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# Durability of blended cement against sodium sulphate attack and alkali-silica reaction

Giri Raj Adhikari  
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# **DURABILITY OF BLENDED CEMENT AGAINST SODIUM SULPHATE ATTACK AND ALKALI-SILICA REACTION**

**By:**

**Giri Raj Adhikari, B. Eng.  
Tribhuvan University, Kathmandu, Nepal, 1994**

**A Thesis**

**Presented to Ryerson University**

**In partial fulfillment of the  
Requirements for the degree of  
Masters of Applied Science  
In the program of  
Civil Engineering**

**Toronto, Ontario, Canada, 2007  
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## **Abstract**

### *Durability of blended cement against sodium sulphate attack and alkali-silica reaction*

**Giri Raj Adhikari**

**2007, MASc, Department of Civil Engineering, Ryerson University**

Blended cements were studied for their efficacy against sulphate attack and alkali-silica reaction using six different types of fly ashes, a slag, a silica fume and four types of General Use Portland cement of different alkalinity. The study results showed that low calcium fly ash, silica fume and ground granulated blast furnace slag enhanced the sulphate resistance of cement with increased efficacy with the increase in the replacement level. However, slag and silica fume, especially at low replacement levels, exhibited increased rate of expansion beyond the age of 78 weeks. On the contrary, high calcium fly ashes showed reduced resistance to sulphate attack with no clear trend between the replacement level and expansion. Ternary blends consisting of silica fume, particularly in the amount of 5%, high calcium fly ashes and General Use (GU) cement provided high sulphate resistance, which was attributable to reduced permeability. In the same way, some of ternary blends consisting of slag, high calcium fly ash and GU cement improved sulphate resistance. Pre-blending optimum amount of gypsum with high calcium fly ash enhanced the latter's resistance to sulphate attack by producing more ettringite at the early stage of hydration.

In the context of alkali-silica reaction, permeability was found to be a contributing factor to the results of the accelerated mortar bar test. High-alkali, high-calcium fly ash was found to worsen the alkali silica reaction when used in concrete containing some reactive aggregates. Ternary blend of slag with high calcium fly ash was found to produce promising results in terms of counteracting alkali-silica reaction.

## **Acknowledgements**

I would like to express my sincere gratitude to my supervisor Professor Dr. Medhat Shehata for accepting me as M.A.Sc. student at Ryerson University and for providing guidance, moral and financial support during the steps of this research. His invaluable time, warmth welcome for discussion, encouragement, motivation and stimulation for creative thinking helped develop confidence at me to handle and accomplish this research work within the expected time frame.

I address my sincere thanks to Nidal Jaalouk, Dan Peneff, Dominic Valle and Robin Loung for providing me invaluable supports ranging from prompt acquirement of materials, tools and equipments to handle and operate them safely.

Also I would like to express my thankfulness to Shaun Radomski, Chris Christidis, Waleed Mikhael, Ramy Zahran and Riad Rahman for their kind support in the form of their valuable ideas and direct and indirect helps in preparation of samples and running the test in the course of this research study.

Finally, I would like to thank my spouse for her warmth love, relentless support and sharing all of the difficulties.

## **Dedication**

**To My Late Parents**

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## **List of Abbreviations**

**AASHTO** : American Association of State Highway and Transportation Officials

**ACI** : American Concrete Institute

**ASR** : Alkali Silica Reaction

**ASTM** : American Society of Testing and Materials

**CH** : Calcium Hydroxide

**CSA** : Canadian Standard Association

**FA** : Fly Ash

**FHWA** : Federal Highway Administration

**GGBFS** : Ground Granulated Blast Furnace Slag

**GU** : General Use

**GUPC** : General Use Portland Cement

**HCFA** : High Calcium Fly Ash

**HCHA** : High Calcium High Alkali

**HCLA** : High Calcium Low Alkali

**LCLA** : Low Calcium Low Alkali

**MCLA** : Moderate Calcium Low Alkali

**PB** : Pre-blending

**RCPT** : Rapid Chloride Permeability Test

**SCM** : Supplementary Cementing Material

**SF** : Silica Fume

**SRC** : Sulphate Resistance Cement

**SSR** : Sulphate Susceptibility Ratio

# **Chapter 1**

## **Introduction**

### **1.1 General**

Portland cement, due to its versatility, availability and economy has been widely used as construction material for centuries. Properly designed, proportioned, mixed, placed and cured structures constructed with Portland cement have been found to be standing up to design life period without any sign of deterioration in environment that are free from harmful species. But the environment free from such harmful species is not possible to be found everywhere. Either naturally or as a result of human activities such as emergence of industries using different types of chemicals, use of different types of fertilizers and haphazard disposal of industrial effluents and domestic wastes, such species are found in the ground or ground water or sea water. Accumulation of such species beyond the prescribed limit (150ppm of sulphate ions as per ACI committee 318) can turn the environment into aggressive and can pose the looming threat to the structures constructed in such environment. Among the several types of such harmful species, sodium sulphate has been found to be one. Sodium sulphate ions present in the sulphate bearing medium, mostly the ground water, enters the hardened concrete by one or more mechanism of adsorption, vapor diffusion, liquid assisted vapor transfer, saturated liquid flow or ionic diffusion under saturated condition (Hearn and Figg 2000) and react with tricalcium aluminate or monosulphate to form expansive and disruptive ettringite (Mehta and Monteiro 2006, Mindess et al 2003) leading to softening, spalling, expansion and cracking. Thousands of structures constructed at the sea shore in the State of California have been reported to be suffering from sulphate attack (Haynes and O'Neill 1994,

Travers 1997, Lichtman et al 1998, Haynes 2000). Deteriorations were ranged from post tensioned floor slabs, garage floors, footings, foundations, driveways, retaining walls to street curbs (Skalny et al 2003). Several millions of prefabricated pre-stressed steel-reinforced railway ties and other concrete products were damaged in between 1980 and 1984 in Germany. Similar cases were documented in the United States, Canada, Finland, ex-Czechoslovakia, South Africa, Sweden and several other countries in the world. Deterioration of bridge foundation was observed in the UK in 1998 (Skalny et al 2003). In the same way, several stretches of pavement in California, Nevada and Delaware were reported to be deteriorated due to alkali-silica reaction (ASR) (source: FHWA) as a result of reaction between alkali available in cement and some types of poorly crystalline siliceous aggregates. Sulphate attack and ASR, therefore, are serious problems and need to be addressed with great attention. Sulphate resistant cement has been developed to address the problem of sulphate attack. However, some of studies carried out on sulphate resistant cement show that it is not effective in higher sulphate bearing environment (Stephens and Carrasquillo 2000, Sahmaran et al 2007). So, the sulphate resistant cement can not be a reliable solution particularly for environment containing higher degree of sulphate concentration. Low alkali cement can be effective in combating ASR but modern cement plants have produced high alkali cement. Therefore, it has been necessary to find alternative solutions to prevent sulphate attack and ASR. One of the best alternatives could be use of supplementary cementing materials (SCMs). However, some of the studies (Cohen and Bentur 1988, Al-moundi et al 1995) show that none of the SCMs are effective in sulphate resistance against magnesium sulphate bearing environment. Therefore, the present research has confined its study only on durability of blended cement against sodium sulphate attack and Alkali-Silica-Reaction

(ASR). General Use cement contains higher amount of sodium sulphate susceptible compound as tricalcium aluminate and hydration product as calcium hydroxide. In the same way, the GU cement being produced from the modern cement plant contains higher amount of alkali which is sustain to ASR. Incorporation of Supplementary Cementitious materials (SCM) in the general use cement can eliminate or alter sulphate susceptible compounds as well as binds alkali in the hydration product as a result of their specific roles which will be explained later in the role of the SCMs subsection. Different types of SCMs are commercially available in the market and are being used as a partial replacement of cement nowadays. The predominantly used SCMs are Fly Ash, Silica Fume, Ground Granulated Blast Furnace Slag (GGBFS) and Natural Pozzolan. Each SCM has its own physical, chemical and mineralogical composition and hence has its own specific role and advantages for use in cement. Among these SCMs, fly ash is one which have been widely produced and used as a cementitious material. The present thesis will include the study result of the effects of incorporation of SCMs in General Use Cement for sulphate resistance and ASR resistance. Most emphasis will be given to fly ash due to its wide range of composition.

## **1.2 Background**

Technological advancement and rapid urbanization have caused the emergence of increased number of industries using different types of fuels and producing large amount of byproducts. The majority of these byproducts includes from fly ash to silica fume and granulated blast furnace slag (GGBFS). As per the Annual Survey Report of American Coal Ash Association, 64,501,920 metric tons of fly ash was produced in the USA (source: American Coal Ash Association). Latest record of exact amount of production of silica fume

is not available. However, as per a report (Malhotra and Carrette 1982), silica fume production was estimated to be in the order of 2000,000 to 5000,000 metric tons in USA. Slag cement consumption has been increased from 3211000 metric tons in 2005 to 3299000 metric tons in 2006 (source: Slag Cement Association). Out of total production of fly ash, 13,598,890 metric tons was used for concrete/concrete product/grout application and 186,005 metric tons was used for road base/sub-base/pavement application in 2005 (source: American Coal Ash Association) which is 21.08% and 0.3% of total fly ash production respectively. However, in the context of silica fume, all of the produced amounts have been reported to be consumed each year (source: Silica Fume Association). Similar consumption trend as silica fume seems for GGBFS.

It is reported that the production of every ton of Portland cement contributes to the production of one ton of carbon-dioxide into the atmosphere (source: Natural Resource Canada) which in the long run causes greenhouse effect and eventually causes the global warming problem. Replacement of cement with one ton of SCM is worth in the reduction of one ton of carbon-dioxide emission in the atmosphere. In addition to the reduction in the emission of carbon-dioxide, replacement of cement with SCMs helps to lessen pressure on rapid depletion of natural resources, reduce energy consumption and minimize the land area of disposal. Moreover, the approach is cost effective. Apart from this, SCMs incorporation enhances the required engineering properties of concrete in terms of durability in aggressive environment. So at the present time, it has been essential for engineers to create awareness and encouragement to use SCMs as many application as possible. Hence it is important for them to carryout extensive research work on SCMs to make use of even at aggressive

sulphate bearing and ASR prone environment without compromising concrete strength and durability.

### **1.3 Objectives**

The main objective of this thesis was to explore different possibilities to enhance the durability of concrete in sulphate bearing and ASR prone environment with the incorporation of the fly ash as the sole SCM and in combination with other SCMs such as Silica Fume and Ground Granulated Blast Furnace Slag (GGBFS). Several mortar bars and concrete prisms were prepared as per ASTM C 1012, ASTM C 1260 and ASTM C 1293 with addition of varied amount of fly ashes in Portland cement. In some instances, other SCMs such as silica fume and slag were added to the fly ashes while replacing a part of Portland cement. Tricalcium aluminate and gypsum balancing approach was investigated against sulphate attack by addition of gypsum to two high calcium fly ashes.. Other testing such as Rapid Chloride Permeability Test (RCPT) and x-ray diffraction of the efficient blend were carried out for analysis of the results.

## **Chapter 2**

### **Literature Review**

Relevant literature was reviewed and the findings were summarized both for sulphate attack and alkali-silica-reaction.

#### **2.1 Sulphate attack**

Sulphate attack is a rather complex process that may involve all of the hydration products produced by Portland cement. The damage caused by sulphate attack may involve cracking and expansion of concrete as a whole, as well as softening and disintegration of cement paste (Mindess et al 2003).

The problem of external sulphate attack was first identified by the United States Bureau of Reclamation in 1908 (Bellport 1968). Since then, lots of efforts have been made in the identification of causes, mechanism, consequences and its prevention. Almost all of the investigation reports on sulphate attack have pointed out that General Use Cement alone is inefficient in sulphate bearing environment. The chemical compounds of general use cement primarily the tricalcium aluminate ( $C_3A$ ) and the hydration product, calcium hydroxide (CH) have been considered to be the compounds susceptible for sulphate attack. Sulphate ions enter the hardened concrete and react with tricalcium aluminate or monosulphate to form expansive and disruptive ettringite (Mehta and Monteiro 2006, Mindess et al 2003). Sulphate ions also react with CH and forms gypsum in the hardened concrete. Excessive formation of gypsum in the hardened concrete causes gypsum corrosion (Mindess et al 2003).



Potential external sources of sodium sulphate have been found to be industrial chemicals, fertilizers, sea water, sewer water, sea shore and ancient sea bed soil. In the same way, added gypsum in the cement during its production, sulphate available in the Supplementary Cementing Materials (SCM) and some gypsum contaminated aggregates has been found to be the internal sources (Neville 1996, Skalny et al 2003).

### **2.1.1 Sulphate attack mechanism**

Sodium sulphate has been reported to attack the cement paste through two distinct mechanisms- physical and chemical (Mehta and Monteiro 2006, Mindess et al 2003, Skalny et al 2003).

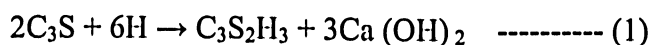
#### **2.1.1.1 Physical attack due to salt crystallization**

When a permeable concrete structure is subjected to sulphate bearing aqueous environment, sulphate (salt) solutions enter the concrete through various ways such as diffusion, sorptivity or capillary suction. These salt solutions rise up in the structures through capillary action. As these solutions approach the evaporation front, start crystallization due to gradual loss of moisture. Some types of salt like sodium sulphate and magnesium sulphate changes its phase upon crystallization depending upon the temperature of the environment. If the temperature of the surrounding is more than 32.4°C, anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) crystal will be formed. If the temperature of the surrounding is less than 32.4°C, hydrous sodium sulphate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) crystal will be formed. Upon the fluctuation of temperature above and below 32°C, sodium sulphate continuously changes its phase. Similarly, magnesium sulphate changes its phase from anhydrous magnesium sulphate ( $\text{MgSO}_4$ ) to monohydrate

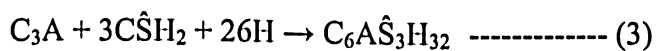
(MgSO<sub>4</sub>.H<sub>2</sub>O) and from monohydrate to hexahydrate (MgSO<sub>4</sub>.6H<sub>2</sub>O) and from hexahydrate to septahydrate magnesium sulphate (MgSO<sub>4</sub>.7H<sub>2</sub>O) (Bucea et al 2005). The volume of these sulphates increases upon crystallization. Due to changing of phase and expansion, these sulphate crystals exert crystal growth pressure (Flatt 2002, Brown 2002) on the concrete surface; as a result flaking, spalling and cracking occur on the surface (Mehta 2002). If the rate of migration of salt solution due to capillary action is lower than the rate of evaporation, crystallization occurs below the ground surface (Mehta 2002).

#### 2.1.1.2 Chemical attack

Chemical attack is caused by the presence of sulphate ions in the hardened concrete. To get better understanding of the mechanism of sulphate attack, it is essential to understand the hydration mechanism of ordinary Portland cement. Portland cement is composed of tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. Gypsum covers four to six percent (Kosmatka et al 2002). When cement is mixed with water, dicalcium silicate and tricalcium silicate reacts with water and forms calcium hydroxide and calcium silicate hydrate(C-S-H)



Gypsum reacts with tricalcium aluminate and forms stable ettringite.

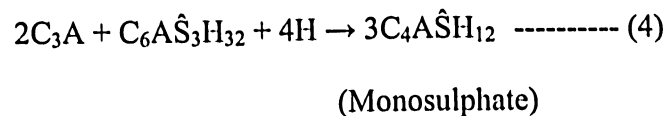


(Ettringite)

The ettringite forms in equation 3 during the hydration of the cement at the initial age when the concrete is in the plastic stage. Ettringite formation at the initial stage of hydration is a

complementary part of hydration reaction of cement. It helps in preventing flash set by retarding early hydration of  $C_3A$ . The ettringite formed at the initial stage of hydration causes no expansion crack to concrete as concrete is still in the plastic state and can accommodate volume change.

If the quantity of gypsum in the cement is adequate, it reacts with all tricalcium aluminate of the cement paste and forms only ettringite as in equation 3; otherwise excess tricalcium aluminate reacts with ettringite and converts it to monosulphate.



#### **2.1.1.2.1 Chemical attack due to external sources of sulphate**

If the concrete structure is situated in the sulphate bearing environment and permeable, sulphate ions can ingress the concrete through diffusion, sorptivity or capillary suction and react with hydration products and forms ettringite and gypsum. Formation of ettringite and gypsum in the hardened concrete is harmful.

The rate of sulphate attack increases with an increase in the strength of solution, but beyond a concentration of about 0.5 percent of magnesium sulphate or 1 percent of sodium sulphate the rate of increase in the intensity of the attack becomes smaller (Neville 2006).

)

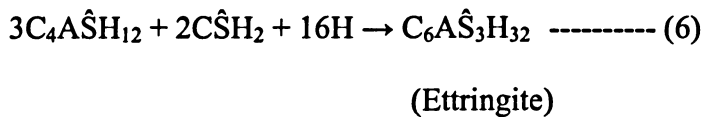
#### 2.1.1.2.1.1 Ettringite formation in hardened concrete

Ettringite can form in hardened concrete from one or combination of more than one mechanism.

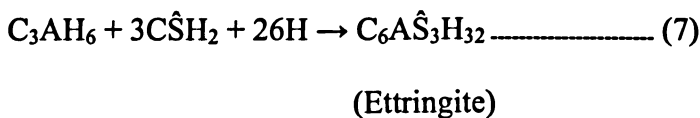
As sulphate ions enter the concrete structures, it reacts with calcium hydroxide and forms gypsum ( $\text{C}\hat{\text{S}}\text{H}_2$ ).



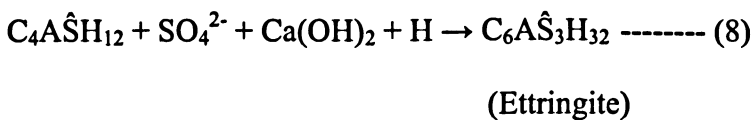
Gypsum reacts with monosulphate formed as in equation 4 and forms ettringite.



Gypsum also forms ettringite with the reaction of calcium aluminate hydrate.



Ettringite also forms with the reaction of sulphate ion, monosulphate, calcium hydroxide and water.



The formed ettringite in equation (8) occupies 55% more solid volume causing a volume expansion within the paste generating internal stress and leading to cracking (Mindess et al 2003). The volume expansion may also be caused by water absorption when ettringite is in a microcrystalline form (Mindess et al 2003). Removal of successive layers (of a specimen subjected to sulfate attack) and analysis of the resulting surfaces has shown the presence of gypsum, then ettringite, then monosulfate, from the surface towards the core of the specimen, with decrease of the quantity of portlandite from the core towards the surface (Taylor 1997).

Ettringite forms in the surface layer, which leads to cracking in this layer and to a lower amount of cracking in the subsequent layers into which sulfate ions have not ingressed yet. When ettringite is formed in this second layer, it induces cracking in the next non- invaded layer, whereas its own expansion is being restrained by the presence of the third layer (Santhanam and Cohen 1998).

#### **2.1.1.2.1.2 Gypsum formation**

Reaction equation of gypsum formation is shown in equation 5. If there is no monosulphate and/or calcium aluminate hydrate for gypsum to react with or if there is excessive amount of gypsum formation due to reaction with excessive amount of calcium hydroxide, gypsum inside the concrete remains in the free state. Formation and accumulation of gypsum inside the hardened concrete itself is a form of sulphate attack. Most structures subjected to sulphate attack due to the formation of gypsum are characterized by spalling on the exterior, softening of the concrete surface texture and loss of compressive strength (Aziz et al 2005). According to P.K. Mehta (Mehta 1973), gypsum formation occurs in the concrete only if the range of pH solution is in between 8 to 11.5. However, controversies exist over the effect of the formed gypsum in the hardened concrete. According to a school of thought, the formation of gypsum in the hardened paste causes expansion (Mindess et al 2003, Santhanam et al 2003, Tian and Cohen 2000a, Tian and Cohen 2000b, Mehta 1992) while according to the other school of thought, the gypsum doesn't cause expansion (Hansen 1963, Mather 1996).

#### **2.1.1.2.2 Chemical attack due to internal sources of sulphate**

Gypsum is one of the internal sources of sulphate which is added in the cement during final grinding of clinker to regulate setting time and for early strength. Apart from gypsum, cement concrete may contain other internal sources of sulphate such as slowly soluble sulphate contained clinker, gypsum contaminated aggregate and admixtures such as fly ash (Skalny et al 2003, Neville 1996). With time and favorable environment, these sulphates may become available to react with the  $C_3A$  or Monosulphate or C-A-H and forms ettringite in the hardened concrete and causes expansion and disruption which is termed as internal sulphate attack.

#### **2.1.2 Prevention of sulphate attack**

From the above equations (equation 1 to 8), it is clear that the sulphate attack is the consequence of reaction involving the sulphate ion and tricalcium aluminate and/or calcium hydroxide. Therefore, reduction or elimination of presence of one or more of the above agents in the hardened concrete can prevent the sulphate attack. Minimization of presence of sulphate ions to the concrete from the external sources can be achieved by preventing entry of the ions with the reduction of the permeability of the concrete. Reduction in the permeability can be achieved with minimization of water cementitious material (w/c) ratio and with the use of certain types of SCMs (Mehta and Monteiro 2006, Neville 1996). Reduced expansion was observed (Khatri et al) at the lower permeability for samples prepared with low w/c ratio for a given type of binder. Similar result (Sahmaran et al 2007) was obtained in an experiment on low sulphate resistant cement with higher  $C_3A$ . Better sulphate resistance was obtained with reduced permeability (Rasheeduzzafar 1992); reduced chloride diffusion

coefficient (Thomas et al 1999) and with incorporation of silica fume in the cement. Production of calcium hydroxide can be limited by reducing the  $C_3S/CH_2S$  ratio as tricalcium silicate ( $C_3S$ ) produces calcium hydroxide 2.2 times more than that of dicalcium silicate ( $C_2S$ ) during hydration (Neville 1996). Increased sulphate resistance was achieved with the use of cement of low  $C_3S/C_2S$  ratio (Rasheeduzzafar et al 1990). Expansion of 0.10% was reached at 148 days for type V cement with higher  $C_3S$  content whereas the same expansion was reached at 1260 days for type V cement with low  $C_3S$  content in the sulphate bearing environment (Gonzalez and Irassar 1998). In another study (Sahmaran et al 2007), poor sulphate resistance was observed on the mortar bars prepared with sulphate resistant Portland cement (SRPC) with high  $C_3S/C_2S$  ratio of 18.3. Production of calcium hydroxide can be minimized with the introduction of SCMs in the cement. Role of different SCMs will be discussed in detail in the subsequence chapter.

Owing to the specific role of  $C_3A$  in the cement, it can not be removed completely.  $C_3A$  and gypsum have the following roles in the cement.

#### **2.1.2.1 Role of $C_3A$**

$C_3A$  can not be removed completely from cement as it is needed to act as a flux to reduce the temperature of burning of clinkers and to bind chloride ion so as to prevent the reinforcement in the concrete from corrosion (Neville 1996). Equations 6 to 8 clearly show that presence of hydration product containing trace of  $C_3A$  such as hydrogarnet ( $C_3AH_6$ ) and monosulphate ( $C_4A\hat{S}H_{12}$ ) in the hardened cement cause the formation of disruptive ettringite either reacting with gypsum (equations 6 and 7) or calcium hydroxide and sulphate ions (equation 8). But the situation whether there will be trace of hydration product of  $C_3A$  or not in the hardened

concrete is governed by the presence of the amount of  $C_3A$  and Gypsum in the cement. Presence of varied amount of gypsum and  $C_3A$  in the cement can produce different hydration product (Table 2.1). If the molar ratio of gypsum and tricalcium aluminate is less than 3, aluminate remains in the form of monosulphate or in the form of hydrogarnet ( $C_3AH_6$ ) in the hydration product which later on becomes available to reacts with sulphate ions to form expansive and disruptive ettringite in the hardened concrete.

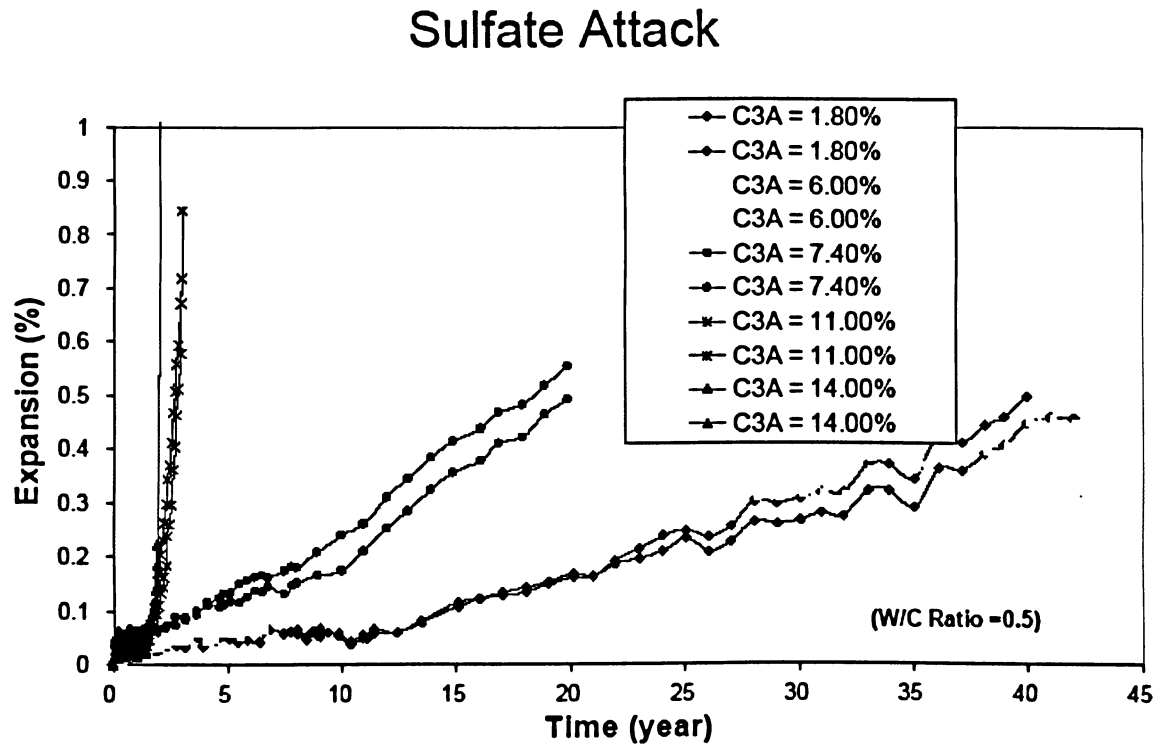
Table 2.1: Role of Tricalcium Aluminate and Gypsum in cement hydration products

$CSH_2/ C_3A$ (Molar ratio)	Hydration Product
>3.0	$C_6A\hat{S}_3H_{32}$
1.0-3.0	$C_6A\hat{S}_3H_{32} + C_4A\hat{S}H_{12}$
1.0	$C_4A\hat{S}H_{12}$
<1.0	$C_4A\hat{S}H_{12}$ Solid solution
0	$C_3AH_6$ (Hydrogarnet)

Source: Mindess et al 2003



Severity of sodium sulphate attack is higher with the increased percentage of  $C_3A$  due to the formation of hydration product containing monosulphate and hydrogarnet (Figure 2.1).



