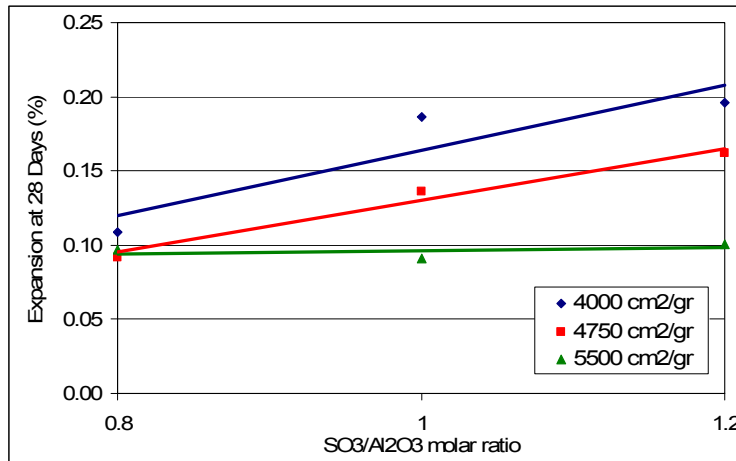


Figure 4.22 The effect of SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio and fineness on the expansion of control cements at 28 days

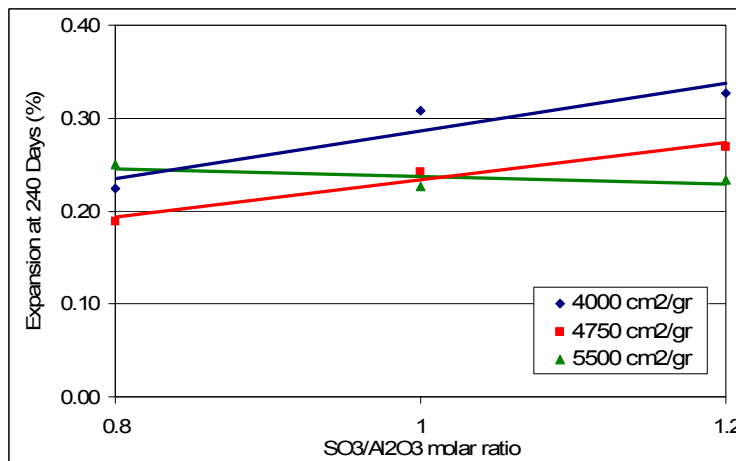


Figure 4.23 The effect of SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio and fineness on the expansion of control cements at 240 days

#### 4.3.2 Samples with Trass Additive

In order to observe the effect of trass additive on expansion, different amounts of ground trass, namely 10%, 30%, and 50%, were added to each of the control samples. In Figures 4.24 to 4.32, the effect of trass on each of the control samples are given.

For the cement types with 4000 cm<sup>2</sup>/g blaine fineness, the increase in trass additive decreased expansion, and 30% of trass addition seems to be the threshold level. Increasing trass additive from this level is not so effective for decreasing the expansion.

For the series with 4750 cm<sup>2</sup>/g blaine fineness, the increase in trass additive decreased expansion proportionally, except the cement with 10% trass admixture and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 0.8. The expansion of this cement is unexpectedly higher than the control cement. It could be due the particle size distribution of the sample.

Finally, for the series with 5500 cm<sup>2</sup>/g blaine fineness, 10% trass additive increased the expansion, however 30% and 50% additive decreased the expansion.

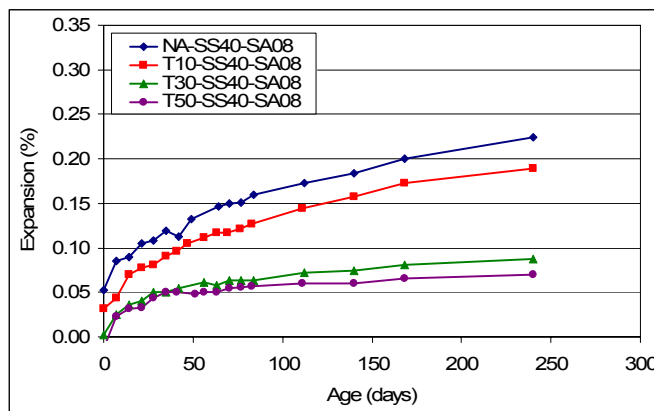


Figure 4.24 Effect of trass on the expansion of control cement with 4000 cm<sup>2</sup>/g fineness and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 0.8

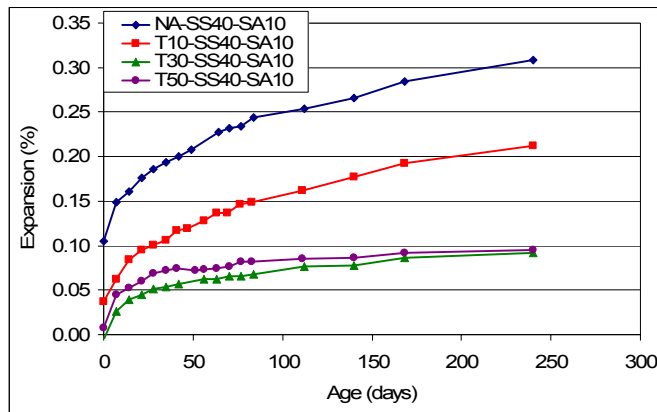


Figure 4.25 Effect of trass on the expansion of control cement with 4000  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

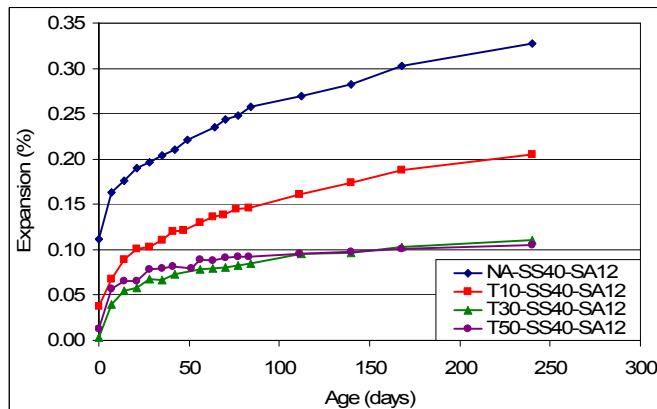


Figure 4.26 Effect of trass on the expansion of control cement with 4000  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

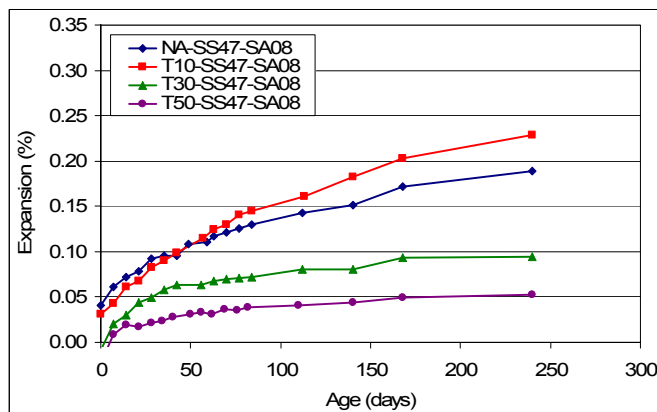


Figure 4.27 Effect of trass on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

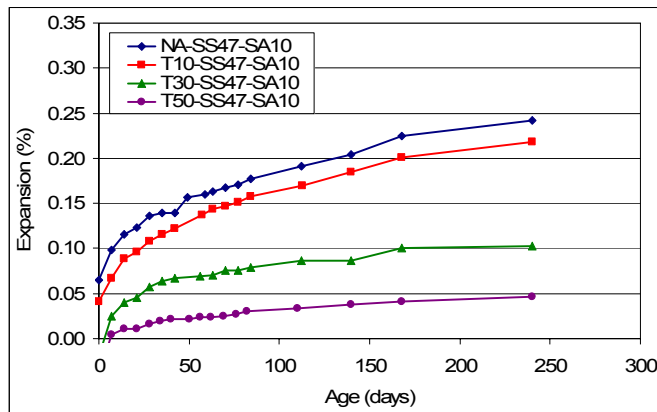


Figure 4.28 Effect of trass on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