**Figure 2.1: Effect of  $C_3A$  in sodium sulphate attack Source: Kurtis**

Sulphate resisting type V cement was introduced with the concept of lowering the amount of  $C_3A$  in the mid-1930s (Skalny et al 2003).

#### 2.1.2.2 Role of Gypsum and Sulphate additives

The role of gypsum and other sulphate additives is equally crucial as the role of  $C_3A$  in Portland cement. With the presence of higher amount of gypsum causes consumption of all the  $C_3A$  during initial period of hydration and no  $C_3A$  will be available to react with sulphate

ions in the hardened cement paste as a result the cement will be free from sulphate attack. However, the presence of excessive amount of gypsum and other sulphate additives in the cement can cause gypsum corrosion, a form of sulphate attack (Mindess et al 2003). Presence of balanced amount of  $C_3A$  and gypsum makes the cement effective sulphate resistance. Sulphate resistance of cement may be achieved by increasing its gypsum content, while still staying within the acceptable  $SO_3$  range (Gollop and Taylor 1996). Detail explanation about the effect on addition of gypsum and other sulphate bearing additives have been provided in the subsequent chapter under the heading of “Role of SCMs”.

### **2.1.2.3 Role of SCMs**

Each SCM has its own chemistry and mineralogy, so efficacy of sulphate resistance of cement with the addition of SCMs varies from one SCM to another. The effect the addition of one SCM causes in alteration of the chemistry and mineralogy of the cement will not be the same with addition of equal amount of other SCM.

#### **2.1.2.3.1 Fly Ash**

Fly ash, one of the widely accepted and specified mineral admixtures in cement and concrete (Joshi and Lohtia 1997) is the by-product of coal combustion. When pulverized coal is burnt in the furnace as a fuel to generate electric power from the thermal power plant, the most of the coal part is burnt and the remaining unburned carbon, mineral matter present in the coal such as clay, quartz and feldspar remained in suspension is carried away by the flue gas and is collected using cyclone separators, electrostatic precipitators and bag houses as fly ash (Joshi and Lohtia 1997). Until past seven decades, whole amount of fly ash thus produced

used to be disposed in the ponds and open land considering it as one of industrial wastes. But after suggestion from R.E. David and his team in 1937 as fly ash to be a material having similarity in properties with volcanic ash, higher pozzolanic reactivity (Hossain and Lachemi 2006), when used as a pozzolan or additive to cement concrete (Joshi and Lohtia 1997), its use as engineering materials in cement concrete has started increasing. But even at the present time, in comparison to the amount of production, its use in cement concrete application is very low.

Depending upon the sources and types of fuel, types and efficiency of power plant and load of power plant operation, the properties of fly ash produced are different. The power plant that burns anthracite and bituminous coal derived from Midwest and eastern states of the United States and some of the eastern Provinces of Canada as a fuel produces fly ash with very low amount of calcium oxide and the power plant that burns lignite derived from North Dakota and Texas and sub-bituminous coal derived from Wyoming and Montana produces fly ash with high calcium oxide. CSA has classified the fly ash as type F (low calcium), type CI (intermediate calcium) and type CH (high calcium) for the percentage of calcium oxide (CaO) content of less than 8%, between 8 to 20% and higher than 20%, respectively. Generally the class CI and CH fly ash is called as class C fly ash.

When fly ash is present in cement either as an admixture or blend, the calcium hydroxide reacts slowly with amorphous alumino-silicates, the pozzolanic compound present in the fly ash and forms the additional hydration product having property similar to C-S-H gel called secondary C-S-H gel which imparts additional strength to the concrete. As the pozzolanic

reaction is much slower than the cement hydration reaction, incorporation of fly ash generally reduces early strength but the ultimate strength may be equal or higher. The rate of strength gain, however, depends upon the properties of the fly ash and cement used, mix proportions as well as curing conditions of the fly ash concrete (Joshi 1979). But in the case of fly ash which has cementitious properties as in the case with class C fly ash, additional strength producing reaction occurs. Although this reaction is complex, it is generally considered to be similar to normal hydration reaction of Portland cement. So incorporation of class C fly ash may not cause reduction in the early strength (Joshi and Lohtia 1997). Due to difference in hydration reaction process for concrete containing fly ash, its fresh and hardened properties are different than that of normal concrete.

Fly ash is indeed a highly heterogeneous material where particle of similar size can have different chemistry and mineralogy (Das and Yudhbir 2005). There could be variation in properties for fly ash produced from different sources, from the same sources but with time (Winter and Clarke 2002), with collection point and with variation in load generation (Source: FHWA). This variation is expected to be higher in class C fly ash (Diamond 1986). Fly ash which is produced at base loaded electric generating plants is usually very uniform (Source: FHWA). Therefore, it is very important for engineers to characterize the fly ash from the different sources before using them in cement concrete application. Fly ash is characterized on the basis of its physical, chemical and mineralogical properties.

#### **A. Physical Properties**

The physical properties of fly ash are summarized as:

### **i) Particle morphology**

Morphological study on particle shape and surface characteristics of fly ash shows the fly ash particles to be of spherical in shape with varied proportion of solid sphere, hollow sphere (also called ceno-sphere) and plero-sphere, a sphere containing small solid spheres. The exterior surface of class C fly ash seems rough due to surface coatings of materials rich in calcium against the smooth surface of class F fly ash (Mehta 1984).

### **ii) Fineness**

Fineness of fly ashes has been found to be in the range of  $10\mu\text{m}$  to over  $100\mu\text{m}$  (Source: FHWA). Fineness is one of the prominent characteristics of fly ash that relates to its pozzolanic activity.

### **iii) Specific gravity**

Specific gravity of fly ashes has been found to be in the range of 1.3 to 4.8 (Joshi and Lohtia 1997). Specific gravity of class C fly ash has been observed slightly higher than that of class F fly ash due to absence of ceno-sphere (Das and Yudhbir 2005).

## **B. Chemical Properties**

The chemical properties of fly ash are summarized as:

### **i) Total oxides**

Presence of higher amount of sum of oxides of silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and iron ( $\text{Fe}_2\text{O}_3$ ) in fly ash represents higher pozzolanic reactivity of fly ash whereas presence of higher amount of calcium oxide ( $\text{CaO}$ ) shows hydraulic characteristics. Class F fly ash has

been found to be rich in pozzolanic characteristics whereas class C fly ash in both pozzolanic and hydraulic characteristics.

#### **ii) Sulphur Trioxide ( $\text{SO}_3$ )**

Compressive strength of concrete has been found to be higher with the increase in amount of  $\text{SO}_3$  content for up to its optimum limit (Joshi and Lohtia 1997). The amount in excess of the optimum limit could lead to lower ultimate strength due to internal sulphate attack. ASTM C 618 has limited maximum amount of  $\text{SO}_3$  as 5%.

#### **iii) Magnesium Oxide ( $\text{MgO}$ )**

Presence of magnesium oxide in the fly ash can form brucite and cause soundness problem in the concrete. ASTM C 618 has limited the maximum amount of  $\text{MgO}$  in fly ash as 5%.

#### **iv) Moisture**

Presence of moisture in the fly ash could lead to hardening of class C fly ash during transportation and storage due to its cementitious properties and can loose its fundamental properties before use. ASTM has limited maximum amount of moisture content in the fly ash as 3%.

#### **v) Carbon Content (Loss on Ignition)**

Carbon content can lead to carbonation of concrete and also can absorb air entraining admixture as a result more dose of air entraining admixtures may be needed than specified. Loss on Ignition (LOI) is a measure of carbon content. ASTM C 618 has limited the maximum amount of LOI as 6%.

#### **vi) Available Alkalis**

The available alkalis refer to those alkalis which are soluble in water and can contribute to concentration of pore solution. ASTM has limited the maximum amount of available alkalis as 1.5% for fly ash.

#### **C. Mineralogical Characteristics**

Petrographical studies have shown class C fly ash to have large amount of crystalline matter ranging from 25 to 45% and somewhat less glassy and amorphous material.



**Figure 2.2: Calcium rich fly ash particle; Source: Joshi and Lohtia 1996**

The crystalline phase could be in the form of anhydrite ( $\text{CaSO}_4$ ), tricalcium aluminate ( $3\text{CaOAl}_2\text{O}_3$ ), calcium sulfo-aluminate ( $\text{CaSAI}_2\text{O}_3$ ) and free lime ( $\text{CaO}$ ). The glassy phase which is believed to contain large amount of calcium makes the surface of class C fly ash highly strained (Figure 2.2). The strained surface is believed to make the fly ash more reactive (Joshi and Lohtia 1997).

As the fly ash particle size increases, the amount of crystalline silica ( $\text{SiO}_2$ ) in the ash increases and the proportion of calcium containing compound decreases. Therefore, large particle size of fly ash is less reactive.

Several studies carried out on the use of fly ash in cement concrete shows that the performance rate of class F fly ash in the aggressive environment is better and consistent (Sahmaran 2007, Thomas et al 1999, Al-Dulaijan 2003, Ramyar and Inan 2007). The reason of the efficacy of low calcium fly ash may be due to its pozzolanic reactivity. Calcium contents of fly ashes have great effect on reactivity (Mehta 1986). Fly ash with calcium content lower than 10% contains mainly aluminosilicate type glass (A-S). Aluminosilicate phase of fly ash reacts with calcium hydroxide (Skalny 2003) and consumes more amount of sulphate susceptible calcium hydroxide (Mindess et al 2003). However, inconsistent results have been reported in the case of incorporation of the high calcium fly ash in the cement (Tikalsky and Carrasquillo 1992, Freeman and Carrasquillo 1995, Freeman and Carrasquillo 1992, Freeman and Carrasquillo 1993).

The main factor behind the inconsistent result of high calcium fly ash is due its varied chemical and mineralogical composition (Mehta 1986, Tikalsky and Carrasquillo 1992, Freeman and Carrasquillo 1995, Freeman and Carrasquillo 1993); varied chemical and mineralogical composition as well as solubility of fly ash (Tishmack et al 2001). High calcium fly ash contains reactive calcium aluminosilicate glass (Thomas et al 1999, Mehta 1986, Tikalsky and Carrasquillo 1992, Freeman and Carrasquillo 1995) as well as cementitious crystalline compounds of calcium such as  $\text{C}_3\text{A}$ ,  $\text{C}_4\text{A}_3\text{S}$ ,  $\text{CS}$ ,  $\text{CaO}$  (Mehta 1986).



Such fly ashes produce more sulphate susceptible calcium aluminate hydrate (C-A-H) during hydration (Mehta 1986) and can not consume more calcium hydroxide due to its high calcium content (Mindess et al 2003).

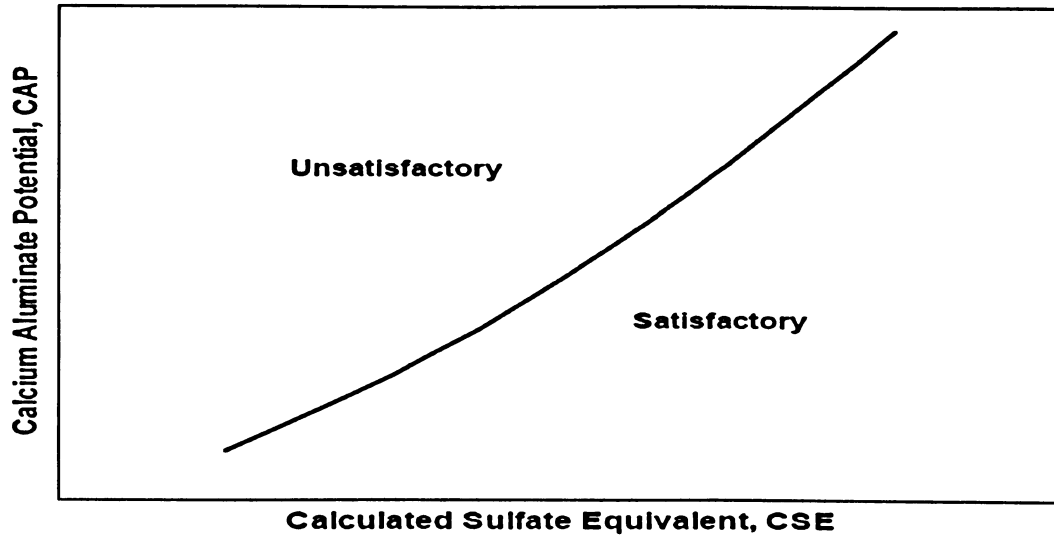
Although study on fly ash as a pozzolan or additive to cement started after David and his team in 1937 (Joshi and Lohtia 1997), its extensive study in the sulphate bearing environment started since 1973 after Bureau of Reclamation began research on use of subbituminous and lignite fly ash in concrete (Dunstan 1987). Before 1973, Bureau of Reclamation had carried out investigation only on the fly ashes produced from the Eastern States of USA which were derived from the bituminous coal and were low calcium fly ashes (Dunstan 1987). Based on the study the Bureau of Reclamation had stated “Fly ash increases the resistance of concrete to sulphate attack” (Dunstan 1987). But around 1973, many new power plants started to be built and operate in the western States which were using lignite and subbituminous coal as a fuel and had produced high calcium fly ashes. Sulphate resistances of some of fly ashes produced from those plants were very poor (Dunstan 1987). So the findings of the Bureau of Reclamation as “Fly ash increases the resistance of concrete to sulphate attack” were proved wrong with these new fly ashes. In 1978, Dunstan discovered an empirical relationship that could be used to describe sulphate resistance. This relationship was called the R-value (Resistance-value). The R-value had been calculated from the result of chemical analysis of the fly ash as:

$$R = (\%CaO - 5) / \%Fe_2O_3 \text{ -----(9)}$$

The constant value of 5 in the equation 9 had been estimated from the result of x-ray analysis of fly ash. From x-ray analysis Dunstan had deduced that around 5% calcium (an

average) of fly ash contains crystalline compound which doesn't contain alumina. The R-value indicates the level of sulphate resistance of fly ash as:  $R < 0.75$  greatly improved; 0.75 to 1.5 moderately improved; 1.5 to 3.0 no significant change and  $> 3.0$  resistance reduced.

Several studies carried out after Dunstan, indicate that R-value is not applicable for every fly ash especially for those which contain high calcium. According to a study result (Rosner et al. 1982), two of fly ashes performed well in the sulphate bearing environment despite their higher R-value as 2.71 and 5.30. Similar result was observed in another study (Mehta 1986). Study carried out on several subbituminous and lignitic Class C fly ashes and bituminous Class F fly ashes with replacement of 25% and 40% of Type I cement having 11% of  $C_3A$  showed that lignitic class C fly ashes with the R-value of 4 were excellent to satisfactory in sulphate resistance whereas the bituminous class F fly ashes with R-value between -0.01 and 1.1 were very poor to satisfactory in sulphate resistance. Principle alumina-bearing phases of class F fly ashes were non reactive mullite and A-S glass whereas N-C-A-S glass and  $C_4A_3\hat{S}$  were in class C fly ashes. Also class F fly ashes were lower in  $SO_3$  in comparison to class C fly ashes. Due to having lower in  $SO_3$ , most of the class F fly ashes produced sulphate susceptible monosulphate whereas class C fly ashes due to having higher  $SO_3$  produced stable ettringite during hydration. Mehta in his conclusion stated that it is neither R-value nor chemical composition but the mineralogical composition of cement-fly ash interaction product that controls the sulphate resistance. From the study, Mehta countered that Dunstan's R factor prediction was flawed because it did not take into account the crystalline form of reactive alumina in fly ash.



**Figure 2.3: Relationship between CAP and CSE Source: Bhatti and Taylor 2006**

Another study (Manz et al. 1987) also showed similar results. Concrete containing different types of fly ashes with R-values from 1.6 to 4.1 showed minimal expansion in the sulphate bearing environment. Based on the reactive components in the fly ash, Manz et al. proposed revised prediction parameters as calcium aluminate potential (CAP) and calculated sulphate equivalent (CSE).

The calcium aluminate potential is expressed as,  $CAP = (C^* + A^* + F^*) / S^*$

Where,

$C^*$  = Bulk CaO – Reactive crystalline CaO (lime, anhydrite,  $C_2S$ ) –inert crystalline CaO (melillite, merwinite)

$A^*$  = Bulk  $Al_2O_3$  – inert  $Al_2O_3$  (mullite)

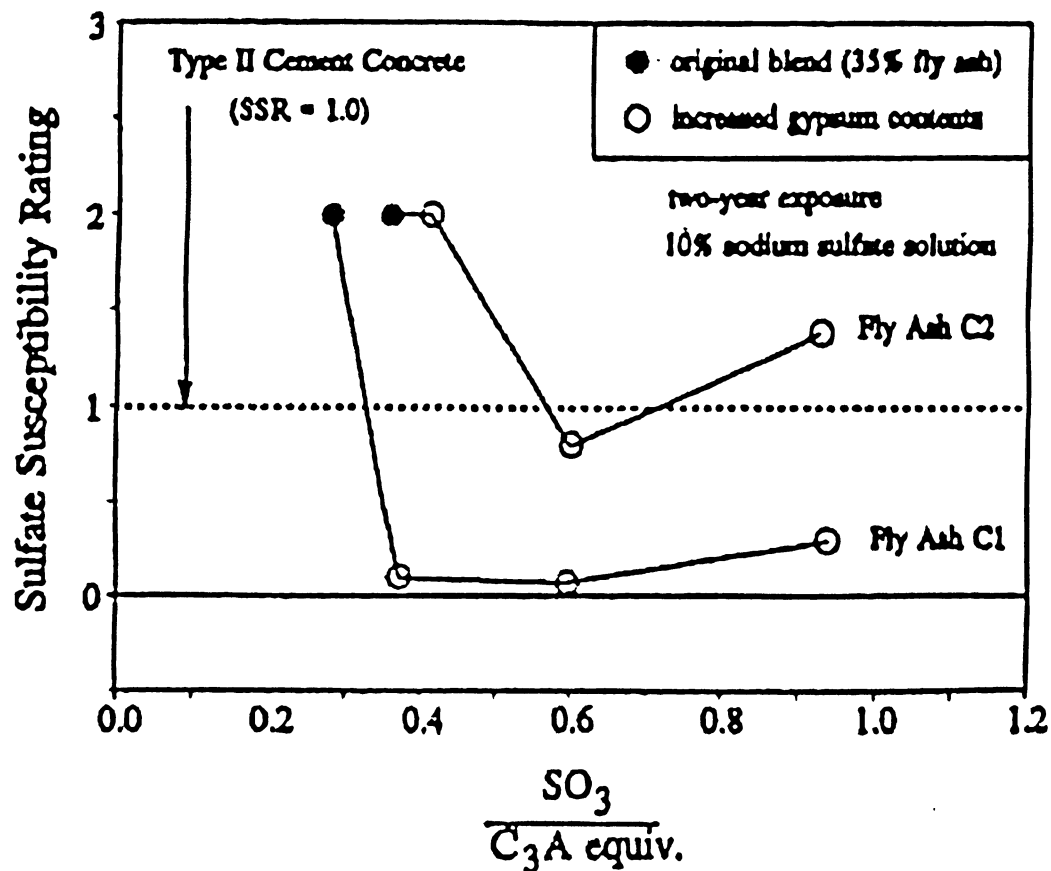
$F^*$  = Bulk  $Fe_2O_3$  – inert crystalline  $Al_2O_3$  (hematite, spinel)

$S^*$  = Bulk  $SiO_2$  – inert crystalline  $SiO_2$  (quartz, mullite)

CAP considers the glassy calcium, aluminate, and iron as detrimental to sulfate resistance and, glassy silica as beneficial to sulfate resistance. CAP factor subtracts the inert crystalline compounds and the crystalline compounds that do not take part in sulfate expansion reaction.

The calculated sulphate equivalent is expressed as,  $CSE = Anhydrite + 1.7\hat{S}$

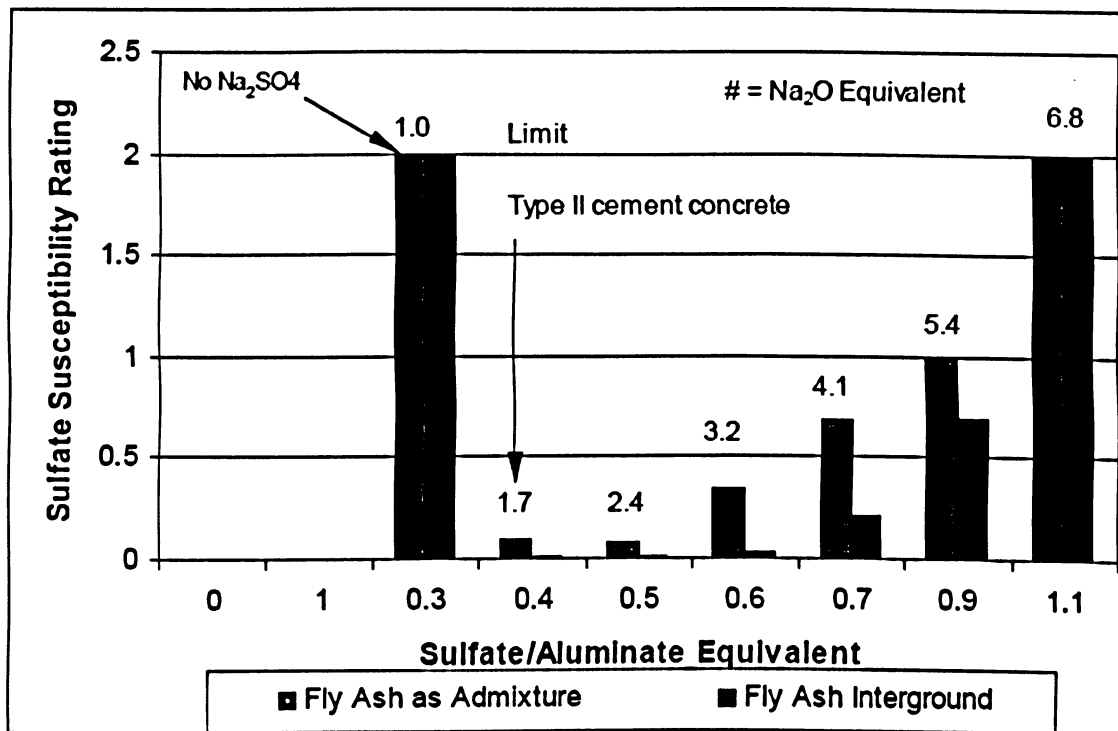
Where,  $\hat{S}$  is the sulphur trioxide present in the fly ash which is considered to be desirable for forming early ettringite. The factor 1.7 accounts for the formation of additional anhydrite from other sulfate sources in the fly ash. The proposed relationship between CAP and CSE in terms of sulfate resistance of concrete is shown in Figure 2.3.



**Figure 2.4: Susceptibility of hardened concrete to sulphate attack**  
**Source: Freeman and Carrasquillo 1995**

In a bid to explore new possibilities, Freeman and Carrasquillo came up with a new concept of gypsum and alumina balancing approach in fly ash/cement system in 1995. In a study, Freeman and Carrasquillo were succeeded in achieving sulphate resistance with the incorporation of non-sulphate resistant high calcium fly ash in type II cement by creating balance between sulphur and alumina with the addition of gypsum.

Several number of mortar bars were prepared varying amount of sulphate with addition of gypsum in the cement.



**Figure 2.5: Sulphate susceptibility of hardened concrete to sulphate attack with  $\text{Na}_2\text{SO}_4$  as a source of  $\text{SO}_3$  Source: Freeman and Carrasquillo (1995b)**

A sulphate susceptibility rating (SSR) was developed as the ratio of 'percentage of liner expansion of mixture to percentage of cement without fly ash'. Value of SSR ( $>1$ ) was the

indication of poorer quality of sulphate resistance and value of SSR ( $<1$ ) was the indication of improved quality of sulphate resistance of mix against the cement without mix. Sulphate to equivalent alumina content ratio ( $\text{SO}_3/\text{C}_3\text{A}$  equivalent) was calculated for the different mixes. A graph plotted using 'sulphate to equivalent alumina content ratio against SSR showed that blended cement having ratio of  $\text{SO}_3/\text{C}_3\text{A}$  equivalent, in the range of 0.35 to 0.60 provided the better sulphate resistant (Figure 2.4). The concept was to consume the calcium aluminate by providing sufficient sulphate ion during hydration.

Another study carried out by the same authors Freeman and Carrasquillo (1995b), adding sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) in the mixing water as source of  $\text{SO}_3$  instead of addition of gypsum also showed the similar trend (Figure 2.5). Fly ash in this test was introduced, however, by two different methods: as an admixture and as an intergrinding. Out of two methods, interground fly ash had provided better sulphate resistance. The better result of interground fly ash was due to the result of granulometric change which resulted in fly ash reactivity by increasing the fly ash surface area exposure and closer proximities of fly ash and cement particles (Freeman and Carrasquillo SP 1995).

In another study, Wu and Naik 2002 were successful in achieving sulphate resistance with incorporation of high sulphate coal ash in high calcium fly ash. The latest studies (Carrasquillo and freeman 1995, Carrasquillo and freeman 1995a, Wu and Naik 2002) give the clear picture that sulphur trioxide ( $\text{SO}_3$ ) of the high calcium fly ash plays equal role as the CaO and reactive aluminosilicate phase in sulphate resistance of the fly ash.

A latest study (Ramayer and Inan 2007) carried out using three types of Portland cement with varied amount of  $\text{C}_3\text{A}$  as 11.39%, 7.73% and 5.48% with replacement of low calcium fly ash

shows sulphate resistance to be depending upon not only  $C_3A$  content but  $C_3S/C_2S$  ratio, concentration of solution and fly ash percentage as well. The study showed the interesting results. Cement having a moderate  $C_3A$  content of 7.73% and a  $C_3S/C_2S$  ratio of 4.38 showed larger sulfate expansion values than PC1 with 11.39%  $C_3A$  content and a  $C_3S/C_2S$  ratio of 3.58. However, the positive effects of lower  $C_3A$  content and lower  $C_3S/CH_2S$  ratio of cement were clearly observed in the expansion value of cement containing 5.48%  $C_3A$ . A mathematical expression was developed to estimate the sulfate susceptibility of cements regarding their  $C_3A$  content,  $C_3S/C_2S$  ratio, mineral additive content as well as concentration of sulfate solution.

$$E = \frac{A^{-0.1277} S^{0.3955} C^{0.5698}}{(100 + K)^{1.0631}} \text{-----} (10)$$

where, E is the 15-week expansion upon exposure to sulfate solution (%), A the  $C_3A$  content of cementitious system (%), S the  $C_3S/C_2S$  ratio of the cement, C the concentration of sodium sulfate solution (%), and K the mineral admixture substitution level (%). The estimated values were in good agreement with the experimental values obtained in this study or reported by other researcher.

Although the test provided good prediction, the fly ash used in the test was low calcium fly ash. Most of the low calcium fly ashes have been found to be sulphate resistant according to many authors. The authors (Ramayer and Inan 2007) did not test the validity of the equation for the high calcium fly ashes, the very ashes which have been proved to be more unpredictable in its behavior than that of low calcium fly ash.

#### **2.1.2.3.2 Silica Fume**

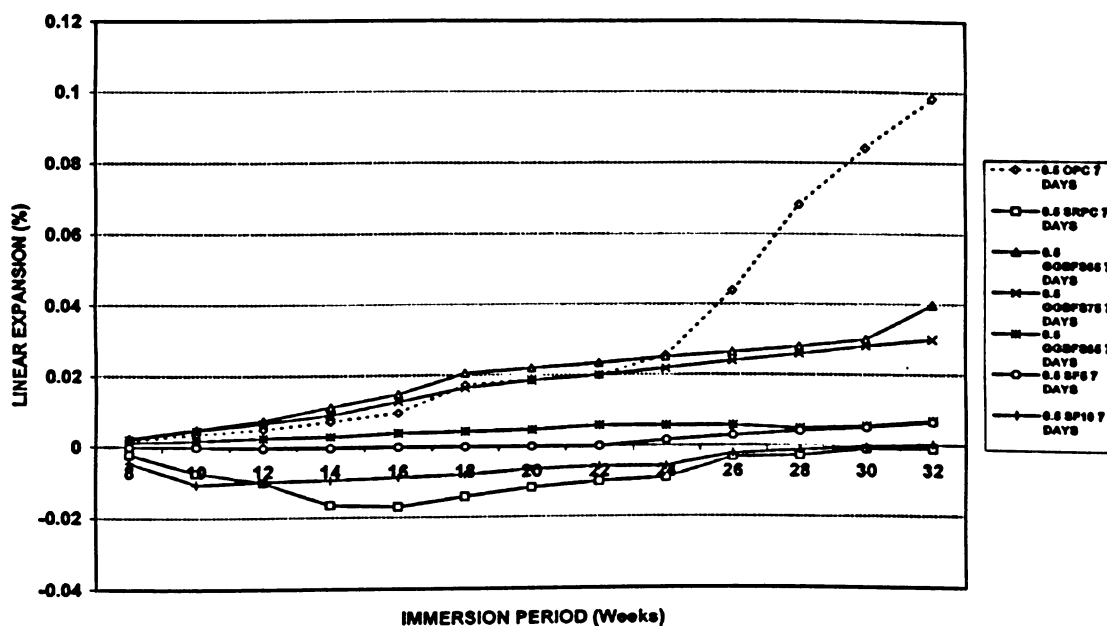
Silica fume is a co-product of the silicon and ferrosilicon metal industry. It is an amorphous silicon dioxide ( $\text{SiO}_2$ ) which is generated as a gas in submerged electrical arc furnaces during the reduction of very pure quartz. This gas vapor is condensed in bag house collectors as very fine gray to off-white powder of spherical particles that average 0.1 to 0.3 microns in diameter (approximately 1/100th the size of an average cement particle) with a surface area of 17 to 30  $\text{m}^2/\text{g}$ . Because of its fine particles, large surface area, and the high  $\text{SiO}_2$  content, silica fume is a very reactive pozzolan when used in concrete. The quality of silica fume is specified by ASTM C 1240 and AASHTO M 307. Silica fume is used in a variety of cementitious (concrete, grouts and mortars), elastomer, polymer, refractory and ceramic applications (Source: Silica fume association).

The one of the main bottlenecks appeared in use of silica fume in the cement concrete application is due to its higher water demand. The higher fineness of the silica fume is attributed to the increased water demand and hindered workability (Carette and Malhotra 1983). Although the potential for use of silica fume in concrete was known in the late 1940s, the material became widely used only after the development of powerful dispersants known as high-range water reducing admixtures or super-plasticizers (Source: Silica Fume Association).

Extensive studies, although not as much as of fly ash, have been carried out for use of silica fume in the concrete in the sulphate bearing environment. Almost all of the study results have shown the silica fume to be efficient in the sodium sulphate bearing environment. Increased sulphate resistance of silica fume is attributed to be the reduced permeability



(Hooton 1993, Al-Dulaijan et al. 2003, Khatri et al 1997); reduced size of pores and total porosity of both cement pastes and concrete, and reduced leachable calcium hydroxide contents of cement pastes which was zero in some cases zero (Hooton 1993). Formation of secondary C-S-H as a result of pozzolanic reaction of silica fume and CH is attributed to the reduced permeability (Al-Dulaijan et al. 2003, Wee et al 2000). Dilution of C<sub>3</sub>A content due to the overall reduction of cement in concrete is another cause of sulphate resistance of silica fume replacement (Al-Dulaijan et al. 2003). Filler action due to the finer particle size of SF (0.1 to 0.2  $\mu\text{m}$ ) further densifies the pore structure to enhance the resistance to sulfate attack (Wee et al 2000).



**Figure 2.6: Linear expansion of concrete mixtures of 0.50 w/b and moist cured for 7 days** Source: Wee et al 2000

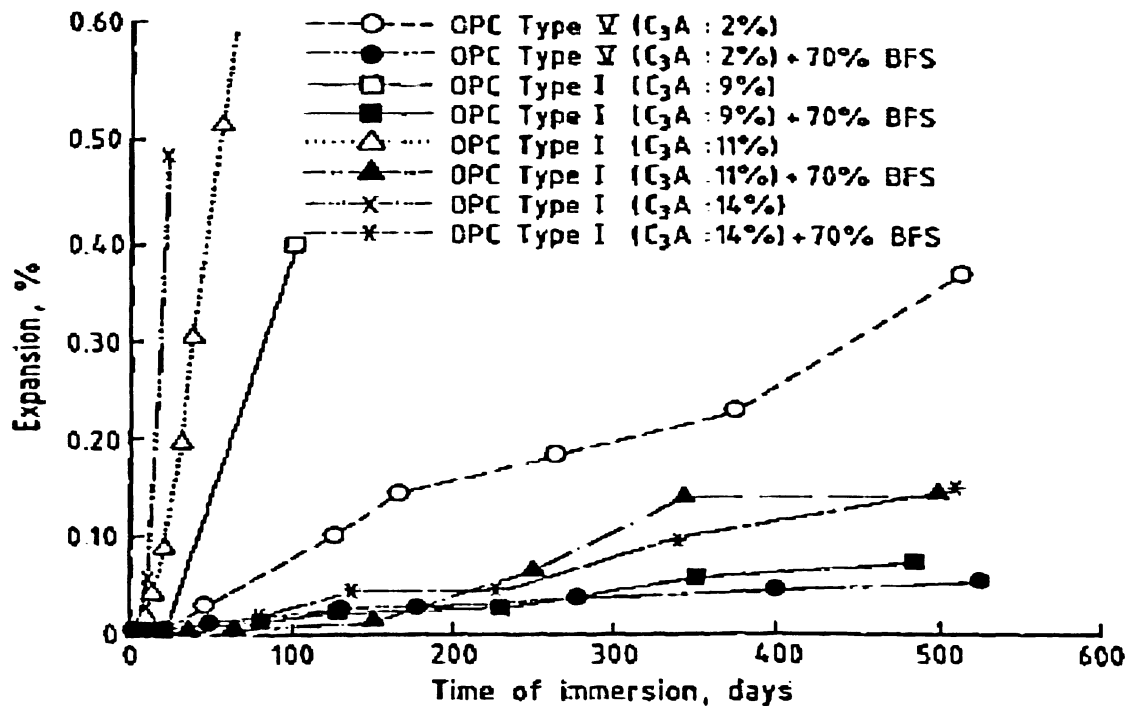
The addition of silica fume reduces the permeability of the transition zone around the aggregate particles as well as the permeability of the bulk paste (Khayat and Aitcin 1992) of silica fume. Influence of silica fume upon permeability of concrete is very large. A 5%

content of silica fume has been reported to reduce the coefficient of permeability of concrete by 3 orders of magnitude (Khayat and Aitcin 1992). However, curing is equally important to get full potential of the silica fume. A study result (Khan and Ayers 1995) shows the curing period of minimum of 3 days to be effective for silica fume blended cement. Effectiveness of silica fume in sulphate resistance has been found to depending upon it replacing level. A study (Hooton 1993) had resulted better sulphate resistance at the replacement level of 10% as per ASTM C 1012 test. Another study (Wee et al 2000), had shown better sulphate resistance at the replacement level of 5 to 10% (Figure 2.6).

The result of Wee et al 2000 had shown the sulphate resistance of silica fume concrete to be independent of the water cement ratio and curing period beyond 3 days. Another study carried out by Lee et al 2000 had also shown the similar trend. Better sulphate resistance was achieved at the replacement level of 5 to 10%.

#### **2.1.2.3.3 Granulated Ground Blast Furnace Slag (GGBFS)**

Ground granulated blast-furnace slag is the granular material formed when molten iron blast furnace slag is rapidly chilled (quenched) by immersion in water. It is a granular product with very limited crystal formation, is highly cementitious in nature and, ground to cement fineness, hydrates like portland cement (Source: FHWA). Although portland blast furnace slag cement, which is made by intergrinding the granulated slag with portland cement clinker (blended cement), has been used for more than 60 years, the use of separately ground slag combined with portland cement at the mixer as a mineral admixture did not start until the late 1970s (Source: FHWA).



**Figure 2.7: Expansion of mortar bars containing different amount of C<sub>3</sub>A and GGBFS; Source: Al-Gahtani et al 1994**

Use of slag or slag cements usually improves workability and decreases the water demand due to the increase in paste volume caused by the lower relative density of slag (Hinczak 1990). The higher strength potential of Grade 120 slag may allow for a reduction of total cementitious material. In such cases, further reductions in water demand may be possible (source: Transportation Research Board).

Several studies carried out on GGBFS show that GGBFS is effective in combating sulphate attack at the higher replacement level (Geissler et al 1995, Wee et al 2000, Al-Gahtani et al 1994, ACI Manual 1991, Osborne 1991). The effectiveness of GGBFS in sulphate bearing environment could be due to: i) GGBFS is glassy in nature and thus reacts with  $\text{Ca(OH)}_2$  in

hydrated cement paste. Higher levels of cement replacement by slag (over 60%) appear to be more effective as the consumption of  $\text{Ca}(\text{OH})_2$  becomes more pronounced (Wong and Poole 1988) ii) Reduction of permeability of the concrete. Test on mortar containing GGBFS has shown that its water permeability is reduced by a percentage of up to 100% (Neville 1996) iii) The denser microstructure of hydrated cement paste due to more of the pore space being filled with C-S-H than in Portland cement paste only (Neville 1996) iv) Reduction of amount of  $\text{C}_3\text{A}$  in cement (Skalny 2003) which is also termed as dilution effect.

A study (Al-Gahtani et al 1994) carried out on GGBFS with cement containing three different content of  $\text{C}_3\text{A}$  (9%, 11% and 14%) and replacement level of 50%, 60%, 70% and 80% shows that the GGBFS to be sulphate resistant at the replacement level of above 70% irrespective of variation in  $\text{C}_3\text{A}$  content (Figure 2.7). However, the cement with high  $\text{C}_3\text{S}/\text{C}_2\text{S}$  ratio has a perceptible adverse-interactive effect and causes sulfate deterioration even with low- $\text{C}_3\text{A}$  sulfate-resistant cement (Al-Gahtani et al 1994). Osborne 1991 studied several blends of cements with GGBFS with respect to sulfate resistance and compressive strength development in concrete. The relative effects of  $\text{Al}_2\text{O}_3$  in slag and  $\text{C}_3\text{A}$  in cements were also investigated. It was noted that a 70% replacement by slag having low/medium  $\text{Al}_2\text{O}_3$  (7.5% to 11.5%) in cement with medium  $\text{C}_3\text{A}$  (9%) produced concrete with good sulfate resistant properties. According to Gallop and Taylor 1999,  $\text{Al}_2\text{O}_3$  will be in short supply in GGBFS concrete as the aluminum ions ( $\text{Al}^{3+}$ ) enter the C-S-H lattice by substituting  $\text{Ca}^{2+}$ , and once again the  $\text{Al}^{3+}$  entering the gel lattice will not be available for ettringite formation. Gallop and Taylor 1999 also showed that the higher the  $\text{Al}_2\text{O}_3$  content in GGBFS, the lower will be the calcium/silica ( $\text{Ca}/\text{Si}$ ) ratio. The  $\text{Al}^{3+}$  is smaller in radius than the  $\text{Ca}^{2+}$ , and hence, from the

view of lattice stability,  $\text{Al}^{3+}$  is preferentially accommodated into the C-S-H lattice by replacing  $\text{Ca}^{2+}$ .

Geiseler et al 1995 had tested the effectiveness of GGBFS from both laboratory-scale work and long term experience in practice and had found that the GGBFS to be higher resistant against sulphate attack. Experimental study of Wee et al 2000 had produced some interesting results. Study was carried out on three different types GGBFS with fineness of 4500, 6000, and 8000  $\text{cm}^2/\text{g}$ ; water-binder ratio (w/b) of 0.40 and 0.50 and moist curing period of 3, 7, and 28 days. Concrete prisms were immersed in a 5% sodium sulfate solution for 32 weeks and periodically monitored for the change in flexural strength and linear expansion. The results demonstrated the resistance of GGBFS concrete to be a complex function of w/b and proportion of GGBFS in the mixture. The 65% GGBFS mixture of 0.50 w/b, moist cured for 7 and 28 days, showed initial signs of deterioration. The same mixture with a lower w/b (0.40) and even with a shorter moist curing period (3 days), however, indicated superior resistance to sulfate attack. The concrete mixtures incorporated with greater proportion of GGBFS i.e., 75 and 85%, however, showed greater resistance to sulfate attack, irrespective of w/b (0.40 and 0.50) and moist curing period (3, 7, and 28 days). Further, for a given proportion of GGBFS (65%), there was no consistent trend between the extent of deterioration and the fineness of GGBFS. Wee et al 2000 attributed the higher sulfate resistance of concrete mixtures with GGBFS to the generation of discontinuous pore structure, which was partly ascribable to a net reduction in portlandite content caused by strong pozzolanic reaction.

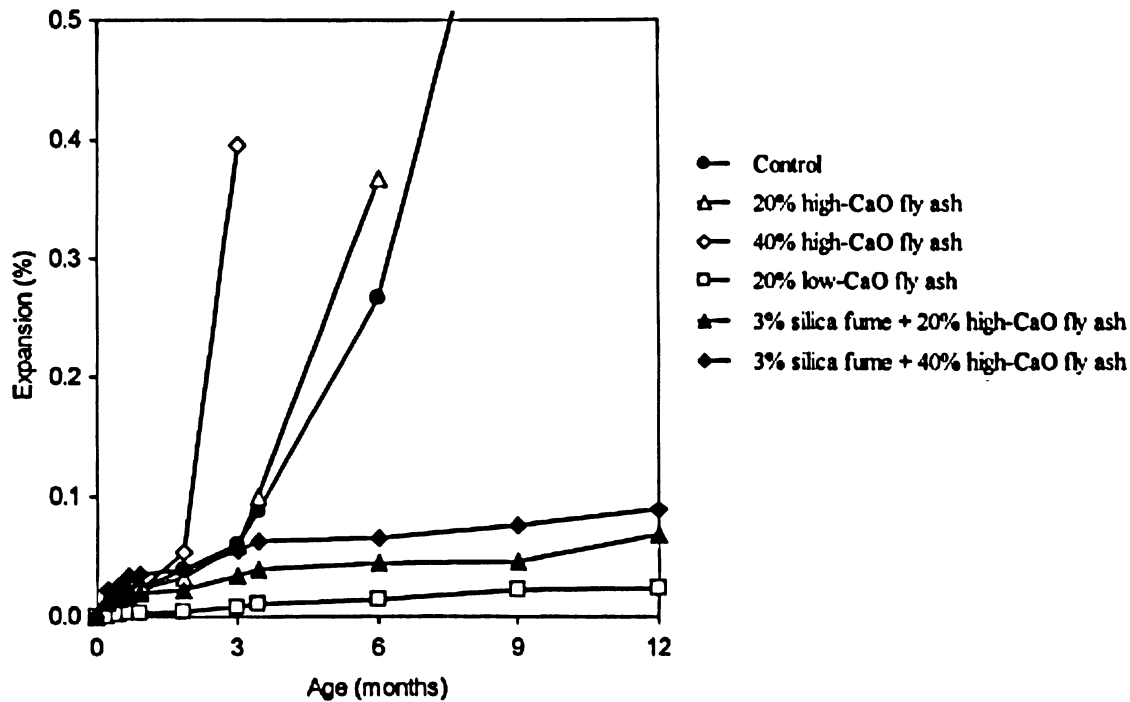
Wee et al 2000 further suggested that the sulfate resistance of GGBFS concrete is not attributed to one factor alone, but due to a combination of factors such as the degree of pore refinement, reduced free portlandite (or lower  $\text{Ca}^{2+}$ ) content,  $w/b$ , proportion of GGBFS, and also the extent of preferential intake of  $\text{Al}_2\text{O}_3$  by the C-S-H gel.

#### **2.1.2.3.4 Ternary blend**

There exist very few records regarding the study of ternary blend in sulphate bearing environment. Binici and Aksogan 2006 had carried out study on blended cement prepared with ternary blend of GGBFS and natural pozzolan at the varied replacement level and had achieved the better sulphate resistance of the blend than general use cement as a reference material. Another study carried out by Shamaran et al 2007 using the ternary blend of natural pozzolan and low calcium fly ash (CaO content of 4.71%) had shown the superior performance in comparison to the blend containing only natural pozzolan. 52 week's expansion results were 0.168%, 0.149%, 0.048% and 0.051% for sulphate resistant Portland cement, cement blended with natural pozzolan of 30.2%, cement blended with low calcium fly ash of 31.8% and blend of cement containing natural pozzolan of 15.3% and fly ash of 20.9% respectively. The blend was found to be even better than sulphate resistant Portland cement.

Study result of Thomas et al 1999 on ternary blend of cement containing silica fume and high calcium fly ash had yielded interesting results. 3% of silica fume was added to each 20 % and 40% of high calcium ash. The high calcium fly ash had performed even worse than control sample prepared with type-10 general use cement. Interestingly, just with the incorporation

of 3% silica fume in the high calcium fly ash, the blend performed well. The expansion reduced significantly and remained well below the prescribed ASTM limit of 0.1% for high sulphate resistant concrete (Figure 2.8).



**Figure 2.8: Effect of silica fume and fly ash on sulphate resistance, Source: Thomas et al 1999**

The author (Thomas et al 1999) ascribes the possible reason of the sulphate resistance of the ternary system as: i) Increased availability of silica results in the formation of more stable calcium-alumino-silicates. ii) The pore structure refinements and increased resistance to the penetration of sulphates.

## **2.2 Alkali Silica Reaction (ASR)**

Alkali-Silica Reaction (ASR) is a reaction between the alkaline pore solution and some types of aggregates that contain poorly crystallized silica. The reaction results in the formation of ASR gel, which upon absorption of water gets expanded. ASR was first identified by Stanton from investigation of cracking in concrete pavements and bridges in 1940 (Stanton 1940). The main effects of ASR are swelling, cracking, and reduction in the mechanical properties of affected concrete (Poyet et al 2006). The damage in ASR starts right from aggregate, propagates gradually outwards and reflects on the surface. Literature reviews on ASR show that ASR depends upon:

- i) Concentration of soluble (available) alkali in the cementing system
- ii) Amount of reactive silica available in the aggregate (aggregate that contains opaline silica as a mineral, occurring as primary or secondary materials, are highly reactive; aggregate that contains chalcedony as a mineral are moderately reactive such as cherts and flints; and aggregate that contains volcanic glass are reactive in some cases such as basalt and rhyolites (Swamy 2003)
- iii) Presence of moisture in the hardened concrete

### **2.2.1 Prevention of ASR**

As the ASR depends upon the above three factors, elimination or minimization of one or more of the above factor can minimize or prevent the ASR.

- i) Soluble alkali ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) can not be eliminated completely from the cement produced from the modern cement plant. In modern cement plants, raw materials are preheated by the hot gases leaving the upper end of kiln (Neville 2006). These gases contain



a significant proportion of the volatile alkalis which ultimately contributes in raising alkalinity in the cement. However, by bleeding off a part of the gases, the alkali content can be controlled (Neville 2006). A low alkali cement with upper limit of 0.60 percent of sodium oxide equivalent ( $\text{Na}_2\text{O} + 0.658\text{K}_2\text{O}$ ) has been standardized and used in the USA for nearly 50 years in the cement to minimize the risk of ASR (Neville 2006) ii) ASR can be prevented by avoidance of use of aggregate containing reactive silica. However, in many instances, due to economical point of view, it is unfeasible to discard such alkali sensitive aggregates. iii) Presence of moisture or free availability of the moisture in the concrete can be controlled by reducing the permeability of the concrete. Use of low water to cementitious materials and use of certain types of SCM namely silica fume can reduce the permeability of the concrete. According to Naville (Naville 2006), if the concrete is thoroughly dried, ASR will stop: there will be no reversal of reaction, but no further damage will occur until re-wetting takes place. Not every ASR is damaging. Sometimes, no more than exudation of alkali-silica gel occurs, and this is only of aesthetic interest, which may or may not be significant. If the gel, which is of the 'unlimited swelling' type is confined by the surrounding hydrated cement paste, internal pressure may arise and may be disruptive. ASR doesn't go forever: if either reactant (silica or alkalis) runs out, the reaction obviously stop. Without excessive alkali content in the mix, ASR will not occur, but the calculated values of the alkali content should not be treated as absolute boundaries.

According to Hobbs 1981, minimum level of available alkalinity in the pore solution should be of  $3.4 \text{ Kg/m}^3$  of acid soluble alkali or  $2.5 \text{ Kg/m}^3$  of water soluble alkali for ASR to occur. It infers that if the reactive siliceous aggregate is present in the concrete, it reacts with the alkaline pore solution of cement paste only when the concentration of pore solution is more

than  $3.4 \text{ kg/m}^3$  of acid soluble alkali. As the reaction proceeds, the alkalinity of the pore solution decreases due to formation of ASR gel. To create the equilibrium between the alkalinity of the pore solution and the hydration product, alkali gets released from the hydration product. Eventually, the reaction ceases when its alkalinity in both hydration product and the pore solution reaches to  $3.4 \text{ Kg/m}^3$ . A study (Rasheeduzzafar and Hussain 1991) however, has proposed the limiting value of alkalinity of  $400 \text{ mM/l}$  for the system containing SCMs.

Like in controlling sulphate attack, literature reviews show that SCMs are found to be effective in controlling ASR. But due to presence of variations in chemical and mineralogical composition and distinct alkali release characteristics, each SCM imparts specific role in controlling ASR. According to Hobbs (Hobbs 1988), fly ash contributes 17% (one sixth), GGBFS 50%, and silica fume 100% of its total  $\text{Na}_2\text{O}_e$  to the pore solution which is nearly in good agreement with the proposed revision of Appendix B of the Canadian CSA A23.1 and A 23.2 standards as 15 % of total  $\text{Na}_2\text{O}_e$  for fly ash, 50% for both GGBFS and silica fume (Duchense and Berube 1994). But the experimental results of studies (Shehata and Thomas 2006, Duchense and Berube 1994) do not agree with the above estimate for the some fly ashes which have been found to release more alkali in the pore solution than the suggested level.

The Role of each SCM in controlling ASR is covered in the coming subsection.

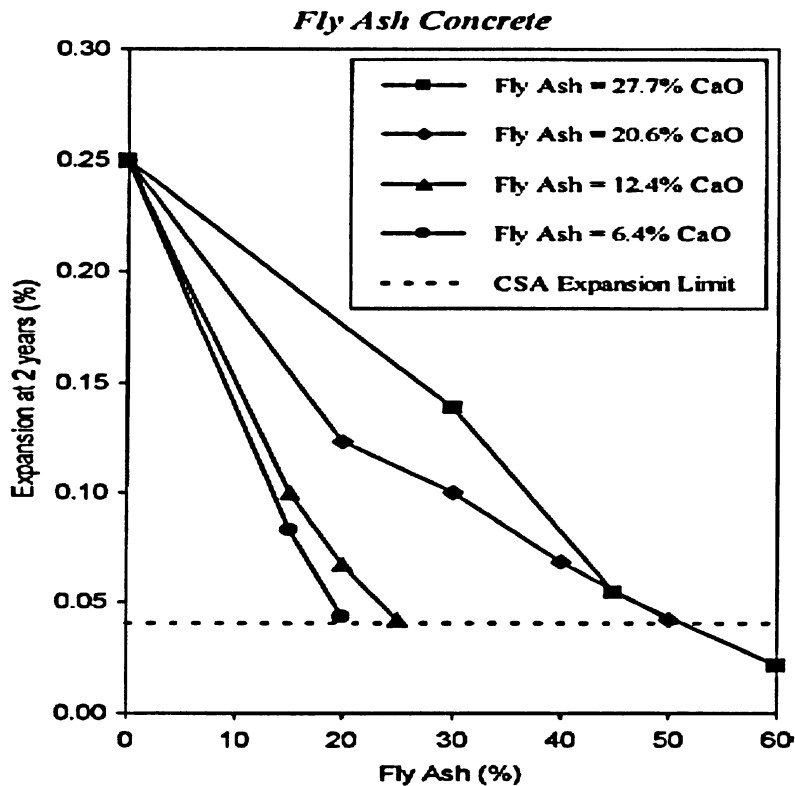
### **2.2.1.1 Fly Ash**

Experimental results elsewhere show that low calcium fly ash is effective in suppressing ASR. The main reason behind the effectiveness of such fly ash is due its higher alkali binding capacity (Shehata and Thomas 2006); reduction of the alkalinity in the pore solution

due to incorporation of more alkalis in the secondary C-S-H gel or negative alkalis contribution ( Duchense and Berbube 1994 II, Duchense and Berube 1994); retardation of transportation of  $\text{Na}^+$  and  $\text{K}^+$  ion towards aggregate due to formation of acidic matrix with a incorporation of fly ash (Chunxiang et al 1994). However, excessive alkali content (a higher SCM alkali content, and a higher overall concrete alkali content) may render the SCM totally ineffective (Duchense and Berbube 1994 II).

Experimental results from several authors show that use of high calcium fly ash is not effective in mitigating ASR, specially, at the lower replacement level. The reason for the lower efficiency of the class C fly ash is likely due the greater portion of the silica in the fly ash that is tied up by lime, lowering the amount of silica available to control the alkali-silica reaction (Mindess et al 2003).

According to study report of Electric Power Research Institute (EPRI), amount of high calcium fly ash required to control expansion varies significantly from one aggregate to another. In the case of extremely reactive aggregate, class C fly ash (CaO of 22.5% and  $\text{Na}_2\text{O}_{\text{eq}}$  of 2.3%) of 50% to 60% would be required to reduce expansion under 0.10%. An experiment (Thomas et al 1999) also shows the similar result. An experiment carried out using reactive siliceous limestone (Spratt), high alkali cement with alkalinity raised to 1.25%  $\text{Na}_2\text{O}_{\text{e}}$ , fly ashes with varied CaO content and equivalent alkalinity less than 3% shows the expansion of less than 0.04% for fly ash containing CaO of 27.7 % with replacement level of 60% (Figure 2.9).