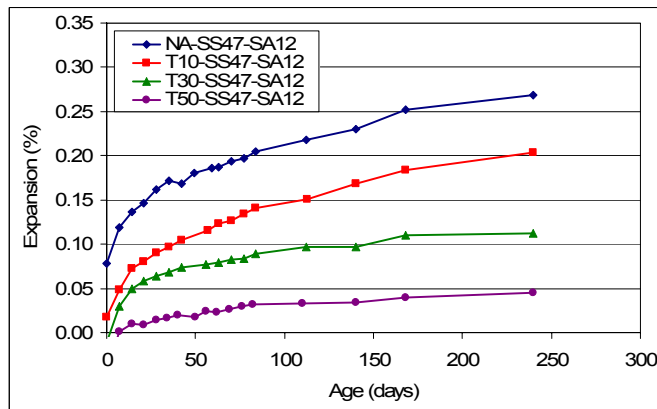


Figure 4.29 Effect of trass on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

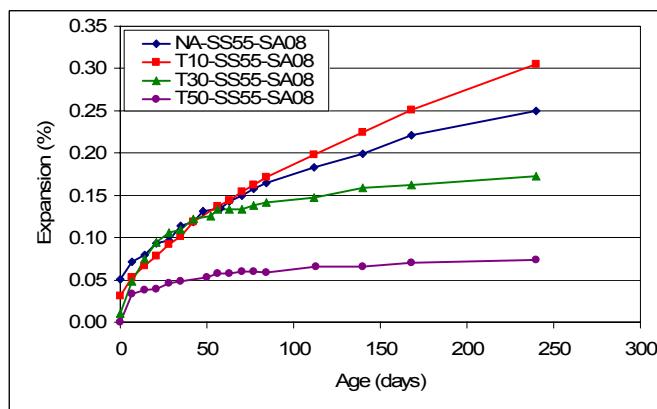


Figure 4.30 Effect of trass on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8



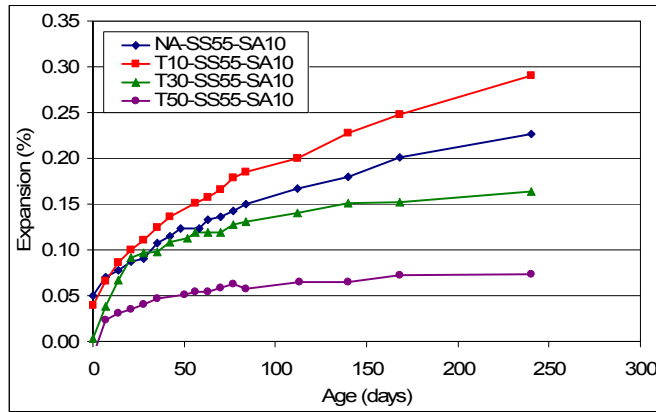


Figure 4.31 Effect of trass on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

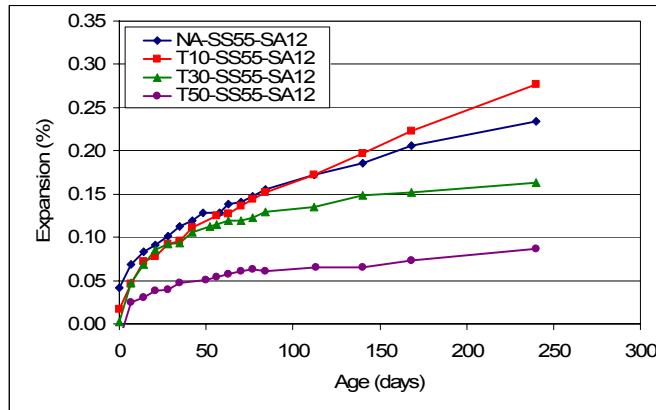


Figure 4.32 Effect of trass on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

In Figure 4.33 the effect of trass on expansion after 240 days is given. For the samples with 4000  $\text{cm}^2/\text{g}$  blaine fineness, the increase in  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio increases the expansion. However, for the finer cements with 4750 and 5500  $\text{cm}^2/\text{g}$  blaine fineness, the effect of  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio reverses.

For all of the samples, except T10-SS55 series, the increase in trass additive caused expansion to be decreased. But, for coarser cement with 4000  $\text{cm}^2/\text{g}$  blaine fineness, the addition of trass more than 30% does not decrease expansion.

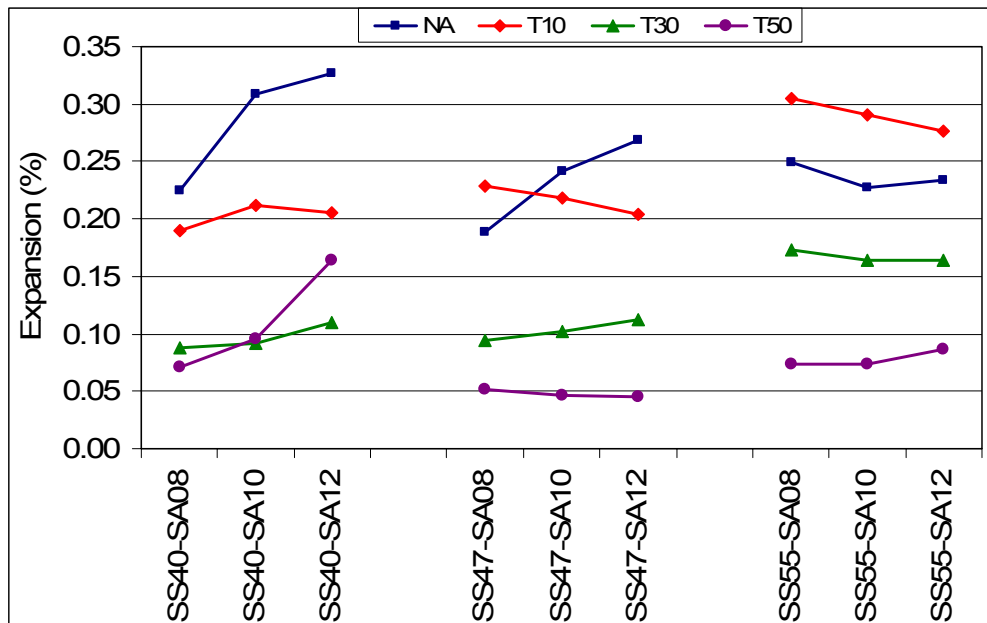


Figure 4.33 Effect of trass additive on expansion after 240 days

#### 4.3.3 Samples with Ground Granulated Blast Furnace Slag Additive

In order to observe the effect of GGBFS additive on expansion, different amounts of GGBFS, namely 10%, 30%, and 50%, were added to each of control samples. In Figures 4.34 to 4.42, the effect of GGBFS on each of the control samples are given.

In general, the addition of GGBFS decreases the expansion. Short term expansion measurements shows that the increase in GGBFS addition has negative effect on expansion, however in the long term the increase in GGBFS additive decreases the expansion more.

Upto 240 days, samples including 30% and 50% GGBFS expanded nearly the same, but the trends of the graphs show that the samples including 10% and 30% GGBFS will continue expanding with higher rates compared with the samples including 50% GGBFS which are nearly stabilized.

For the cement types with 4000 cm<sup>2</sup>/g blaine fineness and with SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 0.8, the long term expansion of all the samples including 10%, 30% and 50% GGBFS additives are nearly the same. But, as SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio increases the sample with 10% additive expands more than the others, which means that after 30% GGBFS addition, SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio is not as effective as at 10% GGBFS addition level.

For the series with 4750 cm<sup>2</sup>/g blaine fineness, SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio is not effective for 10% GGBFS addition. They expanded almost the same, with a value of nearly 0.20%. However, the samples with 30% and 50% GGBFS additives expanded more, with increasing SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. Also 30% GGBFS addition seems to be the threshold value for 240 days expansion. Increasing the additive after 30% does not effective for decreasing the expansion.

Finally, for the series with 5500 cm<sup>2</sup>/g blaine fineness, 10% GGBFS additive increased the expansion, however 30% and 50% additive decreased the expansion with almost the same values except S50-SS55-SA12, which expanded less. It could be due the particle size distribution of the sample.