**Figure 2.9: Effect of fly ash calcium content on expansion due to ASR Source: Thomas et al 1999**

#### **2.2.1.2 Silica fume**

Study results show that silica fume is efficient in controlling ASR. The main reason behind the efficacy of silica fume is due to reduced calcium hydroxide contents of cement paste and pore refinement as an pozzolanic reaction (Rasheeduzzafar and Hussain 1991, Hooton 1993); reduced available alkalis in pore solution (Hooton 1993, Duchense and Berbube 1994 II); formation of non-reactive ASR gel due to rapid reaction at the early age (Mnidess et al 2003). Addition of 20% of micro silica sweeps virtually all the hydroxide ions from the pore solution (Rasheeduzzafar and Hussain 1991). However, to get the full potential of the silica fume in controlling ASR, its quantity should be sufficient in a mix. Efficiency of silica fume gets reduced with the reduction in the replacement level particularly with the replacement

level of lower than 10% (Duchense and Berbube 1994 I, Mindess et al 2003, Hasparyk et al 2000). An experimental result (Gudmundsson and Olafsson 1999) shows that the silica fume to be used in the cement should be free from lumps otherwise the lump could serve as a weak point to form ASR gel around it thereby making the concrete more prone to ASR.

#### **2.2.1.3 Granulated Ground Blast Furnace Slag (GGBFS)**

Review of literature showed that GGBFS is efficient in controlling ASR but at replacement levels higher than those for low-calcium fly ash. Rasheeduzzafar and Hussain 1991 had succeeded to reduce expansion with the use of 60-70% GGBFS in cement of  $\text{Na}_2\text{O}_e$  of 0.65% with Pyrex glass No. 7740 aggregate confirming to ASTM C441 specification. They had ascertained the performance of 60% slag cement is comparable with that of 10% of microsilica cement at the medium alkali cement. However, the effectiveness of slag was found to be decreasing with the increase in the alkali content of cement. Duchense and Berbube (1993 I) had succeeded to keep expansion limit well below 0.04% with the use of GGBFS of 35-50% with cement of 0.74%  $\text{Na}_2\text{O}_e$  with reactive Spratt aggregate. Experimental result of another study (Thomas and Innis 1998) on four alkali-silica reactive aggregate (Siliceous limestone, sandstone, greywake and granite) showed that minimum level of GGBFS required to control expansion to an acceptable level (0.04% in 2 years) varied depending on the nature of aggregate and the amount of alkali present in the concrete. In their study, GGBFS replacement level ranging from 25% to 65% was found to be effective in retarding the rate of expansion. Another study (Malvar et al. 2002) had recommended 40-50% of GGBFS in controlling the ASR. A study by Hester et al. 2005 had shown 50% of replacement of GGBFS to be effective in controlling ASR irrespective of aggregate type or

alkali load, indicating that the alkali level of slag is not a contributory factor at the 50% replacement level. Similar effect was observed in another experiment (Higgins and Connell 2005) at the higher level of replacement of GGBFS. The efficacy of GGBFS was attributed to the dilution effect as well as the stabilization and immobilization of alkalis.

#### **2.2.1.4 Ternary blend**

It is unpractical and unfeasible in the most cases to use more than 50% of high-calcium fly ashes to make it ASR resistant. The problem of high level of replacement can be offset with introduction of certain amount of silica fume in the fly ash cement blend. A study report (Thomas et al 1999) shows that ternary blend of 25% high calcium fly ash and 5% silica fume was successful in keeping the two year's expansion well below the CSA limit of 0.04% with highly reactive Spratt aggregate and high alkaline cement (Figure 2.10).

The possible reason behind the effectiveness of ternary blend in controlling ASR is outlined below.

##### **i) Ability of silica fume and fly ash to bind alkali**

An experimental result (Shehata and Thomas 2002) shows that silica fume has the high capacity to bind alkali at the early age of hydration while the fly ash becomes active in binding alkali at the later age. In silica fume and fly ash incorporated concrete system, silica binds the alkali at the early age of hydration but it can no longer bind much alkali at the later age. But at the later age fly ash becomes active and binds alkali and prevents alkalinity rising in the pore solution. The combined action of silica fume and fly ash has been found very much effective in controlling expansion (Figure 2.11).

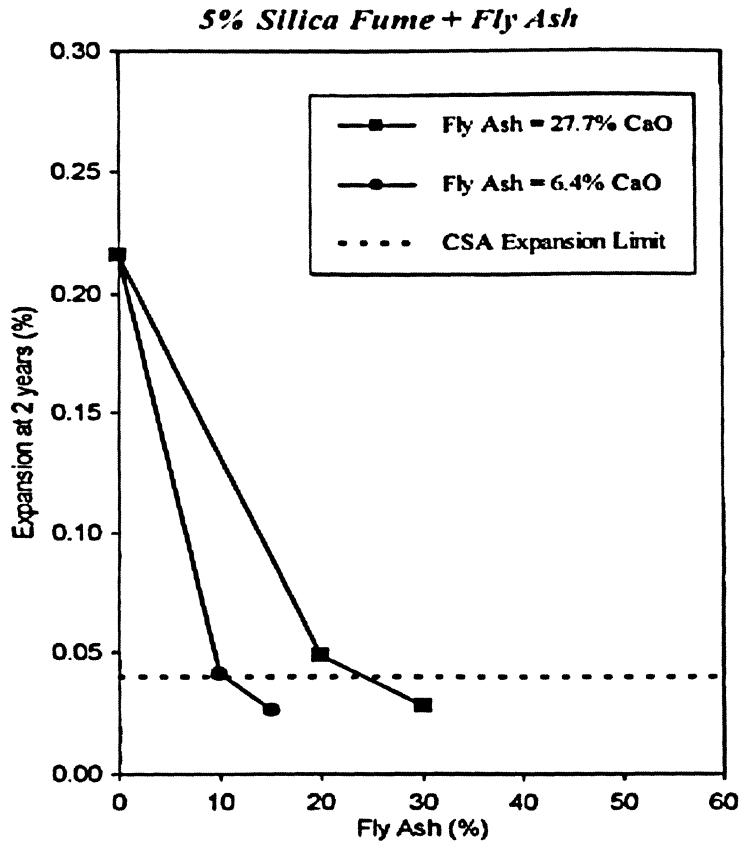


Figure 2.10: Effect of silica fume and fly ash on expansion due to ASR Source: Thomas et al 1999

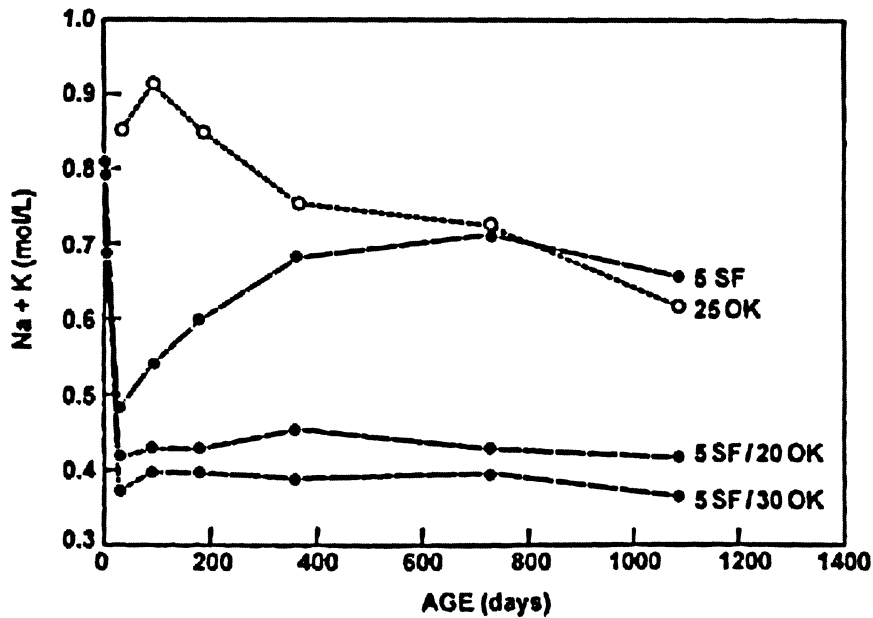


Figure 2.11: Effect of silica fume (SF) and fly ash (OK) on pore solution alkalinity Source: Shehata and Thomas 2002

Reduction in expansion due to combined effect has been found to be far better than the sum of reduction by individual silica fume and fly ash. Shehata and Thomas, 2002, 2006 have termed this enhanced effect as synergic effect.

ii) A study on the alkali release characteristics of various commercially available fly ashes (Shehata and Thomas 2006) has established a correlation between  $\text{Na}_2\text{O}_e$ ,  $\text{CaO}$  and  $\text{SiO}_2$  as a governing factor for the concentration of available alkali in the pore solution.

Available alkali in the pore solution is proportional to  $\text{Na}_2\text{O}_e \cdot \text{CaO} / \text{SiO}_2$  (Figure 2.12). So as per above correlation, addition silica fume in the fly ash cement blend means to reduce the concentration of available alkali in the pore solution.

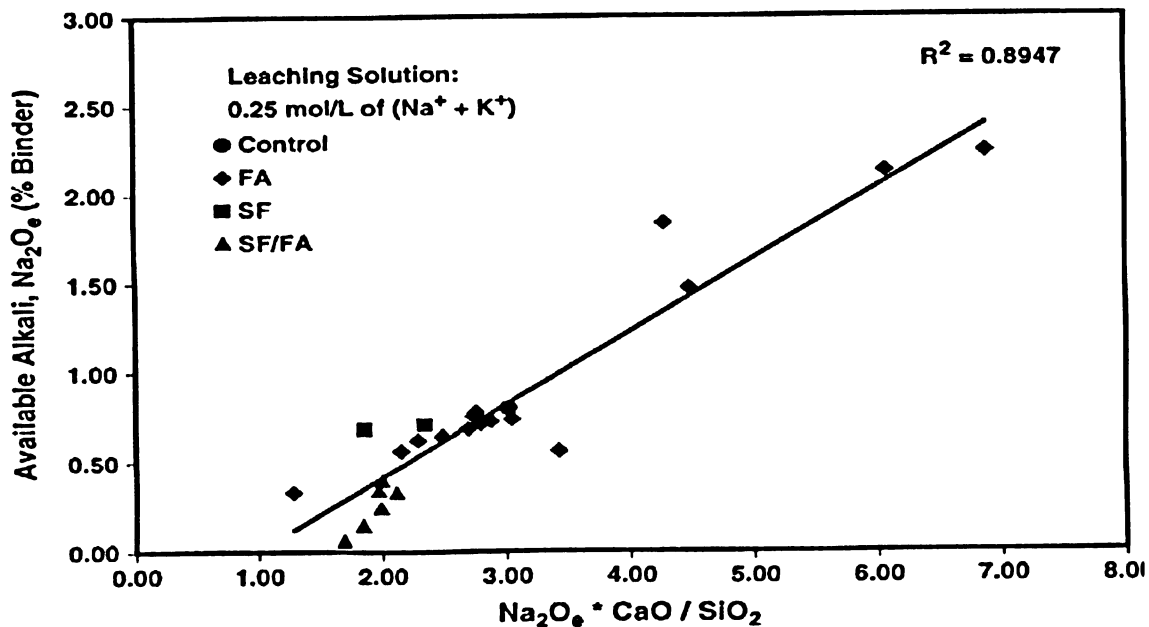


Figure 2.12: Effect of chemical compositions of cementing blends on available alkalies in leaching solution of alkali concentration of 0.25mol/L Source: Shehata and Thomas 2002

iii) According to a findings (Malvar and Lenke 2006), the ASR depends on the ratio of constituents that promotes expansion ( $\text{CaO}_{eq}$ ) to constituents reducing expansion ( $\text{SiO}_{2eq}$ ).



The constituents promoting expansion are: CaO, Na<sub>2</sub>O, K<sub>2</sub>O, MgO and SO<sub>3</sub>. Converting these constituents to molar ratio equivalent to CaO,

$$\text{CaO}_{\text{eq}} = \text{CaO} + 0.905\text{Na}_2\text{O} + 0.595\text{K}_2\text{O} + 1.391\text{MgO} + 0.700\text{SO}_3$$

The constituents reducing expansion are: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. Converting these constituents to molar ratio equivalent to SiO<sub>2</sub>,

$$\text{SiO}_{2\text{eq}} = \text{SiO}_2 + 0.589\text{Al}_2\text{O}_3 + 0.376\text{Fe}_2\text{O}_3$$

Malvar and Lanke 2006 found no significant correlation between Na<sub>2</sub>O<sub>eq</sub> and expansion of test results of 31 different numbers of class F and class C fly ash carried out by several authors as per ASTM C 1260 (Accelerated Mortar bar Test). Addition of silica in the system means to increase the amount of constituents reducing expansion (SiO<sub>2eq</sub>).

#### iv) Reduction of permeability

Silica fume and fly ash incorporated concrete has exhibited extraordinarily low permeability of concrete. The very low range of permeability can reduce the permeation of moisture, a factor for ASR expansion into the concrete. Also the low range of permeability can reduce ionic diffusivity.

#### v) Reduction of porosity

Silica fume in the ternary blend reacts with Ca(OH)<sub>2</sub> and forms C-S-H gel. Since the C-S-H gel takes up more space than Ca(OH)<sub>2</sub>, the pore system becomes finer and less continuous. The reduced porosity limits the ability of alkali to migrate and therefore, reduces the ability of ASR gel to form (Dokter and Eylands 2003).

The literature reviewed in this chapter showed that ground granulated blast furnace slag, silica fume and low calcium fly ash were effective in counteracting both sulphate attack and ASR. However, high calcium fly ashes (HCFA) were less effective in this aspect. Silica fume/HCFA combinations were found to be effective in mitigating expansion due to ASR and sulphate; however, more work is needed to study the long-term performance of SF/HCFA in terms of sulphate attack. Also, the efficacy of SF/HCFA in resisting ASR in concrete containing aggregate of different reactivity needs to be evaluated. Gypsum has been used to improve the performance of HCFA in terms of sulphate attack; however, the study was performed on sulphate resisting Portland cement, and the gypsum was ground with clinker and fly ash. Grinding fly ash, clinker and gypsum during the manufacturing of Portland cement may not be a practical approach in some situations as the produced blended cement will require separate grinding mill and storage in the factory.

## Chapter 3

### Material and Experimental Details

#### 3.1 Sulphate Attack Study:

##### 3.1.1 Materials:

The material used in this study are GU Portland cement ( $C_3A = 10.30\%$ ), reagent grade gypsum, a granulated blast furnace slag (ggbfs), a silica fume, a class F or type F fly ash and two class C or type CH (high calcium fly ash with  $CaO > 20\%$ ) as per ASTM and CSA (Canadian Standard Association), respectively. The chemical analysis of the materials involved in the study is listed in Table 3.1.

Table 3.1: Chemical composition of Cement, Fly ash, Slag and silica fume used in the study

Sn	Description	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
1	General Use Cement (A)	19.58	5.35	2.29	62.84	2.43	4.10	1.13	0.21
2	Fly Ash (CH1)	33.72	18.47	7.04	27.16	5.08	2.84	0.33	1.72
3	Fly Ash (CH2)	40.49	18.50	6.13	22.97	5.00	1.62	0.62	1.36
4	Fly Ash (F)	61.29	16.81	4.62	6.42	2.15	1.12	0.98	3.68
5	Slag (St. Lawrence)	34.40	7.40	0.94	43.20	9.30	0.83	0.58	0.57
6	Silica Fume	96.19	0.35	0.10	0.27	0.91	0.23	0.51	0.11

Compound composition for the given cement as per Bogue's calculation method is:

$C_3S = 56.10\%$ ,  $C_2S = 13.81\%$ ,  $C_3A = 10.30\%$  and  $C_4AF = 6.97\%$

##### 3.1.2 Experimental Details:

Mortar bars were tested in accordance with ASTM C 1012. All supplementary cementing materials were added to the PC during mixing. Gypsum, however, was added to the mixture in two different ways: (a) added to the ingredients at the time of mixing or (b) blended with

the HCFA in a microdeval apparatus (CSA A23.2.23), a jar rolling mill with stainless steel balls of 9.5 mm diameter, for 1 hour. The microdeval was used as means of pre-blending the HCFA and gypsum prior to mixing which would provide intimate contact of fly ash and gypsum. Different levels of gypsum were used as listed in Table 3.2 in which the SO<sub>3</sub> content in the mix is expressed as a percentage of total mass of the dry ingredients (PC + FA + Gypsum).

Table 3.2: Levels of SO<sub>3</sub> investigated in the HCFA/Gypsum samples

Mass of gypsum as a percentage of fly FA, (%)	SO <sub>3</sub> per mass of (FA + gyp.), (%) <sup>1</sup>	Total SO <sub>3</sub> per mass of (PC+FA+Gyp.), (%) <sup>2</sup>	added <sup>3</sup>	Premixed <sup>4</sup>
Fly Ash CH1				
3	4.11	4.10	x	x
4	4.52	4.18	x	x
8	6.07	4.49	x	x
10	6.81	4.64		x
12	7.52	4.78	x	x
14	8.20	4.92		x
15	8.54	4.99		x
16	8.86	5.05	x	x
20	10.12	5.30	x	
Fly Ash CH2				
1	2.06	3.69		x
8	4.94	4.27		x
10	5.70	4.42		x
12	6.43	4.57		x
14	7.13	4.71		x
16	7.81	4.84		x
20	9.10	5.10		x

<sup>1</sup>: SO<sub>3</sub> from FA and gypsum expressed as % of mass of FA and gypsum

<sup>2</sup>: SO<sub>3</sub> from gypsum, FA and PC expressed as % of mass of the three components

<sup>3</sup>: Gypsum as added to the cementing materials as an additive

<sup>4</sup>: Gypsum was pre-mixed with the FA for 1 hour in a Micro-Deval Apparatus



**Figure 3.1: Comparator used for expansion measurement**

Mortars were prepared in accordance with Test Method ASTM C 109 with 1 part of cement and 2.75 parts of Ottawa sand by mass with water cementitious material ratio of 0.485. Mixing was done as per ASTM C 305. Mortar bars were molded in accordance with the Test Method C 157 in the mold containing internal dimension as 25mm X25mm X275mm confirming to requirement of ASTM Specification C 490. Mortar cubes were molded in accordance with Test Method ASTM C 109. Immediately after molding, the molds were covered with glass plate making it water tight and placed in the curing tank in water at  $35 \pm 3^{\circ}\text{C}$  for 24 hrs as per Test Method ASTM C 684, procedure A. The molds were demolded after 24 hrs and all the samples except two cubes were placed in the saturated lime solution at  $23 \pm 1.7^{\circ}\text{C}$  for further curing. After reaching the temperature to the ambient under moist cloths, two cubes were broken for compressive strength test as per Test Method ASTM C 109. Initial reading of the mortar bars were recorded only on the day when the average compressive strength of the

cube reached 20 MPa. Depending upon the types of mixes, the days of curing in the lime water varied from 1 day to 4 days. For some mixes containing more than 40% of SCMs, the day of curing had reached even up to 10 days. After taking initial readings, the mortar bars were placed in the sodium sulphate solution of 5% concentration at  $23\pm 1.7^{\circ}\text{C}$ . Parallel set of mortar bars were immersed in the lime solution at  $23\pm 1.7^{\circ}\text{C}$  for the mixes containing added gypsum to observe the amount of expansion as a result of internal sulphate attack. Expansion measurement of mortar bars were carried out at 1, 2, 3, 4, 8, 12, 13, 15, 26, 39, 52, 78 and 104 weeks using digital length comparator of 0.001mm accuracy (Figure 3.1). Each time after expansion measurement, sulphate solution were replaced with fresh sulphate solution prepared 24 hrs before the replacement. The mortar bars for the test were prepared from the different mixes as shown in Table 3.3. The measurement records have been provided in the Appendix A.

Table 3.3: Mixes used in sulphate attack test

Sample No.	% General use cement	Fly Ash				% Slag	% Silica Fume
		% SCM	Sulphate Addition (%) Replacement of Fly Ash		% Hemi-hydrate		
			Gypsum %				
			Admixture	Premix			
S1	100	0					
S2	80	20 (CH1)					
S3	60	40 (CH1)					
S4	80	19.91 (CH1)	0.10				
S5	80	19.95 (CH1)	0.25				
S6	80	19.90 (CH1)	0.50				
S7	80	19.85 (CH1)	0.75				
S8	80	19.80 (CH1)	1.00				
S9	80	19.61 (CH1)	2.00				
S10	80	19.42 (CH1)	3.00				
S11	80	19.23 (CH1)	4.00				
S12	80	18.52 (CH1)	8.00				
S13	80	17.86 (CH1)	12.00				
S14	80	17.24 (CH1)	16.00				
S15	80	16.67 (CH1)	20.00				
S16	80	19.95 (CH1)		0.25			
S17	80	19.90 (CH1)		0.50			
S18	80	19.85 (CH1)		0.75			
S19	80	19.80 (CH1)		1.00			
S20	80	19.42 (CH1)		3.00			
S21	80	19.23 (CH1)		4.00			
S22	80	18.52 (CH1)		8.00			
S23	80	18.18 (CH1)		10.00			
S24	80	17.86 (CH1)		12.00			
S25	80	17.54 (CH1)		14.00			
S26	80	17.39 (CH1)		15.00			
S27	80	17.24 (CH1)		16.00			
S28	80	14.29 (CH1)		40.00			
S29	80	14.29 (CH1)		40.00*			
S30	80	10.64 (CH1)		88.00			
S31	80	10.64 (CH1)		88.00*			
S32	80	19.95 (CH1)			0.25		
S33	80	19.90 (CH1)			0.50		
S34	80	19.85 (CH1)			0.75		
S35	80	19.80 (CH1)			1.00		

Note: (\*) Star indicates cement, fly ash and gypsum all premixed (pre-blended) at a time

Table 3.3: Mixes used in sulphate attack test (continued)

Sample No.	% General use cement	Fly Ash				% Slag	% Silica Fume
		% SCM	Sulphate Addition (%) Replacement of Fly Ash		% Hemi-hydrate		
			Gypsum %				
			Admixture	Premix			
S36	80	20 (CH2)					
S37	60	40 (CH2)					
S38	80	19.91 (CH2)	0.10				
S39	80	19.95 (CH2)	0.25				
S40	80	19.90 (CH2)	0.50				
S41	80	19.85 (CH2)	0.75				
S42	80	19.80 (CH2)	1.00				
S43	80	19.95 (CH2)		0.25			
S44	80	19.90 (CH2)		0.50			
S45	80	19.85 (CH2)		0.75			
S46	80	19.80 (CH2)		1.00			
S47	80	18.52 (CH2)		8.00			
S48	80	18.18 (CH2)		10.00			
S49	80	17.86 (CH2)		12.00			
S50	80	17.54 (CH2)		14.00			
S51	80	17.24 (CH2)		16.00			
S52	80	16.67 (CH2)		20.00			
S53	80	19.95 (CH2)			0.25		
S54	80	19.90 (CH2)			0.50		
S55	80	19.85 (CH2)			0.75		
S56	80	19.80 (CH2)			1.00		
S57	80	20 (F)					
S58	60	40 (F)					
S59	80					20	
S60	70					30	
S61	60					40	
S62	70		15			15	
S63	60		20			20	
S64	50		20			30	
S65	40		40			20	
S66	97						3
S67	95						5
S68	77	20 (CH1)					3
S69	75	20 (CH1)					5



### **3.1.3 X-ray diffraction:**

To study the different hydration products in samples containing HCFA with silica fume or gypsum, three different pastes of mix containing a) 80% Portland cement and 20% CH1 Fly Ash b) 80% Portland cement and 20% CH1 Fly Ash and Gypsum (16% of Gypsum out of 20% Fly Ash) and c) 75% Portland cement, 20% CH1 Fly Ash and 5% Silica Fume were prepared using high-speed, high-shear food blender. The water to cementing material ratio was maintained as 0.50. The blender was run for one minute followed by rest period of one minute with a total run time of three minutes with total rest period of two minutes. Each paste was then poured into polyethylene cylinder of 50mm diameter and 100mm height and capped from the top and placed in the warm water at 35°C for curing for 24-hour. Each cylinder was cured further for 27 days in saturated lime solution at 23°C constituting total curing period of 28 days. After 28 days, each cylinder was taken out from lime solution, cleaned with tap water to remove the lime clusters and was then broken into small pieces using ceramic bowl and ceramic hammer. Before breaking and each time after breaking, the ceramic bowl and hammer were rinsed with acetone to prevent any impurities from going into broken sample, which might otherwise, alter the result of X-ray diffraction. After breaking, each sample was submerged in reagent grade alcohol for 7 days for drying as a solvent replacement method. Each sample, after removal from alcohol solution was put inside a desiccator for about two weeks. The desiccator was put under vacuumed condition and temperature was maintained at 30°C. To absorb excess moisture and carbon-dioxide so as to prevent the formation of skewed hydration product, Silica Gel and Soda Lime were placed at the bottom of the desiccator. Each sample was then removed from desiccator, ground to fine powder using ceramic bowl and hammer, sieved from # 200-sieve (75µm sieve) and the powder passing

from the sieve (about 5 gram) was put inside the clean and airtight small glass bottle for X-ray diffraction. The Diffraction patterns were collected using Scintag XDS 2000 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.540562 \text{ \AA}$ ).

#### **3.1.4 Rapid Chloride Permeability Test (RCPT)**

To study the effect permeability has on the different blend in sulphate resistance, RCPT tests were carried out as per ASTM C 1202 procedure. Cylinders were cast with mortar prepared using the identical sand, water cementitious material ratio, mixing procedure and curing method as used in preparing mortar bars in accordance with Test Method ASTM C 109 using mixing method as per ASTM C 305. The size of the cast cylinders were 100 mm in diameter and 150 mm in height. After 24 hours of curing, each cylinder was sliced into three parts each of  $51 \pm 3 \text{ mm}$  using the water-cooled diamond saw for RCPT test. After slicing, some samples were placed in the saturated lime solution for further curing for the prescribed period and some were separated for testing. To get representative results from two cylinders of same mix, a slice from the top of first cylinder and two slices from the second cylinder were taken. Each sample to be tested was allowed to surface dry for about half an hour. After air drying, samples were conditioned in the following order. Samples were placed inside a desiccator and vacuumed for three hours. After three hours, leaving the vacuum pumps in running condition, the distilled water was allowed to run inside the desiccator turning the stopcock on until the samples were submerged fully with distilled water. The vacuum pump was allowed to run further one hour. After one hour, the vacuum pump was turned off and the air was allowed to go inside the desiccator by turning the vacuum line stopcock on. The sample was left inside the desiccator under soaking condition for  $18 \pm 2$  hours.

After 18±2 hours, the samples were removed from the desiccator, blotted excess water, mounted rubber gasket and put in the test chamber. One cell of the chamber was filled with 3% NaCl solution and the other cell with 0.3N NaOH solution. A voltage of 60V was applied. The total charge passed at 6 hours was measured using automated computerized measuring system. Based on the total charge passed (coulombs) in six hours, the relative chloride ion permeability was assigned for the given mix. The test results have been provided in the Appendix A1.

### 3.2 Alkali-Silica Reaction (ASR) Study:

#### 3.2.1 Materials:

Materials used in this study were four types of GU Portland cements (total alkalinity,  $\text{Na}_2\text{O}_e$ : 0.89%, 0.95%, 1.02% and 1.05%), four types of fly ashes, one slag and one silica fume. The chemical analysis of the materials involved in the study is listed in Table 3.4.