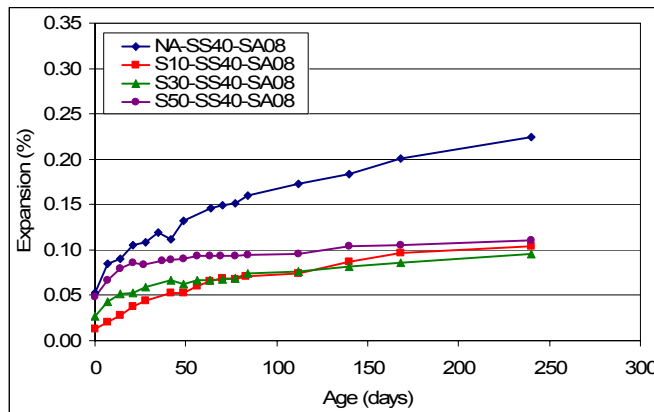


Figure 4.34 Effect of GGBFS on the expansion of control cement with 4000 cm<sup>2</sup>/g fineness and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 0.8

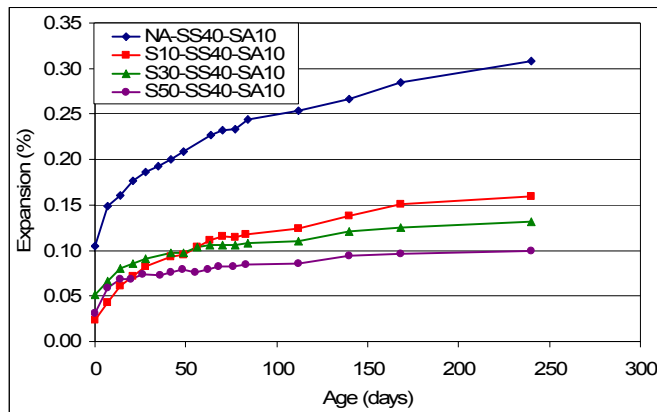


Figure 4.35 Effect of GGBFS on the expansion of control cement with 4000  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

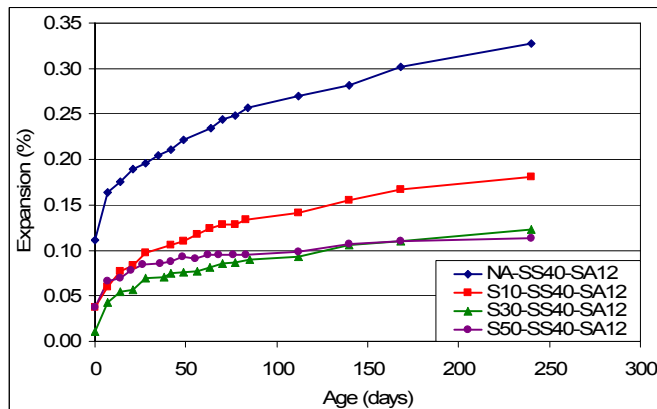


Figure 4.36 Effect of GGBFS on the expansion of control cement with 4000  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

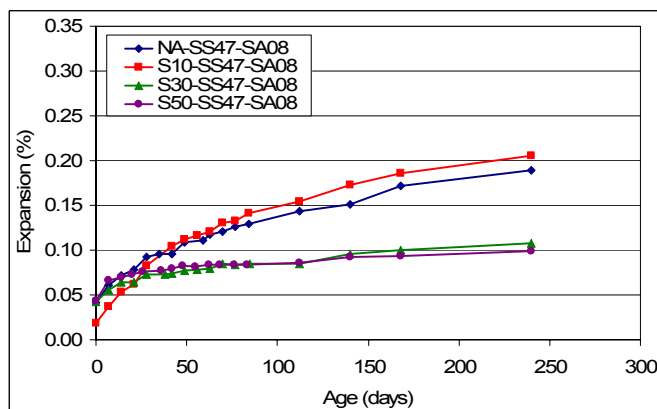


Figure 4.37 Effect of GGBFS on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

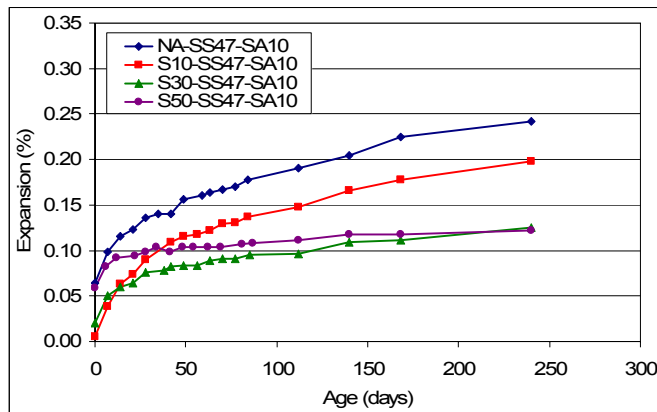


Figure 4.38 Effect of GGBFS on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

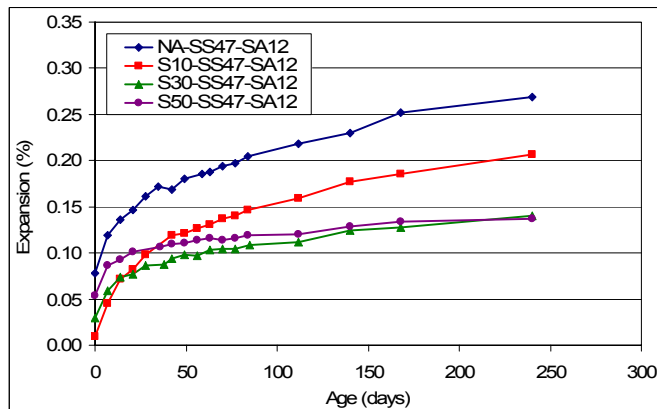


Figure 4.39 Effect of GGBFS on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

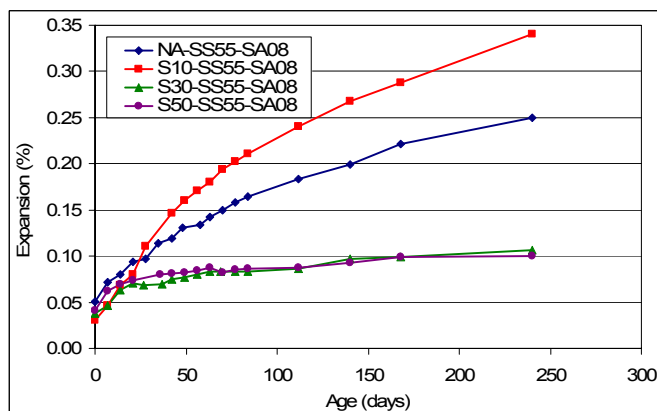


Figure 4.40 Effect of GGBFS on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

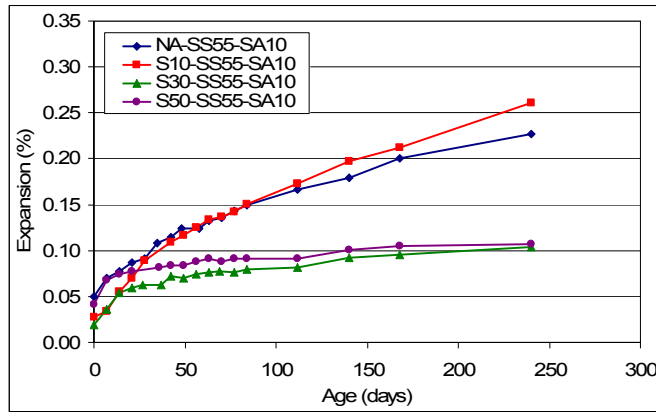


Figure 4.41 Effect of GGBFS on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

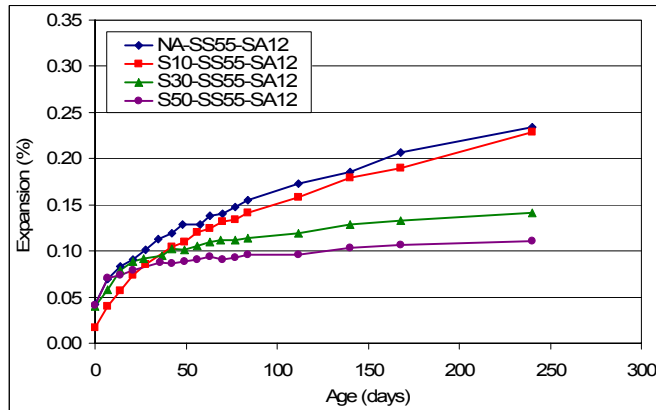


Figure 4.42 Effect of GGBFS on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

In Figure 4.43 the effect of GGBFS on expansion after 240 days is given. For the samples with 4000  $\text{cm}^2/\text{g}$  blaine fineness, 10% addition of GGBFS is enough to control expansion but for the samples with 4750 and 5500  $\text{cm}^2/\text{g}$  blaine fineness values higher replacement levels of GGBFS is needed. For these samples 30% addition of GGBFS is the threshold level. After this level the expansion of the samples are nearly the same. Similar results was obtained by Ramlochan et. al. [2003]. He concluded that sufficient replacement level of GGBFS may control expansion and 25% replacement level may suppress long term expansion with most cements, but higher levels

maybe required when used with cements having very high  $\text{SO}_3$  or alkali content.

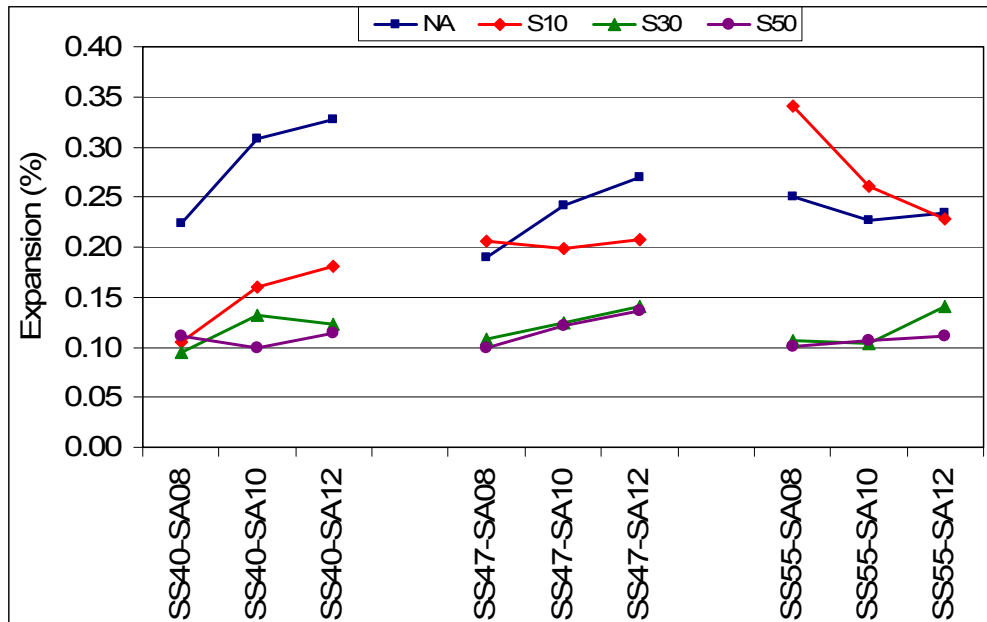


Figure 4.43 Effect of GGBFS additive on expansion after 240 days

#### 4.3.4 Samples with Low Lime Fly Ash Additive

In order to observe the effect of LLFA additive on expansion, different amounts of LLFA, namely 10%, 30%, and 50%, were added to each of control samples. In Figures 4.44 to 4.52, the effect of LLFA on each of the control samples are given.

In general, the addition of LLFA decreases the expansion much more effectively with respect to other additives. 240 days expansion levels are almost the same (nearly 0.05%) for all samples including LLFA additive, however samples including 30% LLFA expanded slightly less than other ones. According to these results LLFA can be used for controlling expansion with minimum replacement levels.

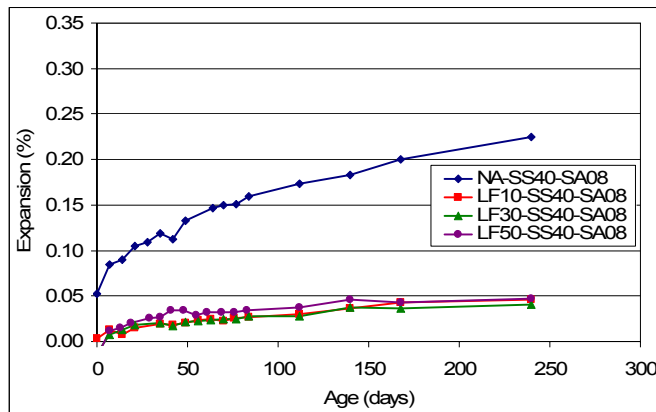


Figure 4.44 Effect of LLFA on the expansion of control cement with 4000  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

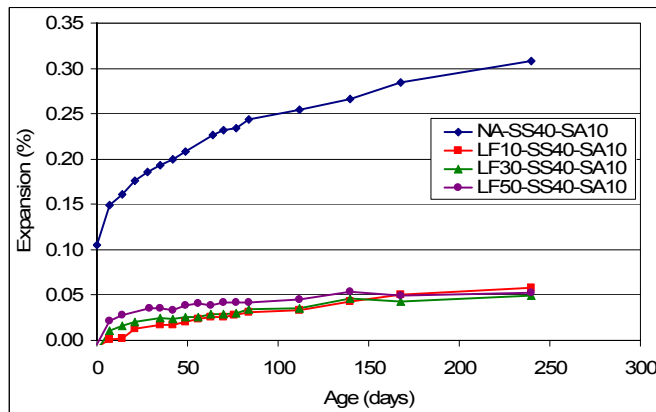


Figure 4.45 Effect of LLFA on the expansion of control cement with 4000  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

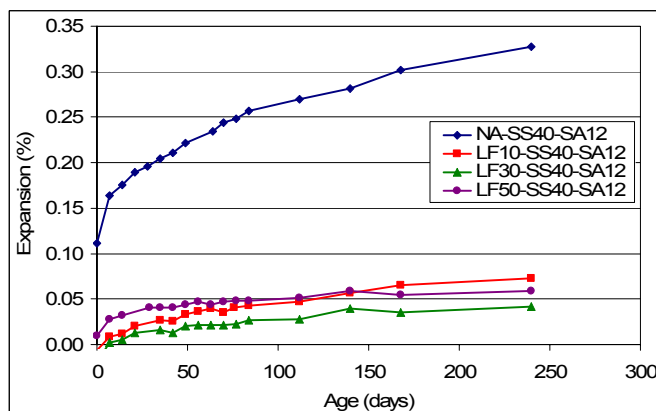


Figure 4.46 Effect of LLFA on the expansion of control cement with 4000  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2



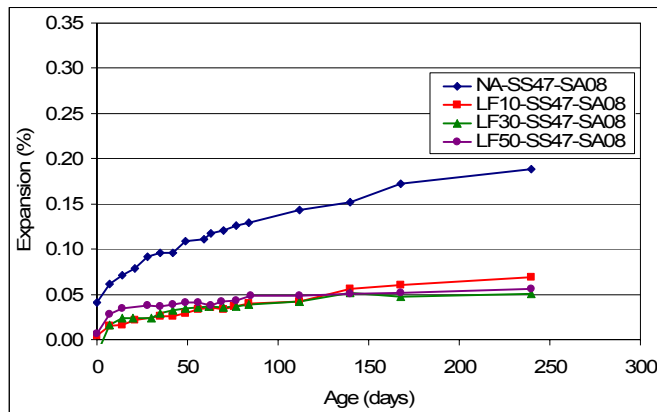


Figure 4.47 Effect of LLFA on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

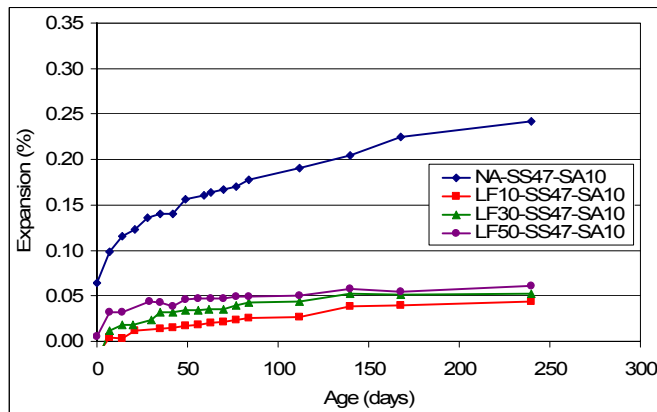


Figure 4.48 Effect of LLFA on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

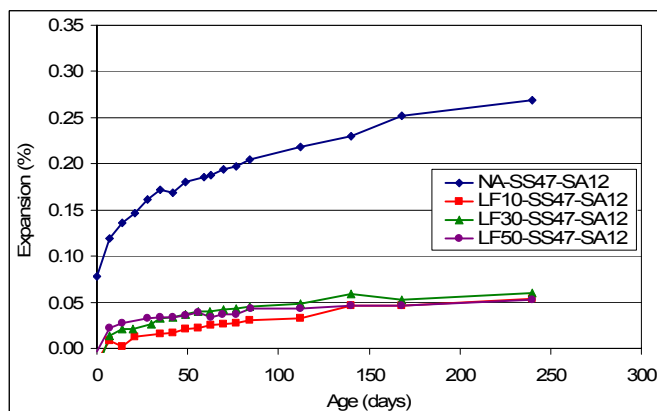


Figure 4.49 Effect of LLFA on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