Table 3.4: Chemical composition of materials used in ASR Test

Sn	Description	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	Sp. Gr.
1	Portland Cement (0.89% $\text{Na}_2\text{O}_e$ ) (B)	19.92	5.57	2.10	63.02	2.55	3.86	1.05	0.20	-
2	Portland Cement (0.95% $\text{Na}_2\text{O}_e$ ) (C)	19.58	5.35	2.29	62.84	2.43	4.10	1.13	0.21	-
3	Portland Cement (1.02% $\text{Na}_2\text{O}_e$ ) (D)	19.40	5.16	2.50	61.50	2.15	4.23	1.17	0.25	-
4	Portland Cement (1.05% $\text{Na}_2\text{O}_e$ ) (E)	19.51	4.94	2.65	62.65	2.56	4.24	1.13	0.31	-
5	High Calcium Fly Ash (Fly Ash CH5)	33.26	18.24	6.45	28.73	5.32	2.59	0.33	1.94	-
6	LCLA Fly Ash 2006 (Fly Ash CI6)	53.10	21.39	7.56	10.46	2.85	0.50	1.39	0.59	2.54
7	MCLA Fly Ash 2006 (Fly Ash CH7)	35.04	18.87	7.19	25.84	5.31	2.47	0.46	1.43	2.16
8	HCHA (Fly Ash CH8)	20.50	12.80	3.92	34.60	3.54	12.06	0.49	8.38	2.55
9	Slag	34.40	7.40	0.94	43.20	9.30	0.83	0.58	0.57	2.94
10	Silica Fume	96.19	0.35	0.10	0.27	0.91	0.23	0.51	0.11	2.40

Note:  $\text{Na}_2\text{O}_e$  is calculated as  $\text{Na}_2\text{O} + 0.658\text{K}_2\text{O}$

In the same way, five different types of fine aggregates and two types of coarse aggregates were used for the study. The properties of aggregates are presented in the Table 3.5.

Table 3.5: Properties of aggregates used in ASR test

Aggregate type	Bulk relative density (Kg/m <sup>3</sup> )	SSD Bulk relative density (Kg/m <sup>3</sup> )	Absorption (%)
<b>Coarse Aggregate</b>			
Limestone (Non-reactive)	2687.33	2718.33	1.15
Siliceous Lime stone (Spratt)	2671.95	2684.63	0.47
<b>Fine Aggregate</b>			
Ottawa Sand	2416.83	2417.79	0
Natural sand (Non-reactive)	2636.25	2666.49	1.15
Britina Sand	2602.42	2644.19	1.61
Jobe Sand	2514.82	2534.07	0.77
Spratt	2560.89	2598.25	1.46

### 3.2.2 Experimental Details:

Experimental works were carried out for ASR test using two set of tests under Canadian Standards Association: i) Test method for detection of alkali-silica reactive aggregate by accelerated expansion of mortar bars (A23.2-25A), a test analogous to ASTM C 1260 or ASTM C 1567, and ii) Potential expansivity of aggregates (procedure for length change due to alkali-aggregate reaction in concrete prisms as 38°C) (A23.2-14A), a test analogous to ASTM C 1293. Some of the mixes were tested for both methods whereas some were tested just for one of the two methods.

Mortar bars were cast using different SCMs at the varied proportion of replacement to the General Use Portland cement, and as control mixes (without SCMs). Mortars were prepared with 1 part of cement and 2.25 parts of sand (passing from 4.75 mm-sieves) by mass with water cementitious material ratio as 0.44. Mixing was done as per ASTM C 305. Mortar bars

were molded in accordance with the Test Method ASTM C 157 in the mold containing internal dimension as 25mm X25mm X275mm confirming to requirement of ASTM C 490. Immediately after molding, the molds were put in the moist curing room containing 100% relative humidity under a shade of glass plate for  $24\pm 2$  h. Molds were removed from moist curing room after  $24\pm 2$  h, demolded and taken the initial length measurement of mortar bars using the digital length comparator of 0.001mm accuracy. The samples were then put in the microwave safe plastic container (ERA WARE®) having internal dimension of 31.5cm in length, 18.8 cm in width and 8 cm in depth filled with 2.5 liter of water. The container was then covered from the top with watertight plastic cover (Glad Press and Seal), placed the lid on the top and put in the oven at temperature of  $80\pm 2^{\circ}\text{C}$  for 24 hrs. After 24 hrs, the container was removed from the oven for taking length measurement of mortar bars. A mortar bar was taken from the warm water, blotted the excess water of the surface, measured the length and placed on a clean paper. Removal of a mortar bar from warm water and its length measurement was completed within 10 seconds. Measurements of other two mortar bars were taken in a similar manner. The measurements were recorded as zero-day reading (initial reading). After completion of measurement recording, all three samples were put in the 1N NaOH solution, covered from the top with water tight plastics cover as had done before and put in the oven of  $80\pm 2^{\circ}\text{C}$ . The time elapsed between the removal of container from oven to its return to the oven was not allowed to exceed 5 minutes. Subsequent measurement of mortar bars were taken at 3, 7, 10, 14 and 28 days in the similar manner. Measurement records have been provided in the Appendix B.

The mixes used in the test are presented in the Table 3.6.

Table 3.6: Mixes used for accelerated mortar bar test

Sample Number	Type and % of Cement	Type and % of Fly ash	% of Silica Fume	% of Slag	Type of Sand
A1	C=100%	-	-	-	Britinia
A2	C=100%	-	-	-	Natural
A3	C=100%	-	-	-	Jobe
A4	C=70%	CH5 -25%	5%	-	Britinia
A5	C=70%	CH5 - 25%	5%	-	Jobe
A6	D=100%	-	-	-	Jobe
A7	D=75%	CI6 - 25%	-	-	Jobe
A8	D=75%	CH7 - 25%	-	-	Jobe
A9	D=70%	CH5 - 15%	-	15%	Spratt

Concrete prisms were cast using different SCMs at the varied levels of replacement to the General Use Portland cement and as control mixes (without use of SCMs). Coarse aggregates were prepared by taking the three equal parts the range (a. passing from 20mm sieve and retained on 12.5 mm sieve, b. passing from 12.5 mm sieve and retained on 9.5 mm sieve and c. passing from 9.5 mm sieve and retained on 4.75 mm sieve). Fine aggregates were prepared by taking the aggregates passing from 4.75mm sieve. Coarse aggregate to fine aggregate ratio was maintained as 60:40. Cementitious material content was maintained as 420 kg/m<sup>3</sup>. Na<sub>2</sub>O<sub>e</sub> of cement was raised to 1.25% and in some cases to 1.40% with consideration of only the mass of cement (without consideration of other cementitious materials). Alkalinity (Na<sub>2</sub>O<sub>e</sub>) was raised by dissolving required quantity of NaOH in the approximately half of the mixing water. Water to cementitious material ratio was maintained as 0.42 for the control mixes and 0.40 for the other mixes containing supplementary cementitious materials. Concrete mixing was done as per ASTM C 192 but to prevent the alkalinity from absorption by coarse aggregate, half of the mixing water (water without NaOH) and aggregate was introduced in the mixture and mixed for about a minute at the beginning of mixing operation.

The concrete was then molded in a designed mould of internal dimension 75mm X 75mm X 285mm as per CSA A23.2-3C but with the use of tamping rod of 10mm diameter using steel stud at the ends to facilitate expansion measurement. Some of the prisms were cured in the moist curing room containing 100% relative humidity under a shade of glass plate for  $23 \pm 2$  h and some were cured using moist burlap. Care had been taken not to allowing dripping of water from the burlap to the concrete surface. Also to prevent the burlap from drying, it was covered from the top with plastic sheet. Burlap was kept slightly above the concrete surface to prevent it from contacting the concrete surface. After completion of the curing period, the molds were demolded and initial measurements of the concrete prism were taken with the digital length comparator of 0.001mm accuracy. Each set of prisms then was put inside watertight bucket of 20 liter capacity. The prisms were rest on the polyethylene grid mounted over one inch high polyethylene pipe of 4 inch diameter. To maintain 100% relative humidity inside the bucket, the inner top and sides were wrapped with wicking cloths (Wypall X70). The side cloths were extended up to bottom to allow wicking of water. Bottom of the bucket was filled with water at the depth of about 20mm. The bucket was then covered with a watertight lid from the top and stored inside the heat room maintained at  $38 \pm 2^\circ\text{C}$ . The bucket was taken out of the heat room and placed in a room containing temperature of  $23 \pm 2^\circ\text{C}$  for  $16 \pm 4$  h before taking regular expansion measurement of prisms and placed again back in the heat room after measurement recording. Expansion measurement of the prism was taken at 1, 2, 4, 8, 13, 18, 26, 39, 52, 78 and 104 weeks. Measurement records have been provided in the Appendix B.

The mixes used in the test are presented in the Table 3.7.

Table 3.7: Mixes used for ASR test (concrete prism)

Sample Number	Type and % of Cement	Na <sub>2</sub> O <sub>e</sub> Raised to	Type and % of Fly ash	% of Silica Fume	% of Slag	Type of Sand	Type of coarse agg.	Method of curing
P1	B=100%	1.25%	-	-	-	Britinia	limestone	moist
P2	B=100%	1.40%	-	-	-	Britinia	limestone	moist
P3	E=100%	1.25%	-	-	-	Britinia	limestone	moist
P4	E=100%	1.40%	-	-	-	Britinia	limestone	moist
P5	B=70%	1.25%	CH5=25%	5%	-	Britinia	limestone	moist
P6	C=70%	1.25%	CH8=30%	-	-	Britinia	limestone	moist
P7	C=60%	1.25%	CH8=40%	-	-	Britinia	limestone	moist
P8	C=50%	1.25%	CH8=50%	-	-	Britinia	limestone	moist
P9	C=40%	1.25%	CH8=60%	-	-	Britinia	limestone	moist
P10	C=50%	1.25%	CH5=30%	-	20%	Natural	Spratt	moist
P11	D=50%	1.25%	CH5=30%	-	20%	Natural	Spratt	moist
P12	D=50%	1.25%	CH5=30%	-	20%	Natural	Spratt	burlap
P13	C=70%	1.25%	CH5=15%	-	15%	Natural	Spratt	moist
P14	D=70%	1.25%	CH5=15%	-	15%	Natural	Spratt	moist
P15	D=70%	1.25%	CH5=15%	-	15%	Natural	Spratt	burlap
P16	C=60%	1.25%	CH5=20%	-	20%	Natural	Spratt	moist
P17	C=40%	1.25%	CH5=40%	-	20%	Natural	Spratt	moist

### 3.2.3 Rapid Chloride Permeability Test (RCPT)

Like in the case of sulphate attack, RCPT tests were carried out simulating all the conditions to that of accelerated mortar bar test. Cylinders were cast with mortar prepared using identical water cementitious material ratio, mixing procedure and curing method as used in preparing mortar bars in accordance with Test Method ASTM C 109 using mixing method as per ASTM C 305. However, in the place of other sand, Ottawa sand was used. The size of the cast cylinders were 100 mm in diameter and 1500 mm in height. After 24 hours of moist curing, each cylinder was cured further in oven containing temperature of 80°C for 7day and 14days. After the prescribed period, each cylinder was taken out from oven and allowed to cool down to room temperature. Subsequent procedure was exactly similar to that followed in sulphate attack test. Test results have been provided in the Appendix B1.



## **Chapter 4**

### **Results and Analysis**

#### **4.1 Effects of binary blend of SCM on Sulphate attack**

Binary blend of a class F fly ash, two class C fly ashes, a silica fume and a slag with GU cement were prepared and efficacy of each SCM was studied in terms of its chemistry and replacement level.

##### **4.1.1 Role of Fly ash**

Role of each fly ash was studied in terms of its calcium oxide (CaO) content and replacement level. Results were observed as follows.

##### **4.1.1.1 Effect of calcium content**

Effects of CaO content of two high calcium fly ashes (class CH1, CaO=27.16% and class CH2, CaO=22.97%) and a low calcium fly ash (class F, CaO=6.42%) on expansion of mortar bars at 20% replacement of GU cement are shown in Figure 4.1. The ASTM C 1157 expansion limits of 0.05% or 6 months and 0.10% for 1 year for high sulphate resistance cement are also shown in the same figure. The figure shows that the expansion of 0.056% at 6 months and 0.094% at 1 year for fly ash class F.

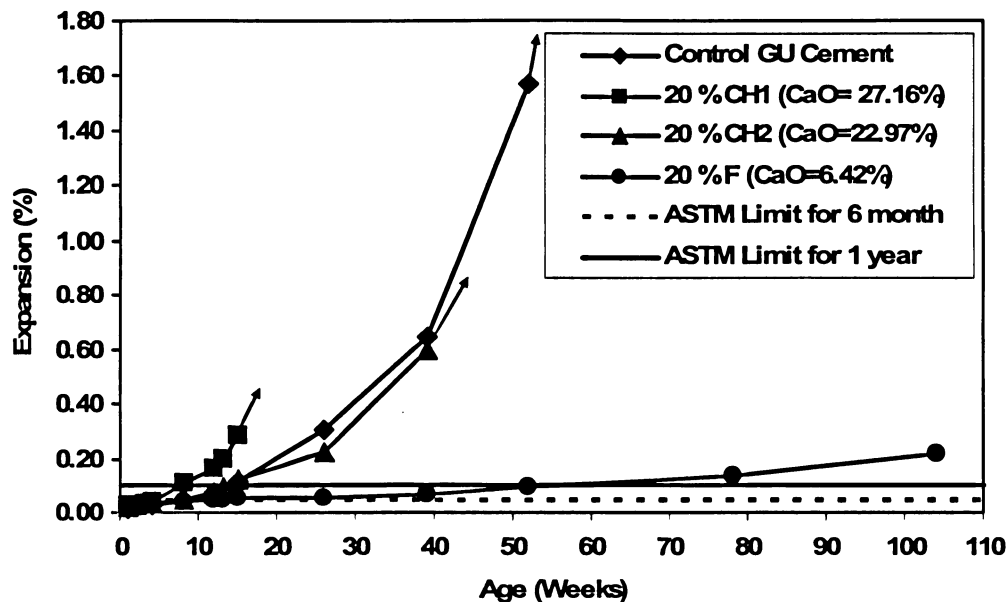


Figure 4.1: Effect of calcium content of fly ashes on sulphate resistance

The expansion level of 0.056% at 6 months is slightly outside the expansion limit of 0.05% for 6 months for high sulphate resistance cement as prescribed by ASTM C 1157 whereas the expansion level of 0.094% is well below the prescribed expansion limit of 0.10% at 1 year for high sulphate resistance cement. Therefore, the binary blend of fly ash containing low calcium content, i.e., class F fly ash in our case can be said to be the highly sulphate resistance. The reason of the efficacy of low calcium fly ash may be due to its pozzolanic reactivity. Fly ash with calcium content lower than 10% contains mainly aluminosilicate type glass (A-S) (Mehta 1986). Aluminosilicate phase of fly ash reacts with calcium hydroxide (Skalny 2003) and consumes more amount of sulphate susceptible calcium hydroxide (Mindess et al 2003). The expansion level of class CH2 fly ash is 0.119% at 15 weeks, 0.222% at six months and the mortar bar disintegrated and broke after 39 weeks whereas the expansion level of class CH1 fly ash is 0.286% at 15 weeks and the mortar bars broke by disintegration

afterwards. The expansion level of 0.119% at 15 weeks of comparatively lower calcium content of class CH2 is quite less than the expansion level of 0.286% of class CH1 fly ash at the same period. Also the mortar bars containing class CH2 fly ash survived up to 39 weeks whereas the mortar bars containing Class CH1 fly ash didn't survive more than 15 weeks. The expansion limit of mortar bars containing class CH2 fly ash is even higher than control sample. The above scenario clearly shows that the efficacy of fly ash depends upon the calcium content of fly ash. The lower the calcium content, the higher is the efficacy of fly ash. The main factor behind the low efficacy of high calcium fly ash may be due to lower consumption of calcium hydroxide. According to Mindess et al 2003, high calcium fly ash can not consume higher amount of calcium hydroxide due to its high calcium content. Similar trend was observed in another experiment (Freeman and Carrasquillo 1992). Mortar bars prepared with Type II cement with interground Class C fly ashes with different percentage of CaO content had shown relatively better sulphate resistance for the fly ashes with CaO content of less than approximately 26%.

#### **4.1.1.2 Effect of replacement level**

Figure 4.2 shows the effect of replacement level of class CH1 fly ash on sulphate resistance. The mortar bars survived for 15 weeks at 20% replacement but didn't survive more than 13 weeks at 40% replacement level. Though the mortar bars at both replacements showed higher expansion and early age disintegration than the control sample, the mortar bars at 40% replacement level showed higher expansion and early age disintegration than that of 20% replacement.

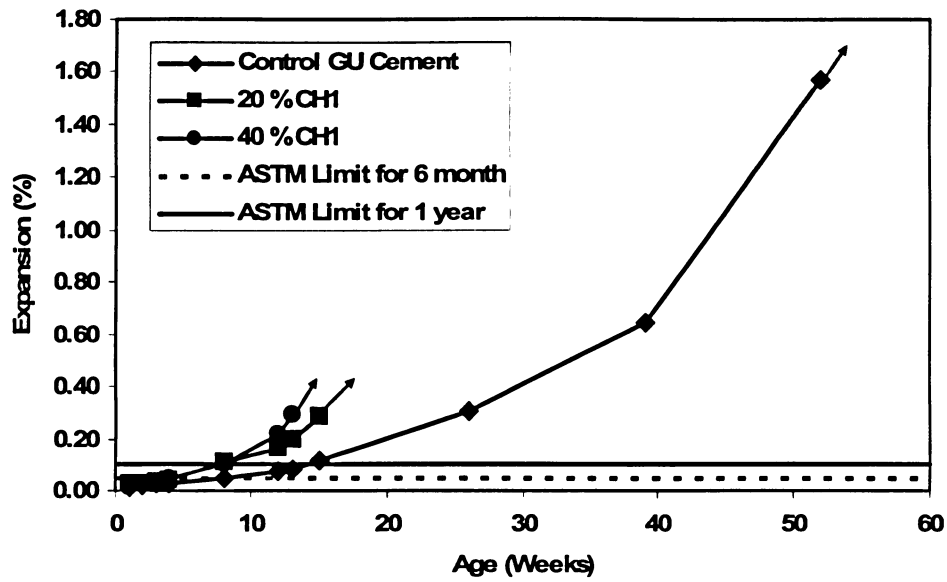


Figure 4.2: Effect of replacement level of class CH1 fly ash on sulphate resistance

However, the scenario was opposite in the case of class CH2 fly ash (Figure 4.3).

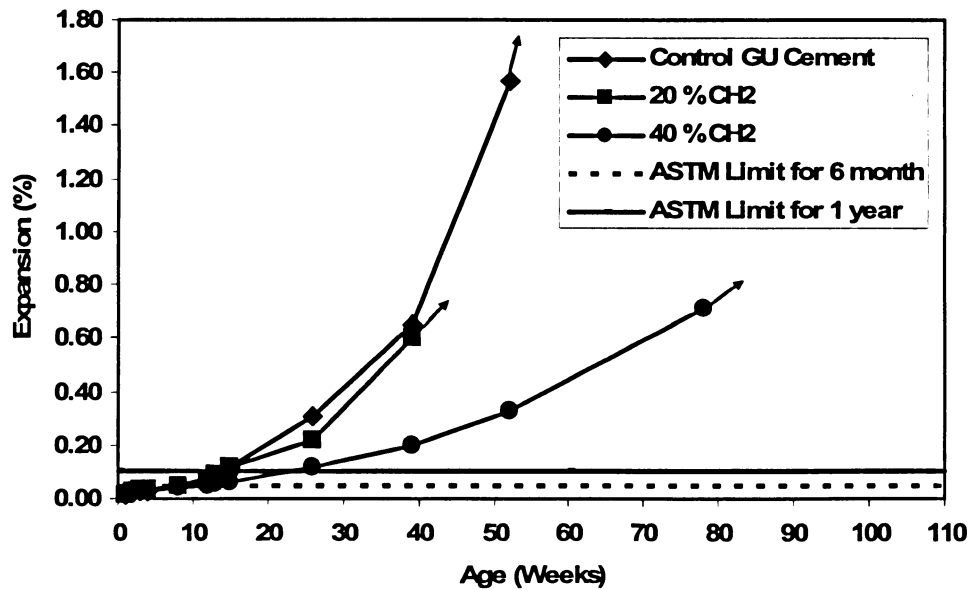
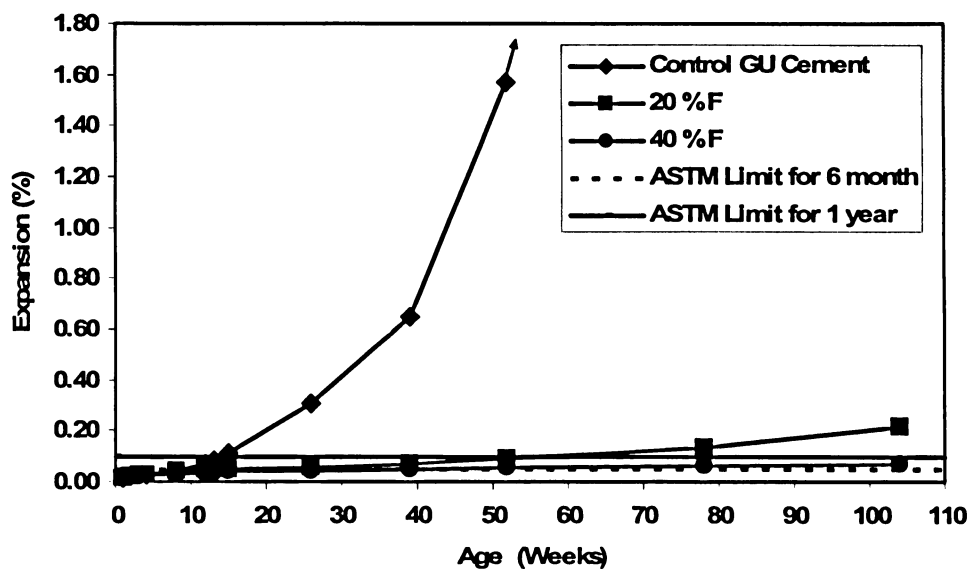


Figure 4.3: Effect of replacement level of class CH2 fly ash on sulphate resistance

Mortar bars prepared with 40% replacement showed relative better result than that of replacement level of 20%.

Mortar bars containing replacement level of 40% showed far better result than that of control sample and survived for 78 weeks with the expansion amount of 0.711% whereas the mortar bars containing 20% replacement level broke after 39 weeks (expansion amount of 0.600%) despite better result than that of control sample.



**Figure 4.4: Effect of replacement level of class F fly ash on sulphate resistance**

Sulphate resistance was quite much enhanced with the increase in replacement level from 20% to 40% in the context of class F fly ash (Figure 4.4). Expansion levels of the fly ash were 0.056% and 0.094% at 6 months and 1 year respectively for 20% replacement level

whereas the quite lower expansion amount of 0.042% and 0.057% were for 40% replacement at the period of 6 months and 1 year respectively.

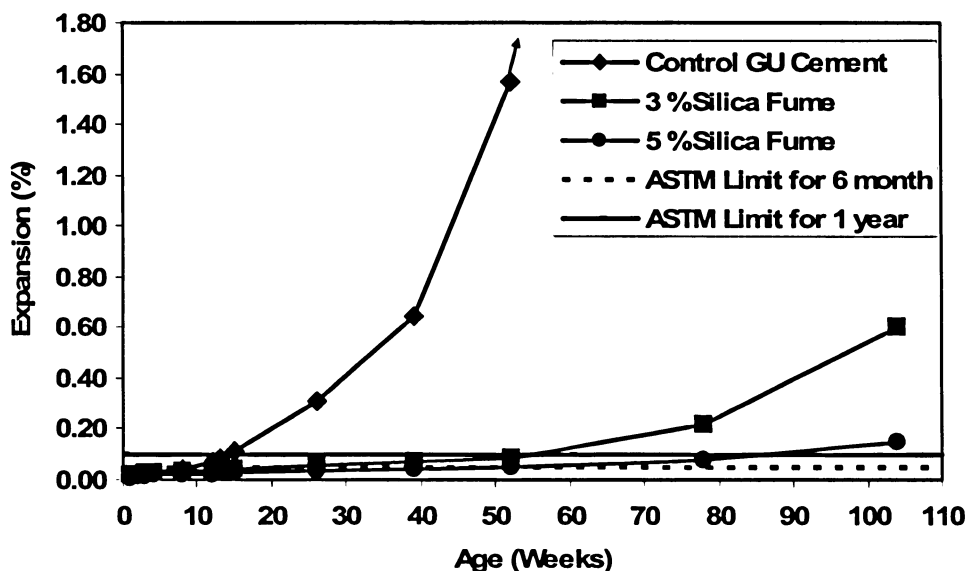
The main factor behind the inconsistent result of high calcium fly ashes (class CH1 and class CH2) may be due its varied chemical and mineralogical composition as observed by other authors (Mehta 1986; Tikalsky and Carrasquillo 1992, Freeman and Carrasquillo 1995, Freeman and Carrasquillo 1993).

Calcium of these fly ashes might have contained reactive calcium aluminosilicate glass as well as cementitious crystalline compounds of calcium such as  $C_3A$ ,  $C_4A_3S$ , CS and CaO and have produced more sulphate susceptible calcium aluminate hydrate (C-A-H) during hydration as observed by Mehta (Mehta 1986) in his experiment.

Based on the above results it can be concluded that the sulphate resistance of high calcium fly ash depends upon both chemical and mineralogical composition. Difference in mineralogy such as presence of varied amount of reactive alumina or glass phase or crystalline aluminate phase of fly ashes is believed to be the main factor that control the ash's performance. Also from the expansion result of the two high calcium fly ashes at two different replacement levels (20% and 40%), no conclusion can be drawn about the relationship between the expansion and replacement level of high-calcium fly ashes. Out of tested two high-calcium fly ashes, CH1 fly ash provided even inferior result at 40% replacement level as opposed to that at 20% replacement whereas class CH2 fly ash provided comparatively better result at 40% replacement.

#### 4.1.2 Role of Silica Fume

Effectiveness of silica fume was studied in terms of its replacement level. Results have been presented in Figure 4.5.