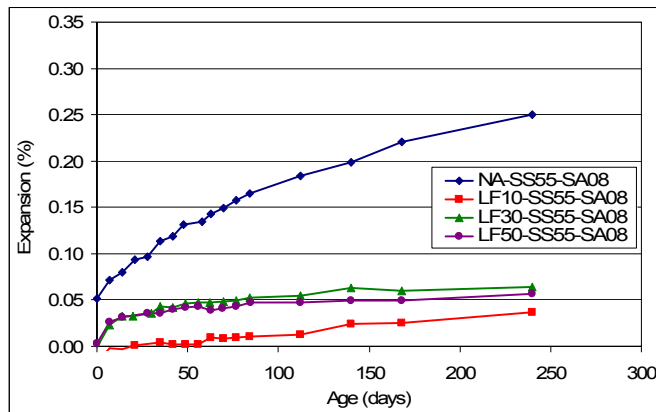


Figure 4.50 Effect of LLFA on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

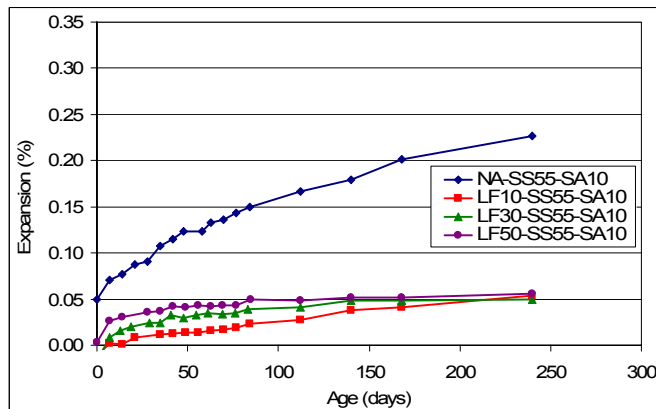


Figure 4.51 Effect of LLFA on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

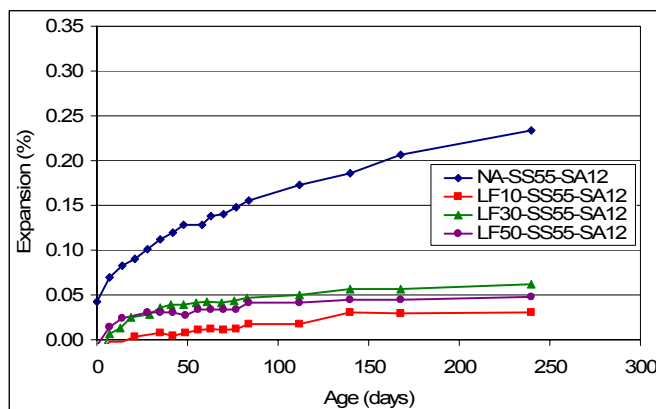


Figure 4.52 Effect of LLFA on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

In Figure 4.53 the effect of LLFA on expansion after 240 days is given. It can be said that LLFA additive decreases expansion very effectively with minimum replacement levels.

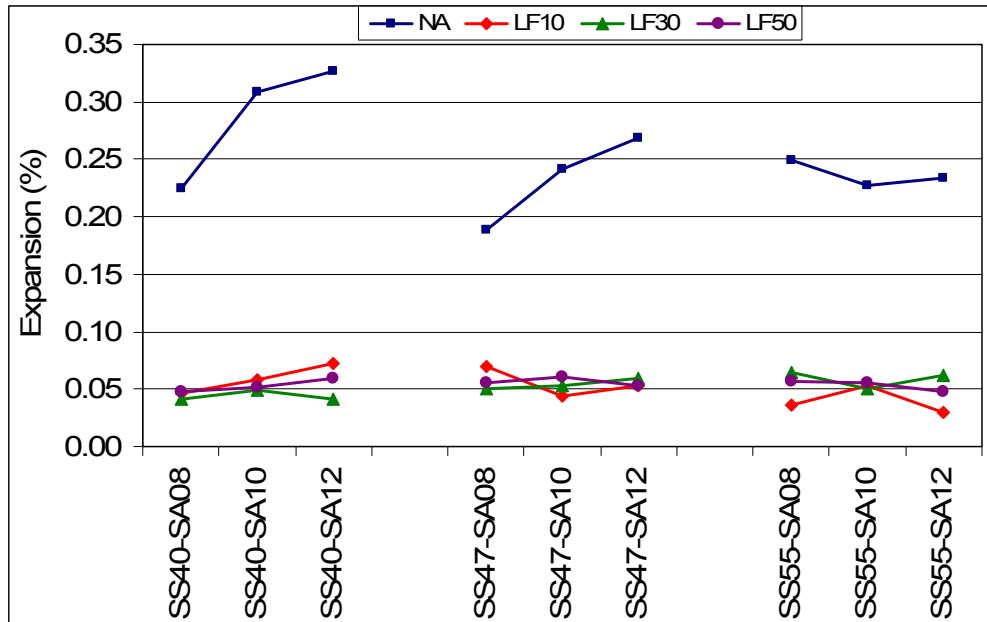


Figure 4.53 Effect of LLFA additive on expansion after 240 days

#### 4.3.5 Samples with High Lime Fly Ash Additive

In order to observe the effect of HLFA additive on expansion, different amounts of HLFA, namely 10%, 30%, and 50%, were added to each of control samples. In Figures 4.54 to 4.62, the effect of HLFA on each of the control samples are given.

For the cement types with 4000 cm<sup>2</sup>/g blaine fineness, the increase in HLFA additive decreased expansion. As SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio increases expansion increases except the sample with 30% HLFA additive which is almost constant.

For the series with 4750 cm<sup>2</sup>/g blaine fineness, the increase in HLFA additive decreased expansion, except the cement with SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 0.8. The expansion of samples including 10% and 30% HFLA is unexpectedly same with the control cement. This could be due to the particle size distribution of the samples.

Finally, for the series with 5500 cm<sup>2</sup>/g blaine fineness, 10% HFLA additive increased the expansion, however 30% and 50% additive decreased the expansion.

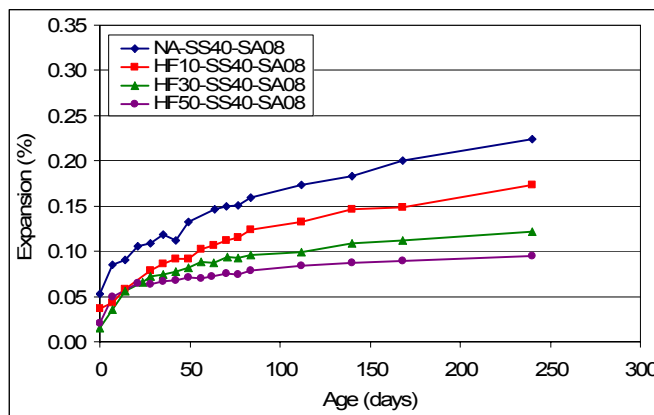


Figure 4.54 Effect of HLFA on the expansion of control cement with 4000 cm<sup>2</sup>/g fineness and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 0.8

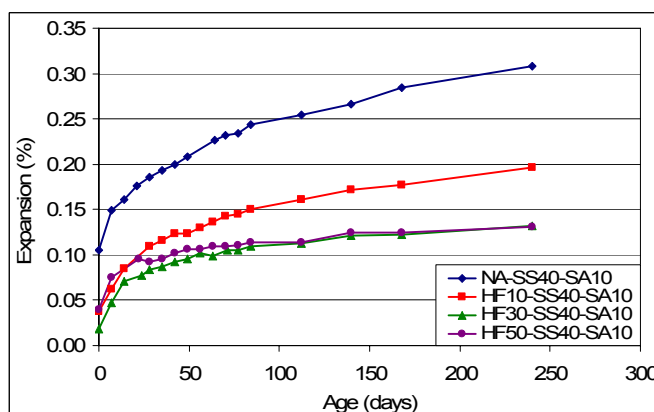


Figure 4.55 Effect of HLFA on the expansion of control cement with 4000 cm<sup>2</sup>/g fineness and SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.0

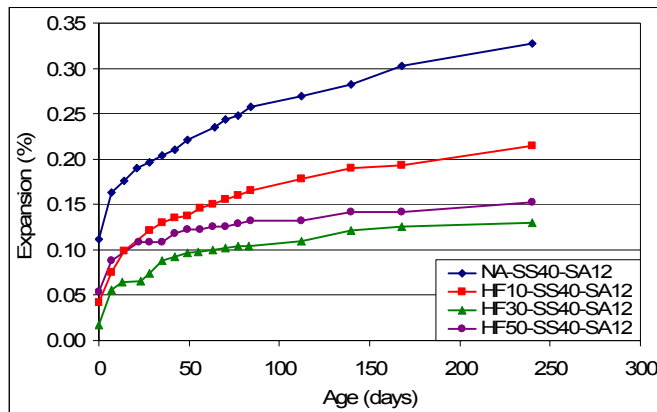


Figure 4.56 Effect of HLFA on the expansion of control cement with 4000  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

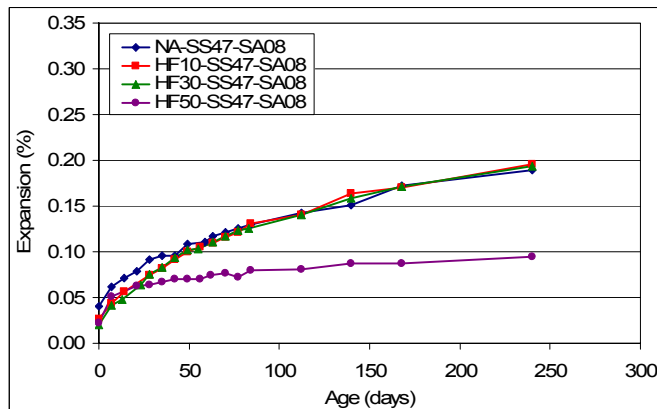


Figure 4.57 Effect of HLFA on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

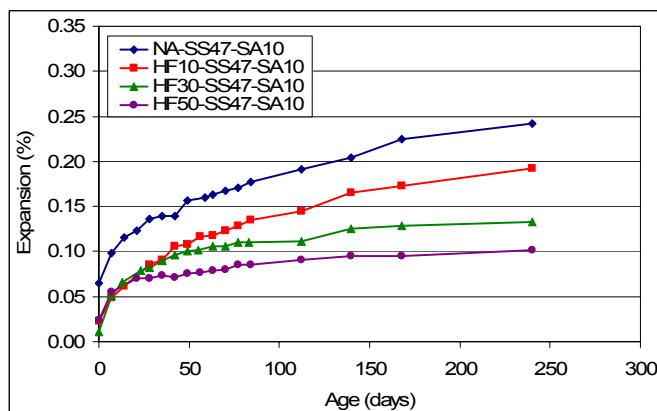


Figure 4.58 Effect of HLFA on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

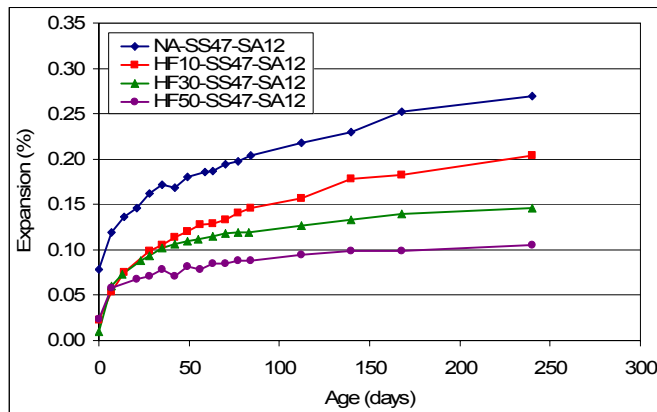


Figure 4.59 Effect of HLFA on the expansion of control cement with 4750  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

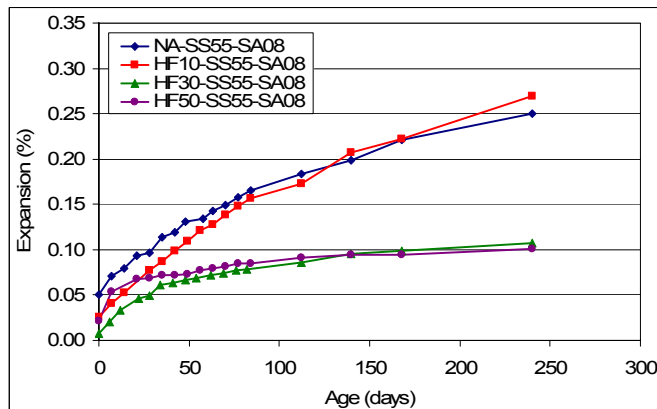


Figure 4.60 Effect of HLFA on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 0.8

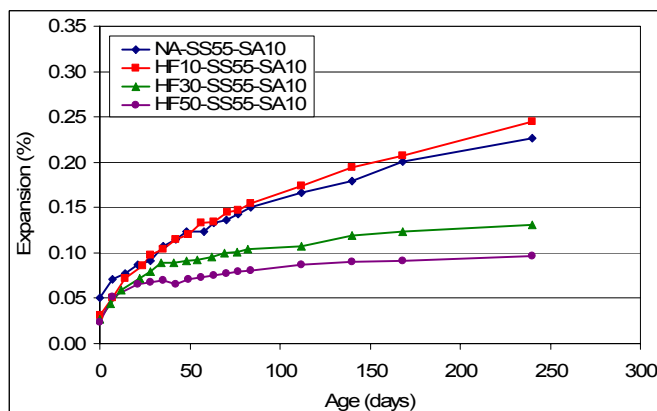


Figure 4.61 Effect of HLFA on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.0

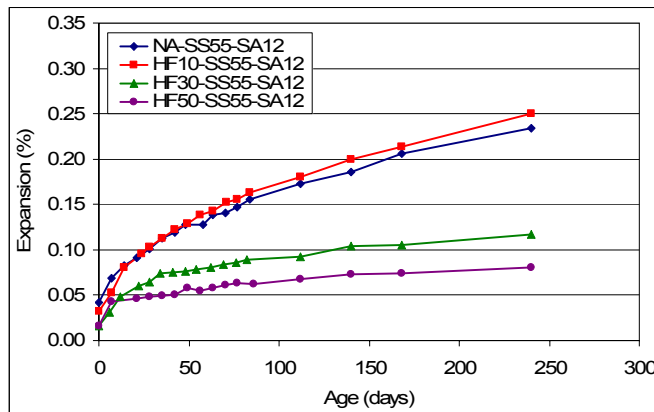


Figure 4.62 Effect of HLFA on the expansion of control cement with 5500  $\text{cm}^2/\text{g}$  fineness and  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of 1.2

In Figure 4.63 the effect of HFLA on expansion after 240 days is given. For the samples with 4000  $\text{cm}^2/\text{g}$  blaine fineness, the increase in  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio increases the expansion.

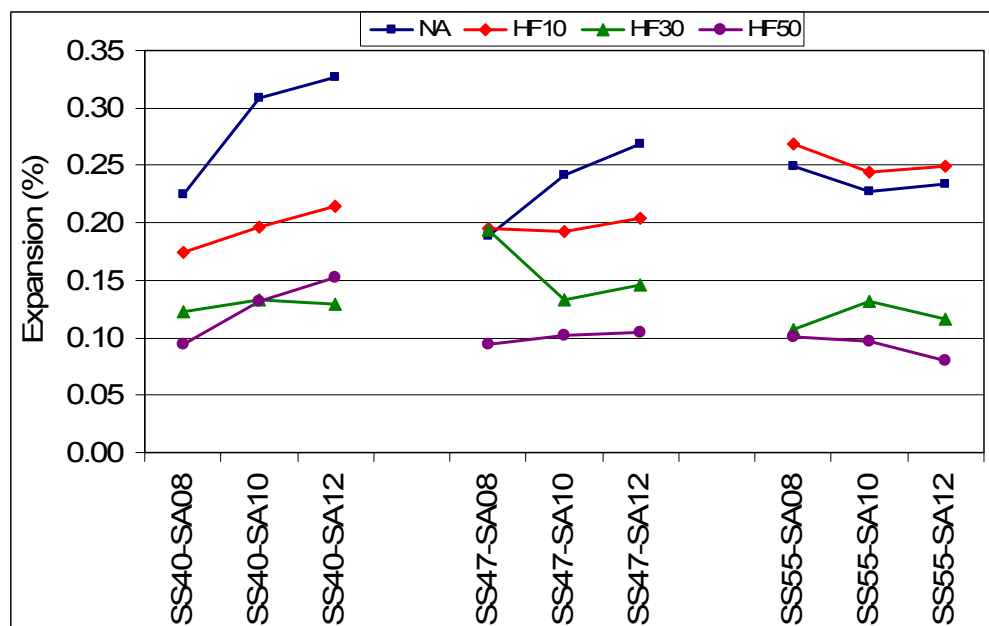


Figure 4.63 Effect of HLFA additive on expansion after 240 days

#### 4.3.6 Comparison of Mineral Admixtures

The expansion results of control cements blended with different types of mineral admixtures are given in figures 4.64 to 4.66.