**Figure 4.5: Effect of silica fume and its replacement level on sulphate resistance**

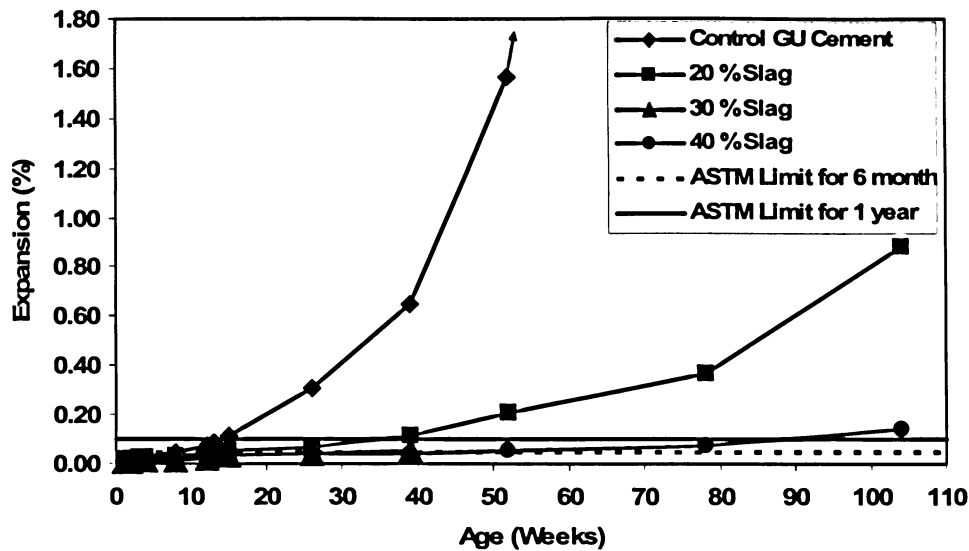
Replacement of silica fume with 5% produced the expansion of 0.036% and 0.048% at 6 months and 1 year respectively as opposed to the expansion level of 0.053% and 0.086% for 6 months and 1 year respectively with the replacement of 3% of silica fume. Although the replacement of 3% had succeeded to keep the expansion level nearly within the ASTM limit for high sulphate resistance cement at 6 months and well within at 1 year, replacement of 5% produced even lower expansion both at 6 months and 1 year. The above results clearly show that the sulphate resistances of GU cement increases with increase in the replacement level of silica fume. The main reason behind the effectiveness of silica fume blended mortar bars is due to its lower permeability as a result of pore refinement. Due to its high pozzolanic

reactivity, silica fume reacts with calcium hydroxide, one of the hydration products and forms secondary C-S-H gel which occupies the space available in the pore and densifies the pore structures thereby reducing the permeability to the large extent. RCPT test result shows very low permeability at replacement of 5% silica fume in GU cement (Figure 4.14). Increase in the replacement level of silica fume causes increase in the consumption of calcium hydroxide. At 20% replacement level, silica fume virtually sweeps all the calcium hydroxide ions from pore solution (Rasheeduzzafar and Hussain 1991).

#### **4.1.3 Role of Ground Granulated Blast Furnace Slag (GGBFS)**

Study was carried out with the replacement of GU cement with 20, 30 and 40% GGBFS. Study results have been provided in Figure 4.6. The study result clearly shows that the efficacy of GGBFS increases with increase in the replacement level. Although samples with all the replacement level has shown lower expansion value than that of control sample, the replacement level of 20% has expanded with 0.069% at six months which is within limit of moderate sulphate resistance as specified by ASTM C 618 at 6 months (1.0%). Samples with 30% replacement level has shown the expansion amount of 0.053% at six months which is slightly above the ASTM limit for higher sulphate resistance and can be approximated as higher sulphate resistance. Samples with replacement level of 40% has shown the higher sulphate resistance with mere expansion of 0.037% at six months and 0.054% at 1 year which is well below the ASTM limit for higher sulphate resistance.



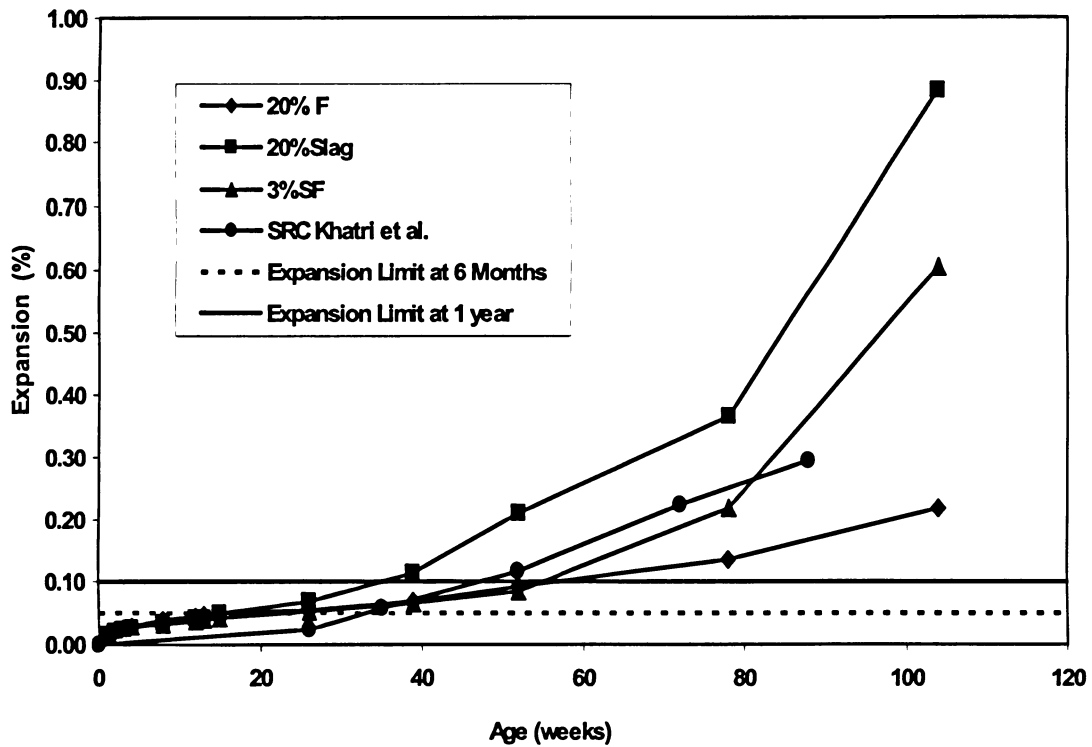


**Figure 4.6: Effect of GGBFS and its replacement level on sulphate resistance**

The increased sulphate resistance of GGBFS with increase in the replacement may be due to a combination of factors such reduced permeability due to pore refinement as a pozzolanic reaction, dilution effect, and preferential intake of  $Al_2O_3$  of the GGBFS by the C-S-H gel as suggested by Gallop and Taylor 1999 .

#### 4.1.4 Comparison of effect of class F fly ash, silica fume and GGBFS on replacement level

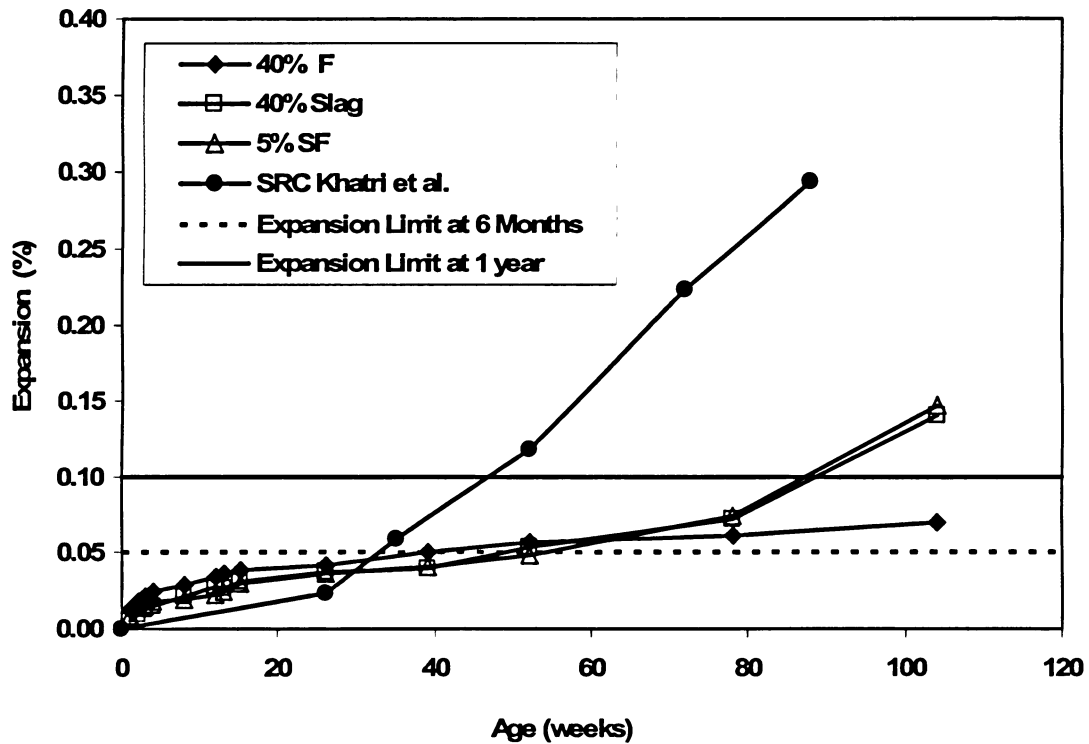
Figures 4.7 and 4.8 show the expansion, up to two years, of samples containing binary blends of silica fume, low-calcium fly ash or slag. The graphs also include, as a reference, the expansion of mortar bar sample containing sulphate resisting cement (SRC) from the study by Khatri et al, 1997.



**Fig. 4.7: Expansion of mortar bar samples containing binary blends of SCM at replacement levels of 20% for low-calcium fly ash and slag, and 3% for silica fume.**

The expansion of this sample was used since the experimental program presented in this research did not include samples containing sulphate resistant cement. In Figure 4.7, the samples containing 20% slag did not meet expansion limits at 6 months or 1 year for high sulphate resistance cement but for the moderate sulphate resistance cement. The samples containing 3% silica fume and 20% low calcium fly ash, however, met both limits. An interesting observation from Figure 4.7, though, is the rate of expansion of samples with 3% SF or 20% slag after the age of 78 weeks. Both samples had expansion rates, before the age of 78 weeks, similar to that of the SRC. However, the rate increased significantly after 78 weeks and exceeded that of the SRC cement. It should be noted that the 3% SF sample met both expansion criteria at 6 months and 1 year. This suggests that reducing permeability may

be the main mechanism by which slag and silica fume enhances sulphate resistance. When enough sulphate ions were able to penetrate the samples to form the amount of ettringite sufficient to generate internal stress to cause microcracking after 78 weeks, the microcracking caused the increased rate of ionic diffusion leading to formation of more ettringite and subsequently more internal stress causing sharp expansion of the mortar bars. It is important to note a fact that the amount of silica fume used in this case was 3% which is the amount quite less than it is needed to consume the all portlandite. According to other research work (Hewlett 2001), higher degree of replacement of silica fume (15%) is needed for ordinary Portland cement to improve the resistance of mortar to sulphate attack at least up to 4 years of immersion. A study report (Hooton 1993) also suggests 10% replacement of silica fume to be appropriate for better sulphate resistance. This is also supported, to some extent, by the pattern of the diffractogram (Figure 4.15) which did not reflect any differences in the hydration products between the CH1 and the SF/CH1 samples, in addition to the presence of monosulphate phase in both samples. Contrary to slag and silica fume, the expansion rate of low-calcium fly ash after 78 weeks is similar to that of the SRC cement. This suggests that low calcium fly ash enhances sulphate resistance by other mechanisms, in addition to reducing permeability, perhaps by reducing the portlandite (calcium hydroxide) content due to its higher pozzolanic reactivity.



**Fig. 4.8: Expansion of mortar bar samples containing binary blends of SCM at replacement levels of 40% for low-calcium fly ash and slag, and 5% for silica fume.**

Figure 4.8 shows the expansion rates of samples containing 40% low-calcium fly ash and slag, and 5% silica fume. There is a slight increase in the expansion rate beyond 78 weeks for the slag and silica fume samples; however, the rate is still lower than that of the SRC cement. One would expect the permeability of samples containing higher levels of SCM to be lower than those with less SCM. Accordingly, the sulphate ions may take longer time to penetrate the samples shown in Figure 4.8, especially the SF and slag samples as there is some increase in the expansion rate already observed after 78 weeks. In other words, the expansion rate of these samples may increase at a later age when the formation of ettringite would be able to cause microcracking leading to increased rate of diffusion of sulphate ions. The low-calcium

fly ash, continue to perform exceptionally well compared to all other samples including SRC cement.

Based on the expansion trend of the binary blend containing silica fume or slag, it can be said that the efficacy of the blend increases with increase in the replacement level. However, the increased rate of expansion after 78 weeks at the lower replacement level suggests that permeability is the main mechanism by which slag and silica fume enhances sulphate resistance. The same can be ascribed for ternary blends containing silica fume and high-calcium fly ash. This is also supported, to some extent, by the pattern of the diffractogram (Figure 4.15) which did not reflect any differences in the hydration products between the CH1 and the SF/CH1 samples, in addition to the presence of monosulphate phase in both samples. When enough sulphate ions were able to penetrate the samples and cause microcracking (after 78 weeks), the microcracking increases the rate of ionic diffusion leading to formation of more ettringite and subsequently more internal stress causing sharp increase in expansion of the mortar bars. The silica fume and slag, therefore, at the lower replacement level do not control the sulphate attack but just postpone it. The eventual sharp rate of expansion after 78 weeks prompts any one to think about how much years of service in the real field environment are represented by this time period. Is the period of one year prescribed by ASTM C 1157 enough to predict the expansion that occurs in the real field? One can argue that the period of one year, for the mortar bar of small cross section (25 mm x 25 mm) and exposed to the severe testing conditions of the ASTM C 1012, is sufficient to represent a long service life for concrete exposed to real field environment. While this argument may be valid, it will be of interest and importance to collect long-term field data on

the performance of blended cement, especially ternary blends of SF /HCFA, against sulphate attack.

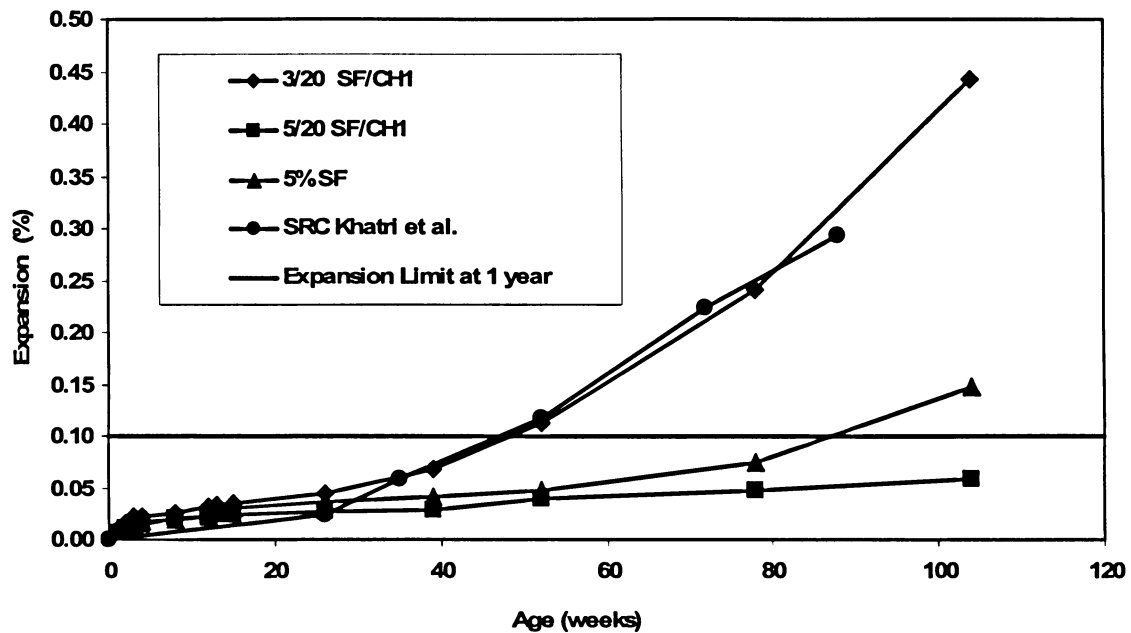
#### **4.1.5 Enhancing the Performance of High Calcium Fly Ash**

Figures 4.1, 4.2 and 4.3 clearly illustrate the low efficiency of high-calcium fly ash in mitigating sulphate attack. Three distinct approaches were adopted to enhance the performance of the same two high-calcium fly ashes which had given the inferior sulphate resistance when studied as a binary blend with GU cement. The first attempt was the creation of ternary blend with the use of small amount of silica fume, high-calcium fly ash and GU cement; the second attempt was the creation of ternary blend with the use of slag, high-calcium fly ash and GU cement and the third attempt was the introduction of gypsum (as a source of sulphate) to fly ash to adjust the sulphur to alumina ratio to produce more ettringite rather than monosulphate at early stage of the hydration.

##### **4.1.5.1 Properties of Ternary Blends of Silica Fume and High Calcium Fly Ash:**

Fly ash CH1 was used in this study as this is the ash that had shown the least resistance to sulphate attack. The expansion results are shown in Figure 4.9. The ternary blend sample containing 3% SF and 20% CH1 met the expansion criterion at 6 months (0.044%) but did not meet the 0.10% expansion limit at 1 year (0.113%). In addition, the expansion of this sample exceeded that of the SRC at ages beyond 78 weeks. On the other hand, adding 5% silica fume to CH1 fly ash significantly enhanced the resistance to sulphate. The expansion of the 5/20 SF/CH1 fly ash sample was 0.07% at 2 years. The expansion rate of this sample

was much lower than that of the SRC and the sample containing 5% SF.

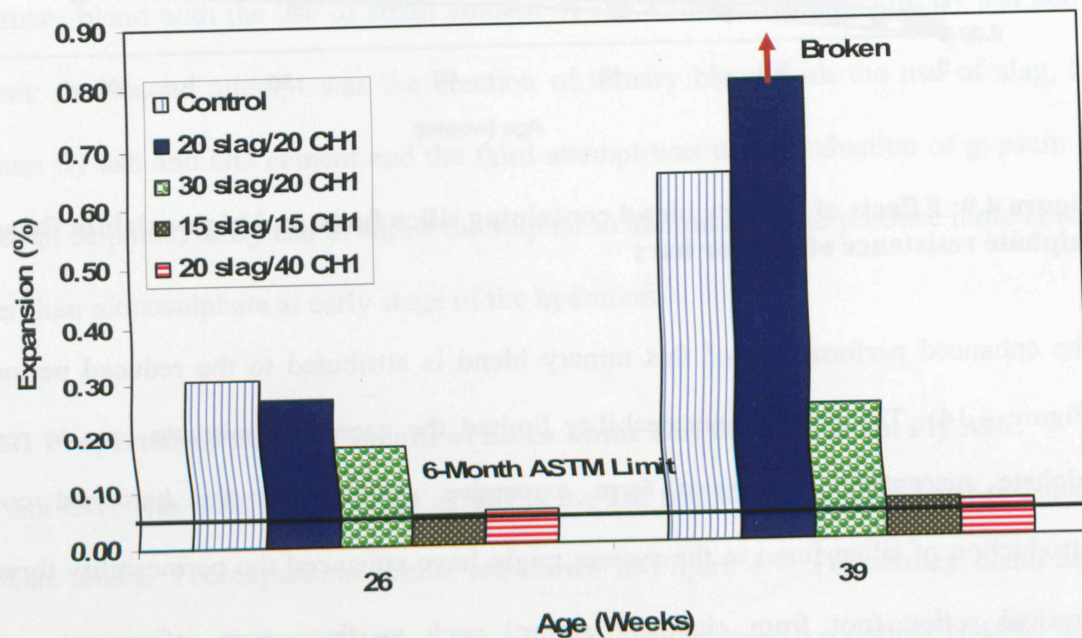


**Figure 4.9: Effects of ternary blend containing silica fume and high-calcium fly ash on sulphate resistance of mortar bars**

The enhanced performance of this ternary blend is attributed to the reduced permeability (Figure 4.14). The reduced permeability limited the access of sulphate ions to reach the sulphate susceptible phases to form expansive ettringite in the hardened concrete. Introduction of silica fume in the system might have enhanced the permeability through its physical action (not from chemical action) such as from pore refinement and pore densification due to its very fine particle sizes. The diffractogram (Figure 4.15) shows almost identical hydration product of the ternary blend containing class CH1 fly ash and silica fume and that of the binary blend containing 20% CH1. The diffractogram of both blends have shown the sulphate susceptible phases as monosulphate, calcium hydroxide and tricalcium aluminate in the similar amount.

#### 4.1.5.2 Properties of ternary blend of slag with High Calcium Fly Ash:

Literature review shows that there have been number of studies for ternary blend consisting of slag and fly ash in terms of its strength. But there is no record of study of the blend against its efficacy in the sulphate bearing environment. Therefore, this is an unprecedented study for this sort of blend against sulphate attack. The result of the ternary blend of fly ash, slag and GU cement with varied level of replacement are shown in figure 4.10.



**Figure 4.10: Effects of ternary blend containing slag and high-calcium fly ash (fly ash CH1) on sulphate resistance of mortar bars**

The results show that the blend containing 15 % slag and 15% CH1 fly ash provided the lowest expansion of all the blends with the expansion value of 0.053% at 6 months. The expansion value of the blend is slightly above the ASTM limit for high sulphate resistance cement at six months. Another blend containing 20 % slag and 40% CH1 fly ash showed



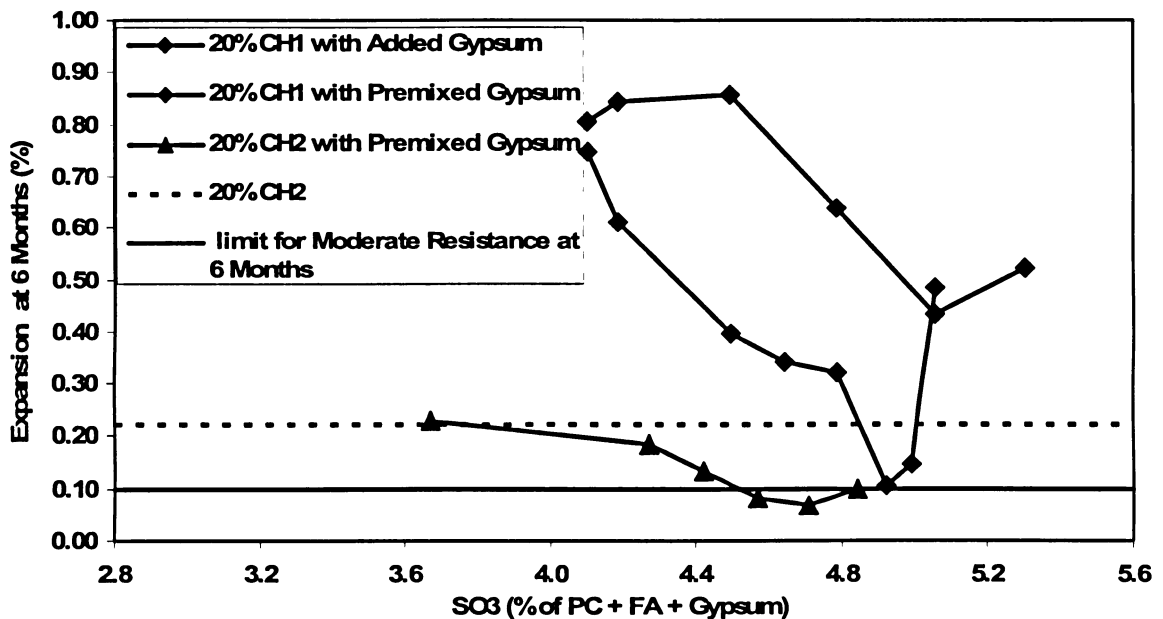
slightly higher expansion than that of the aforementioned blend with the expansion amount of 0.060% at 6 month, however, showing the expansion value well below the limit for moderate sulphate resistance as per ASTM C 618. However, the ultimate expansion result of blend containing 20% slag and 40 % CH1 fly ash at 39 weeks (0.067%) is found to be better than that of the blend containing 15% slag and 15% CH1 fly ash at the same period (0.068%). The blend containing 20 % slag and 20% CH1 fly ash although had shown slightly lower expansion than control sample at 6 months, ultimately broke at 39 weeks showing inferior performance of the all blend. Similar inferior performance is observed for the blend containing of 30% slag and 20% CH1 fly ash. Out of tested three mortar bars for the blend, two of them broke at 39 weeks. The mechanism behind the performance of the aforementioned two blends could not be explained as the previous study on binary blend consisting of slag had shown the increased performance with increase in the replacement level of slag whereas the fly ash CH1 had shown the opposite effect (decreased efficacy with increase in the replacement level). RCPT result of the blend consisting of 15% slag and 15% CH1 fly ash doesn't show much improvement in its permeability over the permeability of the blend of mere 20% CH1 ash (Figure 4.14). Therefore, permeability is not the cause behind their superior performance. There must be another mechanism behind the efficacy of these blends. Further investigation is necessary.

#### **4.1.5.3 Effects of Gypsum addition to High Calcium Fly Ash:**

A study was carried out with addition of varied amount of gypsum to both types of fly ashes each-class CH1 and class CH2- in two ways: (1) addition to the mix ingredients during

mixing or (2) premixed with the fly ash in a microdeval apparatus for 1 hour to allow an intimate contacts or better mixing of fly ash and gypsum

Different levels of gypsum were used as listed in Table 3.2 in which the  $\text{SO}_3$  content in the mix is expressed as a percentage of total mass of the dry ingredients (PC + FA + Gypsum).



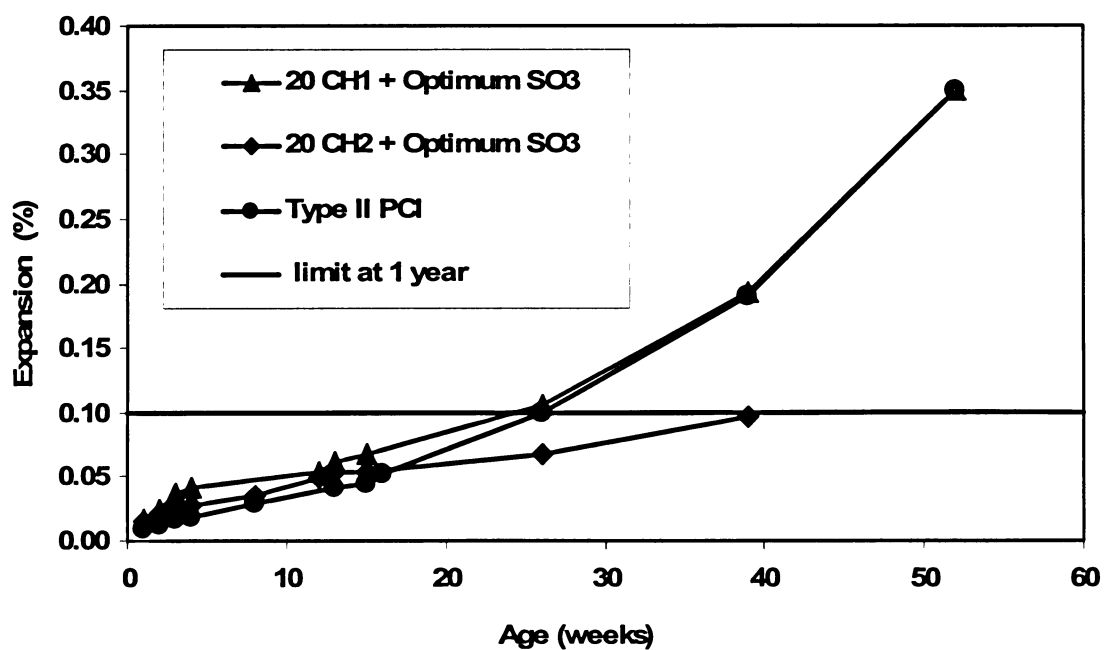
**Figure 4.11: Effects of  $\text{SO}_3$  content of cementing blend (PC + FA + Gypsum) on the 6-month expansion of mortar bars**

Figure 4.11 shows the 6-month expansion results of the two types of high-calcium fly CH1 and CH2 mixed with different levels of gypsum. The graph was plotted between the expansion and the total amount of  $\text{SO}_3$  in the cementing system (PC + Gypsum + FA) as a percentage of total mass of dry ingredients. The graph shows that premixing the gypsum with fly ash resulted in the lower expansion than that of added gypsum at all replacement level. The result clearly suggests that premixing the gypsum with fly ash is much more effective in enhancing sulphate resistance than adding gypsum to the mixing ingredients. For the both types of fly ashes there was the optimum level of  $\text{SO}_3$  content at which the lowest

amount of expansion was observed. However, the optimum amount of  $\text{SO}_3$  content was different for two types of fly ashes. The optimum  $\text{SO}_3$  content for class CH1 fly ash was found to be 4.9%. Addition of 4.9%  $\text{SO}_3$  per total mass of cementing materials (or 8.2%  $\text{SO}_3$  from  $(\text{gypsum} + \text{FA})/(\text{mass of FA and gypsum})$ ) lowered the 6 month expansion to 0.106% for fly ash CH1 which is almost at the limit of moderate sulphate resistance as specified by ASTM C 618. Similar mortar sample with no gypsum had broken before the age of 6 month. This clearly shows that addition of gypsum to the high calcium fly ash improves the sulphate resistance. However, the result exhibits this particular fly ash to be very sensitive to the gypsum contents. Any small change in the optimum gypsum content to the either side of its optimum level results in a significant increase in expansion as shown in Figure 4.11. Knowing that the sample containing fly ash without gypsum broke before reaching the age of 6 months, one can argue that within the gypsum content investigated, the addition of gypsum enhances the sulphate resistance of CH1 fly ash. The optimum  $\text{SO}_3$  content for class CH2 fly ash was found to be 4.8%. Addition of 4.8%  $\text{SO}_3$  per total mass of cementing materials (or 7.2%  $\text{SO}_3$  from  $(\text{gypsum} + \text{FA})/(\text{mass of FA and gypsum})$ ) lowered the 6-month expansion to 0.0067% for fly ash CH2 which is well below the expansion limit of moderate sulphate resistance as specified by ASTM C 618. This type of fly ash, however, doesn't seem to be as much sensitive as the class C fly ash with the variation in the amount of gypsum content. The fly ash was succeeded to accommodate the  $\text{SO}_3$  in the range from 4.5% to 4.9 % to control the expansion within the limit of moderate sulphate resistance as per ASTM C 618. The range can be considered to be the wide and comfortable for producing sulphate resistance cement with gypsum optimization. With the optimum level of  $\text{SO}_3$  of 4.8%, the expansion of

mortar containing this type of fly ash was reduced to 70% of the expansion of the samples containing this fly ash without the addition of Gypsum.