10% addition of LLFA is more effective in decreasing the expansion for cement types with 4000 cm<sup>2</sup>/g blaine fineness. Then comes GGBFS, high lime fly ash and trass, respectively. As blaine fineness increases the effectiveness of these admixtures decreases except LLFA. Also at higher blaine finenesses the addition of trass and GGBFS increase expansion. For these series of cements, as SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio increases, the effectiveness of GGBFS decreases and expansion of samples including GGBFS additives expands nearly same with samples including trass additive.

At the replacement level of 30%, low lime fly ash is more effective than the other admixtures. For cement types with 4000 and 4750 cm<sup>2</sup>/g blaine fineness, the effectiveness of trass is higher than GGBFS, but for cement types with 5500 cm<sup>2</sup>/g blaine fineness it is reversed. HLFA is the less effective additive for the cement types with 4000 and 4750 cm<sup>2</sup>/g blaine fineness, and for cement types with 5500 cm<sup>2</sup>/g blaine fineness, trass is the less effective additive.

Finally, at the additive level of 50%, LLFA is more effective additive like all other samples. For these series, the effectiveness of trass reached nearly to the levels of LLFA. And again HLFA is the less effective one.

In general LLFA appears to be more effective at any replacement level and HLFA is the less effective one, which is also supported with the study of Ramlochan et. al [2003].

As a result, the addition of any amount of mineral admixtures to the cement decreases the expansion of concrete caused by delayed ettringite formation.



In their investigation about the expansion behavior of heat-cured mortars containing pozzolan and slag, Ramlochan et. al [2003] reported similar results that the addition of mineral admixtures reduces the long-term expansion, slows the rate of expansion, and delays the onset of expansion. They added that the efficacy of particular pozzolan or slag in controlling expansion may depend on its  $Al_2O_3$  content.

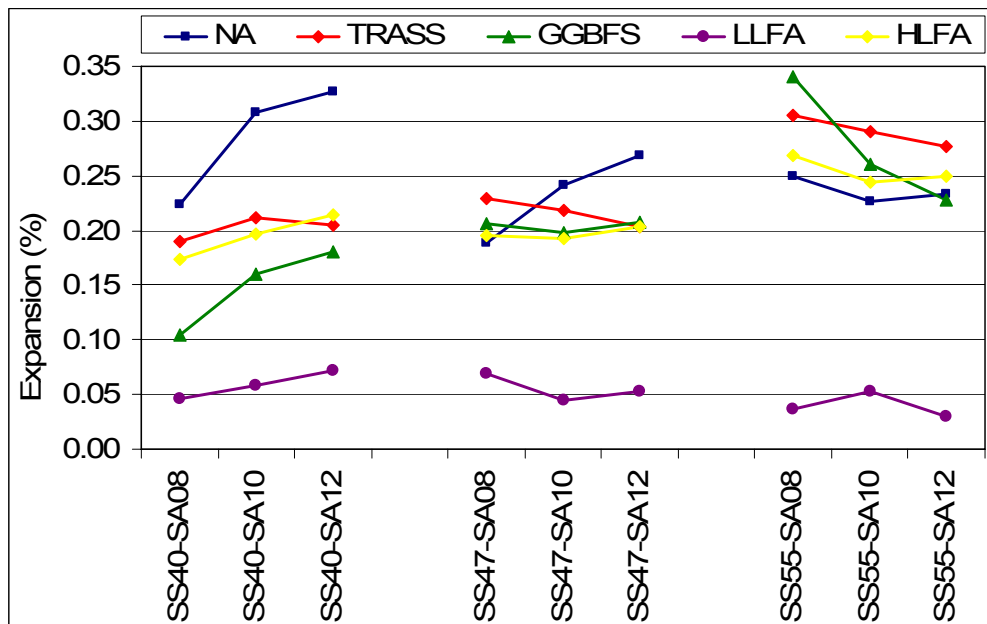


Figure 4.64 Effect of different mineral admixtures at 10% blending level on expansion after 240 days

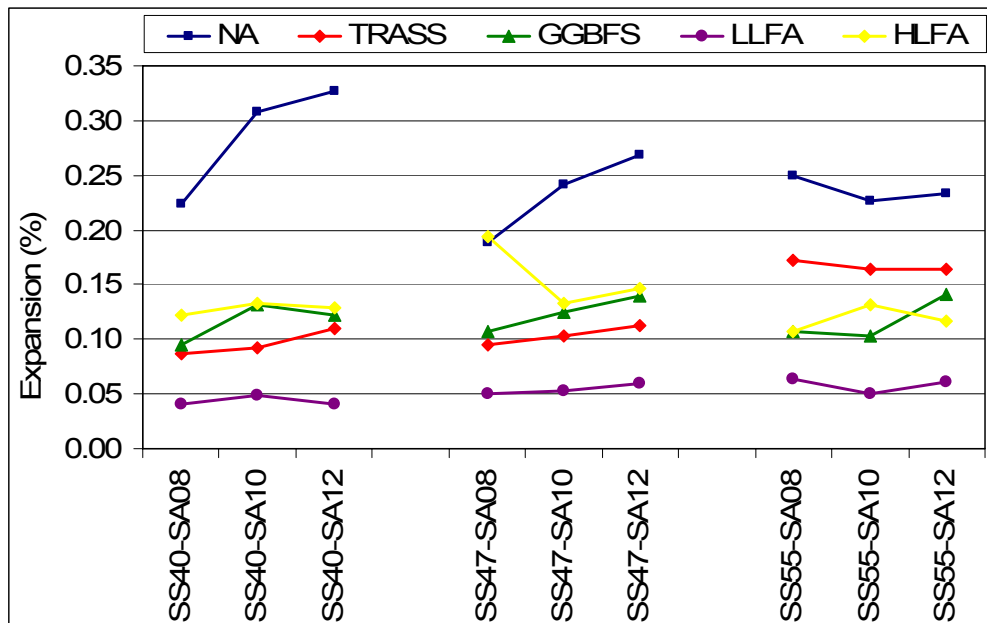


Figure 4.65 Effect of different mineral admixtures at 30% blending level on expansion after 240 days

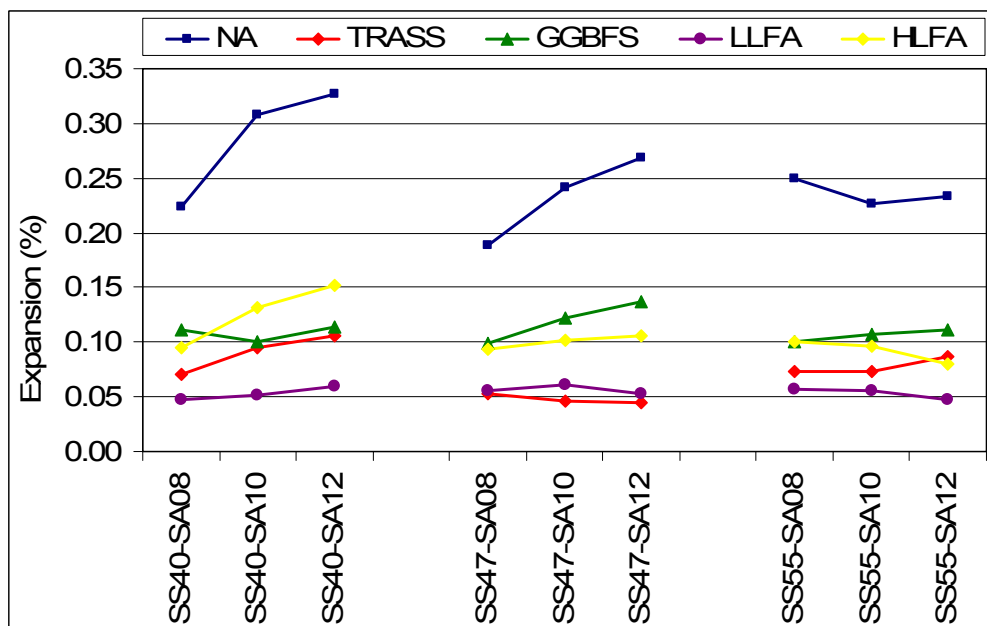


Figure 4.66 Effect of different mineral admixtures at 50% blending level on expansion after 240 days

## CHAPTER 5

### CONCLUSIONS

#### 5.1 General

In this study, the effects of partial cement replacement by different mineral admixtures (trass, blast furnace slag and fly ash),  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio and specific surface area of cement on DEF were investigated. According to the experimental results obtained in this study, the following conclusions can be drawn:

$\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio of the cement is one of the important factors that affects DEF potential. In the literature significant expansions were recorded for  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio ranging between 0.85 and 1.40. In this study the range between 0.80 and 1.20 is chosen and it is observed that as  $\text{SO}_3/\text{Al}_2\text{O}_3$  molar ratio increases, the expansion increases.

The specific surface area of the cement is another important factor that affects DEF. As the specific surface area thus blaine fineness increases the expansion decreases because of the rapid formation of ettringite on the surface of cement particles.

Partial cement replacement by any of the mineral admixtures used reduces the expansion. This effect is mainly due to the dilution of  $\text{C}_3\text{A}$ .

Mineralogical and chemical compositions of the admixtures are the main parameters affecting the decrease in expansion due to DEF. In this investigation, low lime fly ash was the most effective whereas the high lime fly ash was the least effective in controlling the expansions. Effectiveness of a given fly ash at controlling expansion might depend greatly on its CaO content.

Slag can be used for controlling the expansion caused by DEF with higher amounts of replacement levels. Since 30% replacement level is the threshold level, it can be replaced with higher levels because it is known that blending cement with slag increases the final strength and durability of concrete. However, this is not valid for other admixtures where high levels of replacement decrease the strength of concrete.

## **5.2 Recommendations for Future Researches**

Considering the results obtained from this thesis, some recommendations for future researches are suggested below:

In this experimental study cement pastes were prepared by mixing cement samples with different water amounts, which were determined according to water demand analysis. Instead of this, constant water can be used in order to eliminate the possible experimental errors from water demand analysis.

All the samples were prepared from the same Portland cement clinker. So that the mineralogical components like  $C_3S$ ,  $C_3A$  were constant. In order to observe the effects of these minerals on expansion, samples could be prepared with different clinkers like sulfate resisting cement clinkers where  $C_3A$  content is limited to a maximum of 5%.

DEF may be monitored by advanced analysis methods like SEM and XRD and the results may be correlated with the expansion test results in order to fully understand the mechanism of DEF.

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## APPENDIX A

### WATER DEMANDS AND SETTING TIMES

#### A.1 Water demand and setting time of control samples

Table A.1: Water demand and setting time of control samples

<b>SAMPLE</b>	<b>Water Demand (cc)</b>	<b>Initial Setting Time (min.)</b>	<b>Final Setting Time (min.)</b>
NA-SS40-SA08	140	165	205
NA-SS40-SA10	140	170	200
NA-SS40-SA12	140	170	200
NA-SS47-SA08	146	170	220
NA-SS47-SA10	145	180	210
NA-SS47-SA12	146	180	200
NA-SS55-SA08	160	175	205
NA-SS55-SA10	162	180	200
NA-SS55-SA12	163	195	215

## A.2 Water demand and setting time of samples containing trass additive

Table A.2: Water demand and setting time of samples containing trass additive

<b>SAMPLE</b>	<b>Water Demand (cc)</b>	<b>Initial Setting Time (min.)</b>	<b>Final Setting Time (min.)</b>
T10-SS40-SA08	140	150	190
T10-SS40-SA10	141	150	190
T10-SS40-SA12	141	140	180
T10-SS47-SA08	148	160	180
T10-SS47-SA10	147	170	220
T10-SS47-SA12	148	170	220
T10-SS55-SA08	162	170	190
T10-SS55-SA10	163	190	210
T10-SS55-SA12	164	190	210
T30-SS40-SA08	143	140	180
T30-SS40-SA10	146	150	170
T30-SS40-SA12	146	160	180
T30-SS47-SA08	153	160	180
T30-SS47-SA10	153	180	200
T30-SS47-SA12	153	180	220
T30-SS55-SA08	166	180	200
T30-SS55-SA10	166	190	240
T30-SS55-SA12	166	200	235
T50-SS40-SA08	155	170	210
T50-SS40-SA10	156	180	210
T50-SS40-SA12	158	180	200
T50-SS47-SA08	164	180	200
T50-SS47-SA10	163	180	200
T50-SS47-SA12	162	180	205
T50-SS55-SA08	163	160	180
T50-SS55-SA10	164	160	180
T50-SS55-SA12	165	160	190

### A.3 Water demand and setting time of samples containing GGBFS additive

Table A.3: Water demand and setting time of samples containing GGBFS additive

<b>SAMPLE</b>	<b>Water Demand (cc)</b>	<b>Initial Setting Time (min.)</b>	<b>Final Setting Time (min.)</b>
S10-SS40-SA08	142	160	190
S10-SS40-SA10	142	150	180
S10-SS40-SA12	141	160	180
S10-SS47-SA08	148	180	200
S10-SS47-SA10	148	180	200
S10-SS47-SA12	149	180	210
S10-SS55-SA08	163	190	220
S10-SS55-SA10	165	200	240
S10-SS55-SA12	166	190	230
S30-SS40-SA08	146	160	190
S30-SS40-SA10	143	180	220
S30-SS40-SA12	142	170	200
S30-SS47-SA08	149	180	200
S30-SS47-SA10	151	170	210
S30-SS47-SA12	150	170	210
S30-SS55-SA08	160	170	230
S30-SS55-SA10	162	190	215
S30-SS55-SA12	163	200	250
S50-SS40-SA08	143	170	190
S50-SS40-SA10	142	160	180
S50-SS40-SA12	144	170	190
S50-SS47-SA08	148	180	210
S50-SS47-SA10	150	170	195
S50-SS47-SA12	150	180	230
S50-SS55-SA08	158	180	200
S50-SS55-SA10	161	190	250
S50-SS55-SA12	161	190	240

#### A.4 Water demand and setting time of samples containing low lime fly ash additive

Table A.4: Water demand and setting time of samples containing LLFA additive

<b>SAMPLE</b>	<b>Water Demand (cc)</b>	<b>Initial Setting Time (min.)</b>	<b>Final Setting Time (min.)</b>
LF10-SS40-SA08	140	150	170
LF10-SS40-SA10	140	150	170
LF10-SS40-SA12	139	150	200
LF10-SS47-SA08	146	180	210
LF10-SS47-SA10	146	190	230
LF10-SS47-SA12	146	190	230
LF10-SS55-SA08	161	190	220
LF10-SS55-SA10	163	200	220
LF10-SS55-SA12	164	200	240
LF30-SS40-SA08	139	160	180
LF30-SS40-SA10	140	160	180
LF30-SS40-SA12	139	170	190
LF30-SS47-SA08	145	180	200
LF30-SS47-SA10	145	190	210
LF30-SS47-SA12	145	180	210
LF30-SS55-SA08	159	210	230
LF30-SS55-SA10	160	230	250
LF30-SS55-SA12	161	230	250
LF50-SS40-SA08	147	200	230
LF50-SS40-SA10	147	200	240
LF50-SS40-SA12	147	200	250
LF50-SS47-SA08	150	220	250
LF50-SS47-SA10	150	210	260
LF50-SS47-SA12	151	210	240
LF50-SS55-SA08	162	230	270
LF50-SS55-SA10	163	250	290
LF50-SS55-SA12	162	210	240

## A.5 Water demand and setting time of samples containing high lime fly ash additive

Table A.5: Water demand and setting time of samples containing GGBFS additive

<b>SAMPLE</b>	<b>Water Demand (cc)</b>	<b>Initial Setting Time (min.)</b>	<b>Final Setting Time (min.)</b>
HF10-SS40-SA08	141	170	200
HF10-SS40-SA10	142	190	240
HF10-SS40-SA12	139	160	180
HF10-SS47-SA08	147	190	220
HF10-SS47-SA10	146	200	220
HF10-SS47-SA12	147	220	260
HF10-SS55-SA08	160	200	230
HF10-SS55-SA10	162	210	240
HF10-SS55-SA12	163	210	250
HF30-SS40-SA08	138	210	240
HF30-SS40-SA10	138	210	240
HF30-SS40-SA12	135	230	260
HF30-SS47-SA08	145	190	220
HF30-SS47-SA10	143	250	270
HF30-SS47-SA12	140	230	260
HF30-SS55-SA08	150	250	290
HF30-SS55-SA10	148	240	270
HF30-SS55-SA12	151	250	270
HF50-SS40-SA08	127	290	330
HF50-SS40-SA10	126	280	320
HF50-SS40-SA12	123	280	320
HF50-SS47-SA08	129	280	310
HF50-SS47-SA10	129	250	290
HF50-SS47-SA12	126	250	295
HF50-SS55-SA08	134	250	280
HF50-SS55-SA10	132	240	260
HF50-SS55-SA12	130	250	275