The rates of expansion of samples containing CH2 and CH1 with the optimum  $\text{SO}_3$  content are compared to the expansion rate of Type II Portland cement (moderate sulphate resistance) from a study by (Rodriguez-Camacho and Uribe-Afif, year ) in Figure 4.12.



**Fig. 4.12: Comparison of the expansion rates of mortar bars containing Type II (moderate sulphate resistance PC) with bars containing high calcium fly ashes CH2 and CH1 with optimum  $\text{SO}_3$  contents.**

The expansion rate of CH1 with optimum  $\text{SO}_3$  was identical to that of the moderate sulphate resistance cement (Type II). The expansion rate of the CH2 was better than that of Type II cement. The main reason behind the improved performance class CH1 and class CH2 fly ashes is due to the formation of more amount of ettringite at the early stage of hydration. The fact is clearly evidenced by the pattern of the diffractogram (Figure 4.15). The diffractogram

shows that the blend containing introduced gypsum produced the comparatively higher amount of ettringite. Addition of gypsum in such types of fly ash/cement system favors the formation ettringite at the early age as result of a reaction of gypsum with  $C_3A$ . In terms of the permeability, the blend was found to be the one with highest level of permeability of all of the tested samples (Figure 4.14).

The above study results showed that ternary blend of silica fume or slag or gypsum used with high-calcium fly ash in the optimum amount were effective in enhancing the sulphate resistance of the ash. Premixing gypsum with fly ash was found to be more effective over adding the gypsum to the ingredient during mixing (as an additive). Optimum gypsum content was different for the two different types of fly ashes in the study. Fly ash CH1 was more sensitive to the gypsum content. Any small change in the optimum gypsum content to the either side of its optimum level resulted in a significant increase in expansion. CH2 fly ash, however, was not as sensitive as CH1 fly ash to variation in the amount of gypsum content. On the basis of variation in optimum gypsum content for these two fly ashes, one can deduce that it is necessary to establish the optimum gypsum content for each of fly ash depending on its mineralogical composition. In the same way, it is necessary to establish the optimum gypsum content for the cement with different composition, specifically the sulphur and aluminate content. The approach of addition of silica fume or slag seems much more effective over the approach of gypsum optimization as the later was not effective enough to keep the expansion below the ASTM C 1157 one-year expansion limit of 0.10% for high sulphate resistance cement. However, the effects of any cementing blend on the properties of concrete also need to be considered. It has been found that the addition of modest amount of

gypsum (similar to the optimum levels obtained here) has no considerable effects on compressive strength and permeability of concrete (Freeman and Carrasquillo 1995). The addition of silica fume to concrete has been found to enhance the late strength, permeability, ion diffusivity and resistance to alkali-silica reaction (Thomas et al 1999, Radomski et al, 2007) but required more water reducers to achieve the same level of workability as that of concrete with only fly ash (Radomski et al, 2007). Addition of slag in the fly ash enhances the properties of concrete than addition of slag only and produces the higher ultimate strength (Dongxu et al 2000).

#### **4.1.6 Internal Sulphate Attack for Samples with Gypsum Addition :**

With the addition of gypsum, there is always the menace of internal sulphate attack due to excessive amount of  $\text{SO}_3$ . There is a possibility that the reaction of aluminate phase occurs at a higher rate than that of the dissolution of  $\text{SO}_3$  from gypsum. According to a study (Learch 1946) with the added gypsum, the gypsum dissolves in the mixing water together with lime formed by the hydrolysis of compounds present in the cement. The saturated lime-gypsum solution decreases the solubility of alumina in the aqueous solution and thereby retards the hydration of the aluminate phase. The rate of retardation of the hydration increases with increase in the amount of  $\text{SO}_3$  content. The study shows that peak rate of heat of hydration of aluminate phase will be shifted from 2 hours to 50 hours with change of  $\text{SO}_3$  contents from 1.25% to 3.5% respectively. This 50- hour is the period far beyond the period of final setting of Portland cement. So from the above study result, it can be inferred that addition of gypsum beyond the optimum level causes the precipitation of non-reacted  $\text{C}_3\text{A}$  in the hardened paste due to its decreased solubility which at the later age reacts with residual

gypsum to cause internal sulphate attack. However, another theory (Crammond 1984) which contradicts with the above theory states that the coarsely crystalline gypsum within the matrix reacts with cement alkalis to form plates of portlandite along the boundaries of gypsum particles. The conversion of gypsum into portlandite releases sulfate ions into the adjoining cement paste at the later age. The sulphate ions react with aluminate bearing phases (tricalcium aluminate or hydrogarnet or monosulphate) and form ettringite in the hardened concrete and causes expansion and disruption.

To investigate the possibility of internal sulphate attack, identical samples of mortar bars were prepared and stored in lime water.

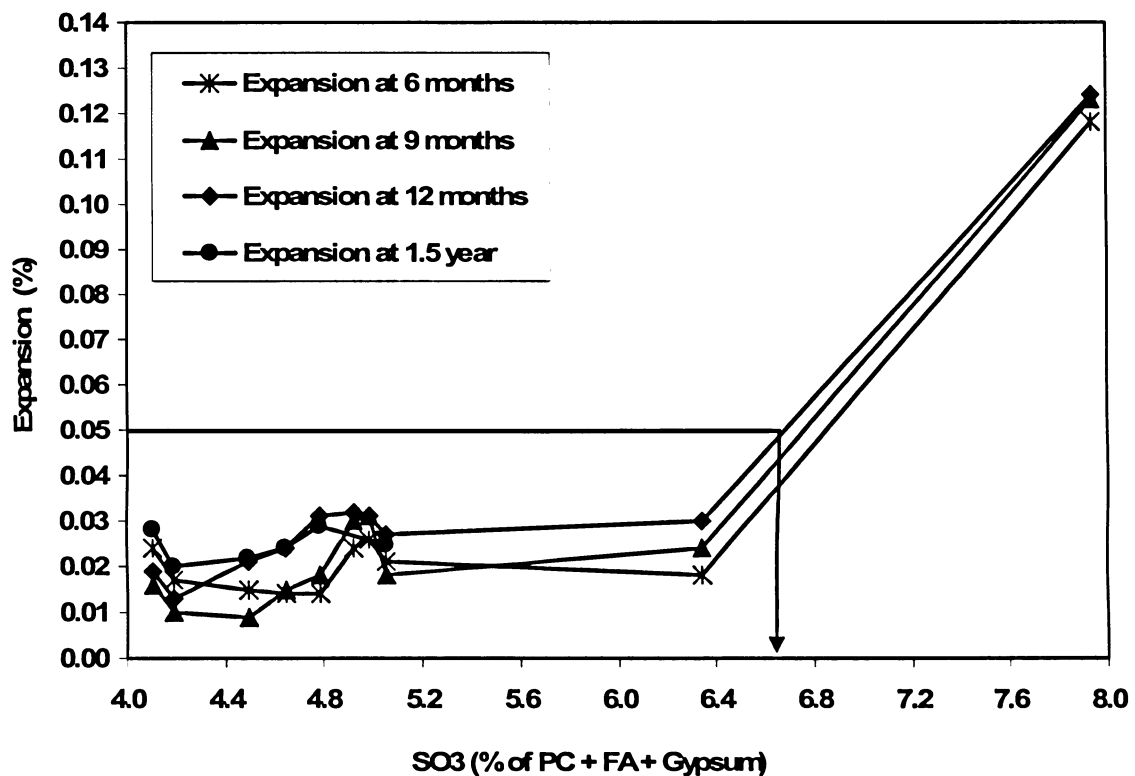
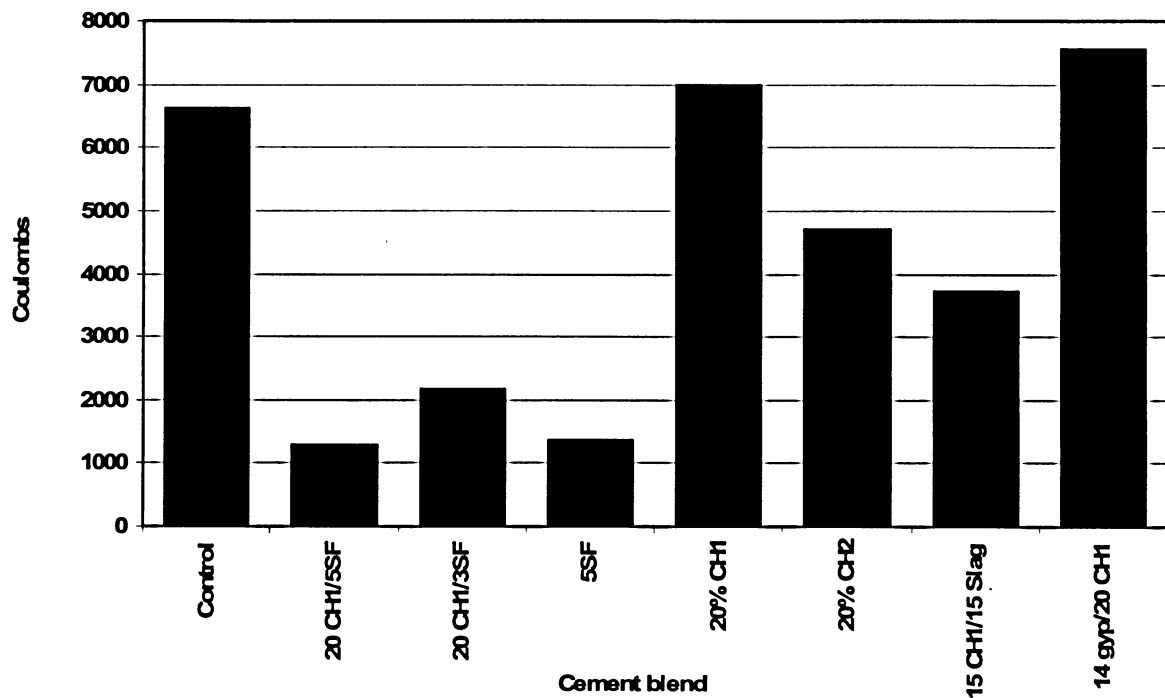


Fig. 4.13: Effects of SO<sub>3</sub> content on the expansion of mortar bars soaked in lime solution

Some of the results are presented in Figure 4.13 which demonstrates that internal sulphate attack occurs only when  $\text{SO}_3$  exceeds 6.6% by total mass of gypsum + FA + PC which is beyond the optimum levels developed for the two high-calcium fly ashes in this research study.

#### 4.1.7. Rapid Chloride Permeability Test (RCPT) results

Samples prepared from 8 different mixes were tested for RCPT to investigate the relative permeability of the mixes. The test results at 56 days are shown in Figure 4.14.



**Figure 4.14: Chloride Ion Permeability of different mixes for 56 days of curing at 35°C**

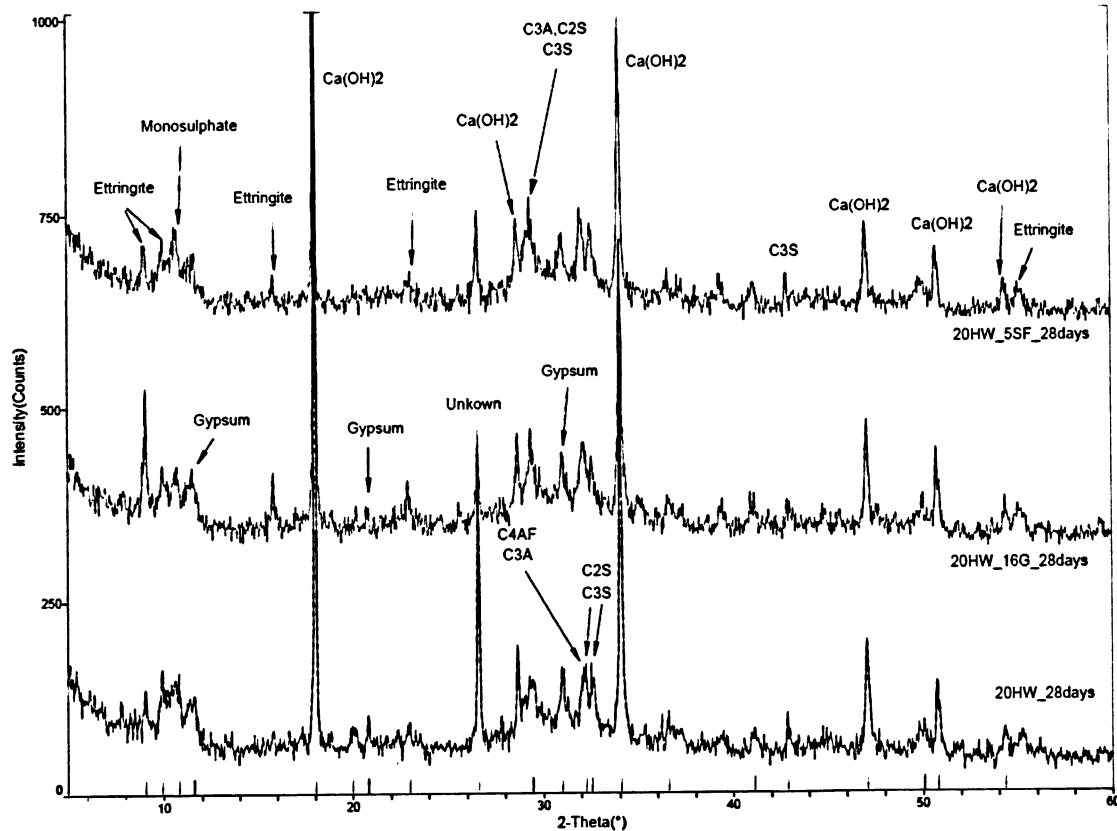


The results show that the ternary blend containing 20% class CH1 fly ash and 5% silica fume provided the lowest permeability with the total charge passed as 1291 coulombs. The permeability of sample containing 5% silica fume was also in the comparable range with the given ternary blend with the total charge passed as 1376 coulombs. In the contrary, permeability of the blend containing 14% gypsum (as a percentage of fly ash) was comparable with the blend containing 20% class CH1 fly ash (total charge passed 6998 coulombs) and the control sample (total charge passed 6627 coulombs). The total charge passed for the blend containing 14% gypsum was 7557 coulombs. From the above permeability result, it is evident that addition of gypsum doesn't significantly change the permeability. Hence the benefit of gypsum addition in fact is the stabilization of reactive aluminate phase.

#### **4.1.8 X-ray Diffraction Patterns**

To study the different phases produced in the hydration products, x-ray diffraction of the three different pastes of mix containing 80% Portland cement and 20% CH1 Fly Ash; 80% Portland cement and 20% CH1 Fly Ash and Gypsum (16% of Gypsum as percentage of fly ash); and 75% Portland cement, 20% CH1 Fly Ash and 5% Silica were carried out. The results of the x-ray diffraction are presented in Figure 4.15. Out of the three studied samples, except for the production of comparatively more amount of ettringite (evidently observed in the form of a sharp peak) in the sample containing 16% of gypsum (as a percentage of fly ash), all the samples produced almost similar amount of monosulphate. The x-ray diffraction result suggests that except for the blend containing introduced gypsum, either there should be other phases in the hydration product that were not detected by x-ray diffraction or there

should be another mechanism behind the performance of other two blends in sulphate bearing environment.

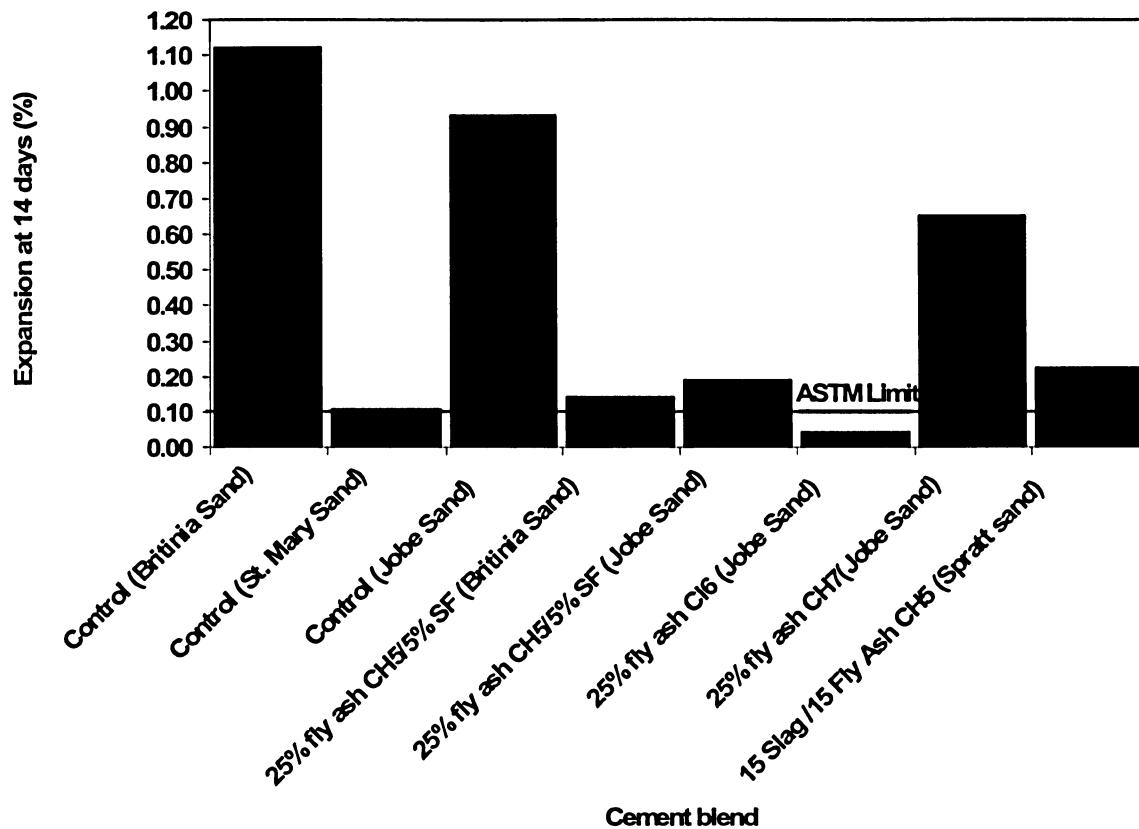


**Figure 4.15: Diffractogram showing the composition of paste samples containing: (1) 5/20 SF/CH1, (2) 20% CH1 + gypsum, and (3) 20% CH1.**

In any case, the x-ray diffraction confirmed that the addition of gypsum produces more ettringite and this, apparently, is the mechanism by which gypsum addition enhances the performance of high-calcium fly ash against sulphate attack.

## 4.2 Alkali-Silica Reaction

Expansion results of mortar bars containing different blend of cementing materials at 14 days are shown in figure 4.16. The ASTM C 1567 expansion limit of 0.10% for innocuous behavior of aggregate for AMBT test is also provided in the same figure.

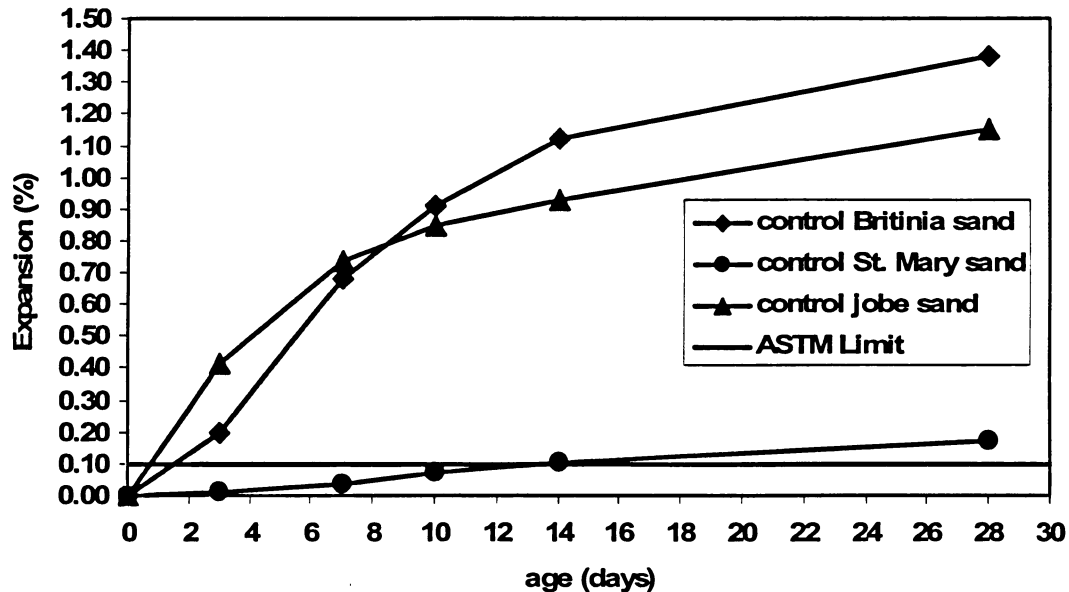


**Figure 4.16: Expansion result of mortar bars containing different blend of cement under Accelerated Mortar Bar Test**

The Figure 4.16 shows that the control sample containing Britania sand from Western Canada showed the highest expansion with the expansion value of 1.121% at 14 days whereas the sample containing 25% fly ash CI6 with sand from New Mexico known as “Jobe Sand” has given the lowest order of expansion with the expansion value of 0.042% at 14days. The expansion results of mortar bars were investigated in terms of reactivity of different aggregate along with different types of SCMs.

#### 4.2.1 Effect of types of aggregate

Three different types of fine aggregates (Britinia sand, Jobe sand and St. Mary sand) were used for the study against ASR in the form of AMBT. The expansion result of mortar bars containing these three different types of fine aggregates are provided in Figure 4.17



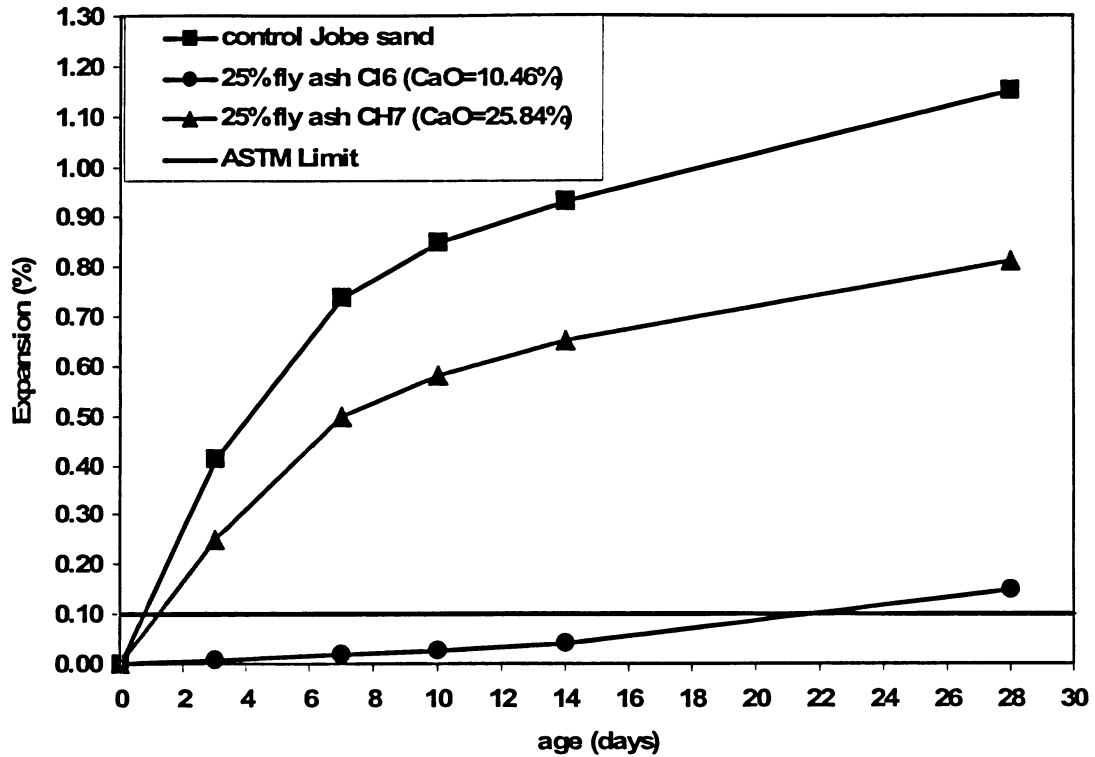
**Figure 4.17: Effect of aggregate type on expansion of mortar bars under Accelerated Mortar Bar Test**

Figure 4.17 clearly shows that the expansion of mortar bars containing St. Mary sand is very low (0.010%) at 3-day and its ultimate expansion at 14-day is 0.107%. The ultimate expansion of these mortar bars at 14-day is slightly above the of ASTM C 1260 limit of 0.10%. Therefore, in terms of reactivity, the St. Mary aggregate can be termed as innocuous. The expansion of mortar bars containing Britinia sand is 0.198% at 3-day whereas the expansion of mortar bars containing Jobe sand is 0.414% which is more than two time the expansion of Britinia sand for the same duration. But the ultimate expansion of Britinia sand at 14 day is 1.121% which is 1.2 times more than that of Jobe sand (0.931%) at the same time

period. As the expansion limit of both sands exceeds 0.20%, they can be termed as deleteriously expansive as per ASTM C 1260. The expansion trend suggests that Britinia sand is highly sensitive to alkalinity. According to a study (Thomas et al 2007), alkali level in the pore solution for high alkali cement remains minimum before immersing in the 1N NaOH solution due to leaching of alkali during storage in water at 80°C for 24hr. As the mortar bar is immersed in 1N NaOH solution at 80°C, alkali from the solution starts to penetrate the mortar bars and the pore solution alkalinity starts increasing. Being alkali sensitive, Britinia sand, therefore, exhibited lower expansion at the 3<sup>rd</sup> day but the higher expansion at the 14<sup>th</sup> day.

#### **4.2.2 Role of fly ash and its CaO content**

A fly ash CI6 (CaO=10.46%, Na<sub>2</sub>O<sub>e</sub>=1.50%) and another fly ash CH7 (CaO=25.84%, Na<sub>2</sub>O<sub>e</sub>=1.73%) were investigated using reactive Jobe sand with replacement level of 25% each. The expansion result of mortar bars is shown in the Figure 4.18. The Figure shows that replacement of cement with both types of fly ash produced better ASR resistance. However, the replacement of cement with fly ash CI6 succeeded to control 14-day expansion well below the prescribed ASTM limit of 10% with the expansion value of 0.04%.



**Figure 4.18: Effect of fly ash and its CaO content on expansion of mortar bars under Accelerated Mortar Bar Test**

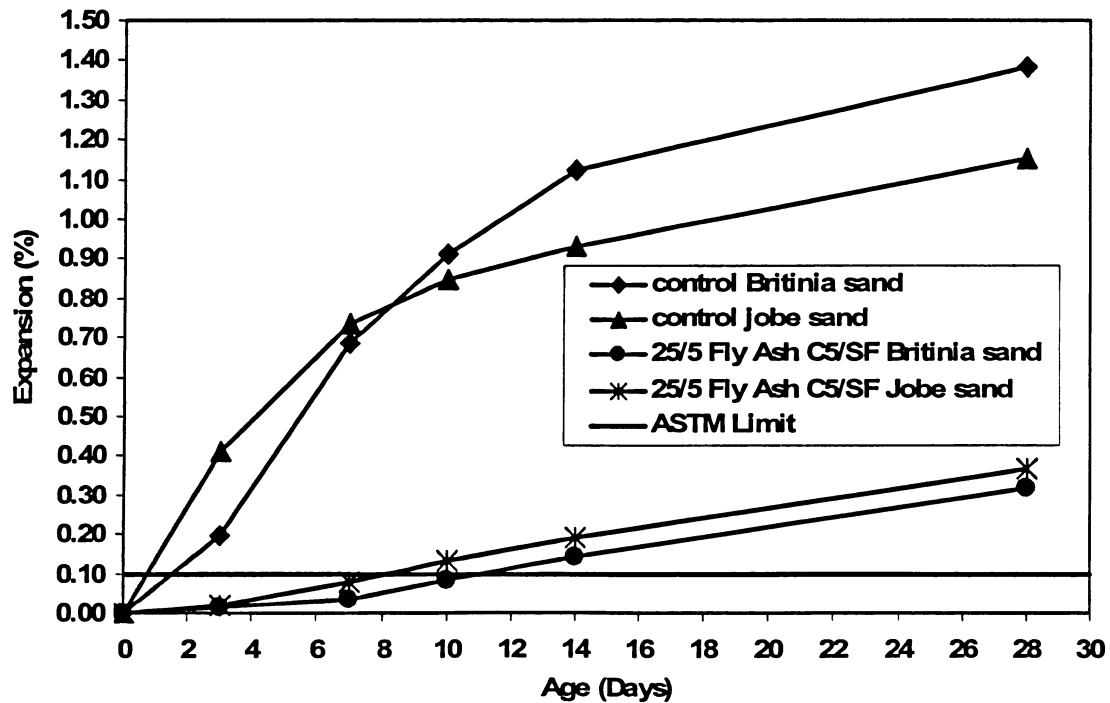
The enhanced efficacy of the fly ash CI6 is due to the following two reasons:

- i) According to a study result (Shehata and Thomas 2006), alkali release characteristics the hydration product consisting of supplementary cementitious material depends upon the ratio of  $(\text{Na}_2\text{O}_e, \text{CaO}) / \text{SiO}_2$ . The fly ashes C6 and C7 have CaO and  $\text{SiO}_2$  content of 10.46% and 53.10%, respectively. Addition of such fly ash in the cement means to reduce CaO content and increase  $\text{SiO}_2$  content which ultimately produces hydration products that release less amount of alkali to the pore solution or in other words, binds alkalis from the concrete pore solution.
- ii) RCPT test result (Figure 4.20 and Appendix B1) shows that the chloride ion permeability of the mix containing fly ash CI6 is very low i.e., 316 coulombs in 6 hrs. Due to its reduced

permeability, rate of penetration of alkali from the NaOH solution is very low. Therefore, due to availability of lower amount of alkali from the external source within the relative short span of test period of 14-day, the rate of ASR is low despite higher reactivity of aggregate. Same principle holds for fly ash CH7 too. It should be stated that earlier studies (Shehata and Thomas, 2000, 2002) have shown low-calcium fly ash to be very effective mitigating ASR in both accelerated mortar bar and concrete prism tests which suggest that the role of permeability is secondary compared to the high ability of low calcium fly ash in binding alkalis. If the accelerated mortar bar test (AMBT) is allowed to run for a longer time, the alkali concentration from the external sources increases causing more expansion. This can also be evidenced from the fact that rate of expansion is in the increasing order for the blend containing fly ash CI6 after 14 days (Figure 4.18). This shows that extending the testing period from 14 to 28 days may underestimate the efficacy of adequate preventive measure such as low-calcium fly ash.

#### **4.2.3 Role of ternary blend**

Ternary blend was prepared with the addition of 5% silica fume and 25% of CH5 fly ash (high-calcium fly ash) to the GU cement and tested for both Britinia sand and Jobe sand. The expansion result of mortar bar is provided in Figure 4.19. The figure shows that with the addition of 5% of silica fume and 25% of class CH5 fly ash, expansion reduced to 0.144% from 1.121% of the control sample containing Britinia sand. In the same way expansion reduced to 0.190% from 0.931% of the control sample containing Jobe sand.



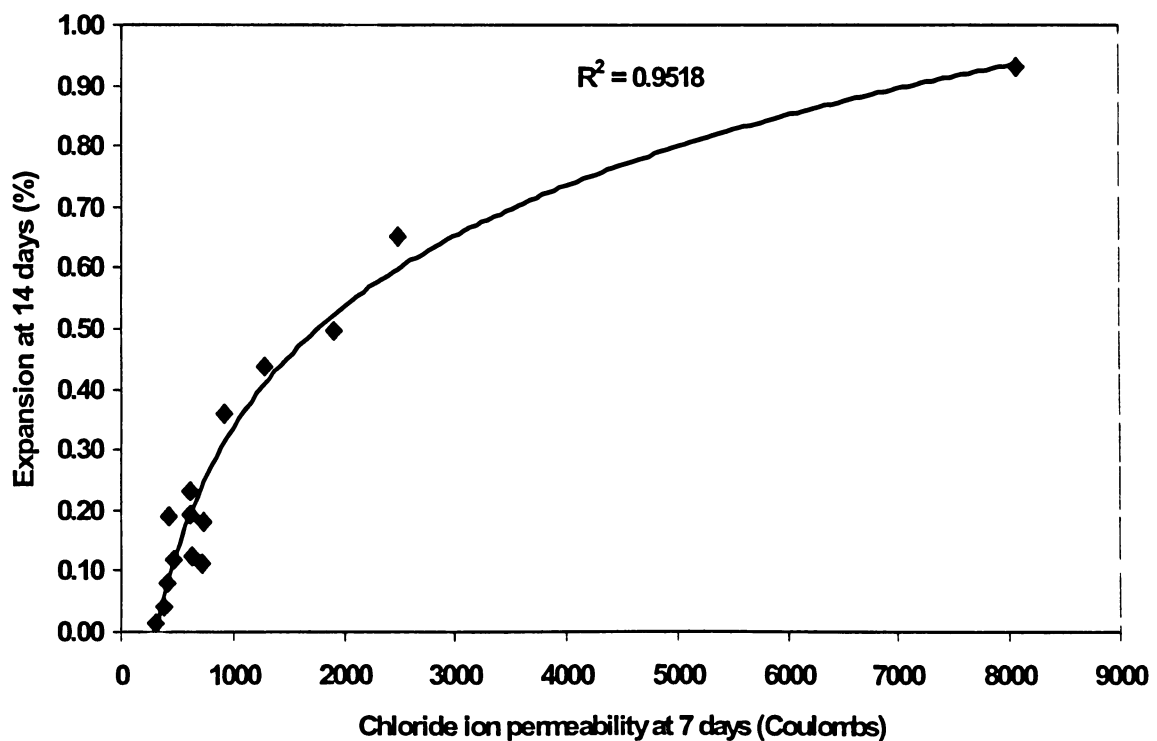
**Figure 4.19: Effect of ternary blend of fly ash and silica fume on expansion of mortar bars under Accelerated Mortar Bar Test with two different types of reactive aggregates**

The amount in the reduction of expansion was found to be higher ( $1.121\% - 0.144\% = 0.977\%$ ) for Britinia sand in comparison to that of Jobe sand ( $0.931\% - 0.190\% = 0.741\%$ ). However, the ternary blend was not successful to keep the expansion below the prescribed ASTM limit of 0.10% for 14 days. The reason could be due to the addition of lower amount of silica fume in the ternary blend. A study result (Radomski 2005) shows that higher amount of silica fume ( more than 7%) needs to be added in the ternary blend with some types of high calcium fly ash and highly reactive sand. The increased efficacy of the ternary blend is due to its reduced chloride ion permeability (411 coulombs) (Figure 4.20 and Appendix B1)) coupled with the higher alkali binding capacity with decreased  $\text{CaO/SiO}_2$  ratio upon the addition of more  $\text{SiO}_2$  in the form of silica fume.



#### 4.2.4 Relationship between permeability and expansion

To study the relationship between permeability and expansion of mortar bars in the AMBT test, mortar cylinders were prepared with varied amount of SCMs, simulated the curing conditions and tested at 7 days to represent the average permeability of the sample during the testing period of 14 days. In order to get the more statistically reliable results, some of the expansion data were taken from Radomski 2005. The relation is shown in Figure 4.20.



**Figure 4.20: Effect of permeability on expansion of mortar bar under Accelerated Mortar Bar Test**

The result shows that there is very strong correlation between permeability and expansion in the form of AMBT. The higher value coefficient of determination ( $R^2=0.9518$ ) shows the higher degree of goodness of fit of the given data. Therefore, from the result, it can be argued that, for the ASR test in the form of AMBT, permeability is a contributing factor in

determination of the expansion. One can also argue that the factors that lead to low permeability also lead to high alkali binding capacity. Increasing the silica content in the cement blend produces more hydration products which reduces the permeability and increases the alkali binding at the same time.

Based on the result of AMBT test it can be said that the performance of fly ash against ASR depends upon its CaO content. It is presumed that the addition of low calcium fly ash helps reduce Ca/Si ratio of the hydration product which binds the alkali by attracting the positive charge  $\text{Na}^+$  and  $\text{K}^+$  ions. But with the addition of fly ash with higher calcium content increases the Ca/Si ratio thereby decreasing the alkali binding capacity of hydration product. However, the graph plotted between expansion and chloride ion permeability (Figure 4.20) clearly shows that the expansion in the AMBT is also governed by the permeability of the samples. The lower the permeability, the lower is the expansion. It should also be mentioned that the factors that leads to low permeability are also the same that lead to high alkali binding capacity. More reactive silica in the system produces more hydration products which enhance the pore structure (reduce permeability) and at the same time bind more alkalis. Therefore, the reduced expansion of mortar bars containing fly ash with low CaO content is due to its lower permeability and high alkali binding capacity. Same can be said to the ternary blend containing silica fume and class CH5 fly ash.

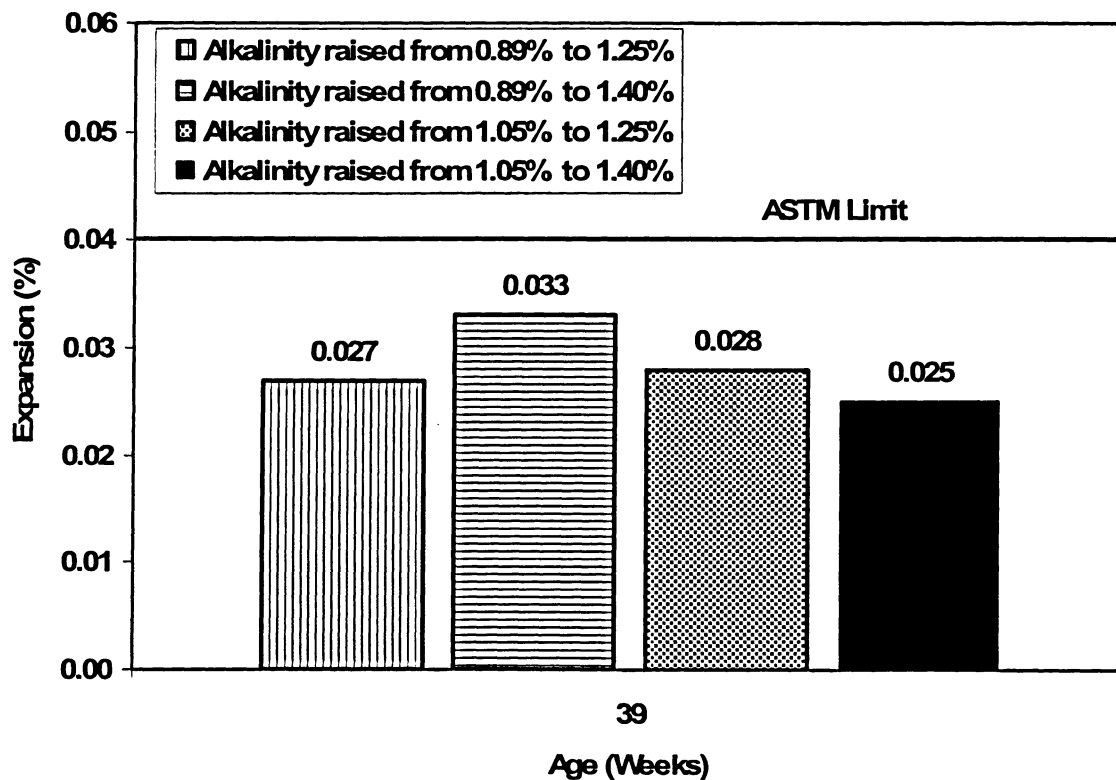
#### **4.2.5 Concrete Prism Test**

Concrete prism tests were carried out with the use of GU cement of four different  $\text{Na}_2\text{O}_e$  content (0.89%, 0.95%, 1.02% and 1.05%), a reactive Britinia Sand, a reactive Spratt coarse

aggregate and, two high calcium fly ashes (fly ash CH5 and fly ash CH8), a silica fume and a slag as variables. Effect of each variable on the concrete expansion was studied.

#### **4.2.6 Effect of alkali content of cement**

Effects of alkali content of cement on expansion of concrete prism containing reactive Britinia Sand are shown in Figure 4.21. The ASTM C 1293 expansion limits of 0.04% for 1 year for ASR resistance concrete cement have also been shown in the same figure. Expansion of concrete prism containing cement with alkalinity of 0.89% at 39- week is 0.027% and that of concrete prism with cement alkalinity of 1.05% is 0.028% at the same time period when tested with raising alkalinity for both cement to 1.25%. This shows that expansion of concrete prism increases negligibly with the increase in the alkali content of cement. But when tested the same cements with alkalinity raising to 1.40%, the cement with alkalinity of 0.89% provided higher expansion of 0.033% in comparison to the cement with alkalinity of 1.05% which provided the expansion of 0.025%.



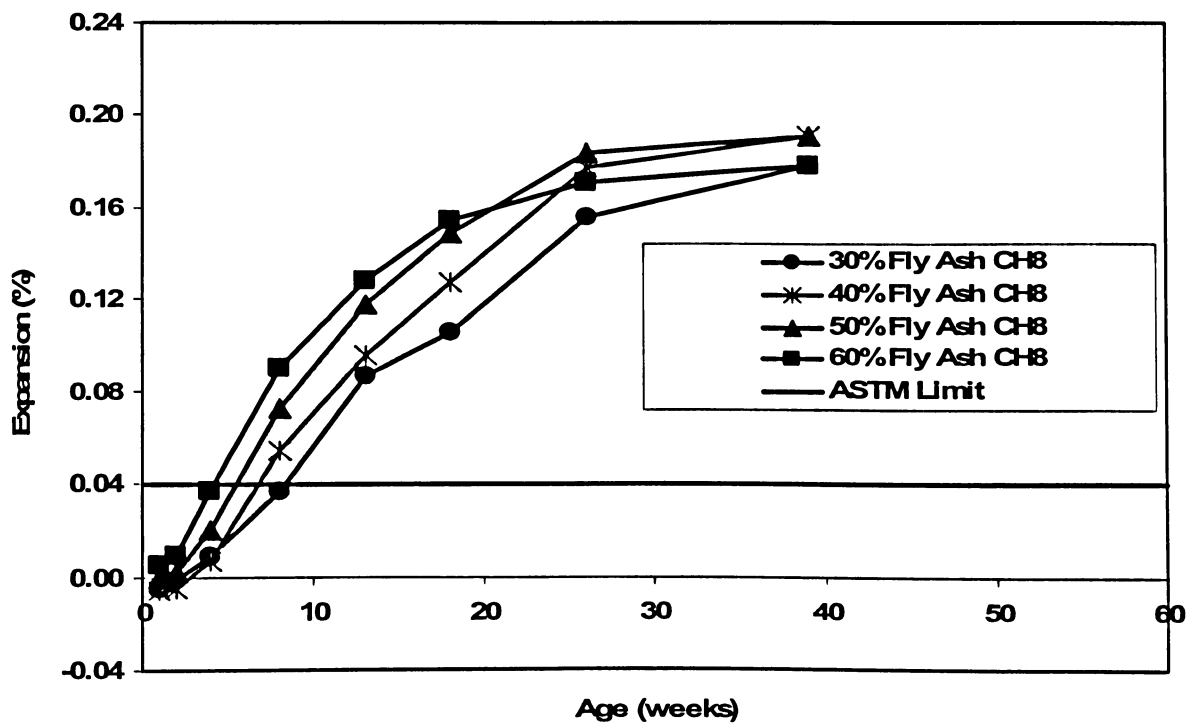
**Figure 4.21: Effect of alkali content and added alkalinity on expansion of concrete prism**

From the above expansion trend, no conclusion can be drawn about whether increase in the alkali content of cement causes increase in the expansion of concrete prism. However, it can be said that the amount of expansion of the prisms for all the above four combination (0.027%, 0.033%, 0.028% and 0.025%) are too much close to each other. This closeness of expansion for all the mixes at different level of alkalinity suggests that there must be a threshold of cement alkalinity above which ASR reaction (or concrete expansion) is less sensitive with fluctuation of cement alkalinity. Shehata and Thomas 2000 had observed very minimum increase of expansion beyond the cement alkalinity ( $\text{Na}_2\text{O}_e$ ) of  $4.20 \text{ Kg/m}^3$  (1.00%). Study carried out on concrete prism with varied level of alkalinity of cement from  $2.89 \text{ Kg/m}^3$  (0.69%) to  $5.25 \text{ Kg/m}^3$  (1.25%) and reactive siliceous lime stone (Spratt)

aggregate showed the minimum level of increase in expansion beyond the 4.20 Kg/m<sup>3</sup> (1.00%) of cement alkalinity. According to Shehata and Thomas 2000, the reaction (or more appropriately the expansion) is limited by some other factors such as the quantity of reactive silica or perhaps the availability of calcium at such high levels of alkali.

#### 4.2.7 Role of fly ash and its replacement level

Effects of fly ash and its replacement level on expansion of concrete prism containing reactive Britinia sand have been shown in Figure 4.22.



**Figure 4.22: Effect of fly ash and its replacement level on expansion of concrete with reactive Britinia sand**

Note that the fly ash used in the study contains the CaO and Na<sub>2</sub>O<sub>e</sub> in the level of 34.60% and 8.70%, respectively. The amount of both CaO and Na<sub>2</sub>O<sub>e</sub> in the fly ash is too high in comparison to the same oxides in the average fly ashes. The graph shows that the rate of

early age expansion of the concrete prism containing 30% fly ash CH8 is the lowest of all the other replacement level whereas the concrete prism containing 60% fly ash CH8 showed the higher rate of expansion at same period. The rate of expansion of all the samples started decreasing, particularly, after 13 weeks. However, the decrease in the rate of expansion was more pronounced for the prisms containing 60% fly ash CH8. Decrease in the rate of expansion was even more after the age of 26 weeks. Ultimately, the expansion of the prism containing 60% fly ash CH8 at 39 weeks was observed to be the lowest and equal to that of the prism containing 30% fly ash CH8 and the expansion value at this age of both blends were 0.178%. However, no replacement level succeeded to control the expansion level within the prescribed expansion limit of ASTM C 1293. Similar result was observed in another study (Shehata and Thomas 2000) for moderate calcium fly ash with  $\text{Na}_2\text{O}_e$  greater than 4%.

The expansion pattern of Figure 4.22 gives insight into the behavior of such types of fly ash. Expansion pattern of such fly ashes are entirely different than that observed in the common fly ash (with medium to low alkali both low and high calcium fly ashes). Indeed, the use of this type of fly ash triggered the expansion in concrete samples that performed better without the addition of the fly ash. This shows that SCM of inadequate composition (alkali content in this case) can cause more harm to concrete containing some types of reactive aggregates.

The higher rate of expansion at the early age at the higher replacement level of fly ash CH8 could be due to immediate availability of some alkali from the fly ash due to its excessively high  $\text{Na}_2\text{O}_e$  content. However, the reason behind the reduced rate of expansion at the later age for the fly ash with higher replacement level could be attributable to the rapid

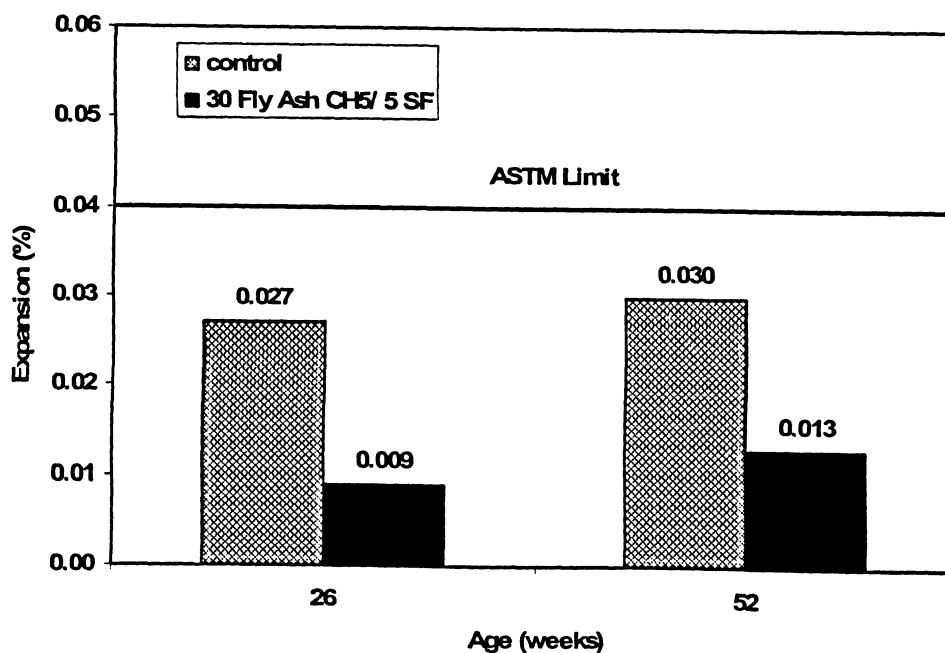
consumption of alkalis by the reactive constituents at early ages leaving less alkalis in the pore solution to fuel further reaction.

#### 4.2.8 Efficacy of ternary blends

Ternary blend was created with the use of two types of SCMs (silica fume and slag) each and class CH5 fly ash (high calcium fly ash).

##### 4.2.8.1 Ternary blend of fly ash and silica fume

Ternary blends were cast using 5% silica fume to 30% of class CH5 fly ash.



**Figure 4.23: Effect of ternary blend of fly ash and silica fume on expansion of concrete prism with reactive Britinia sand**

The expansion result of concrete prism containing Britania sand and ternary blends are shown in Figure 4.23.

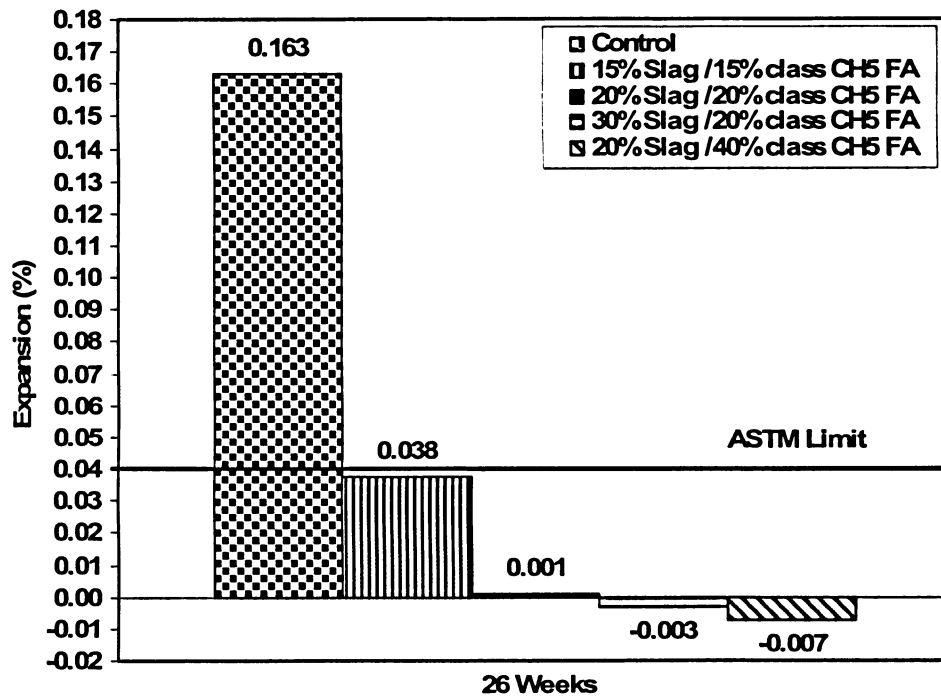
Figure 4.23 shows that with the addition of 5% of silica fume and 30% of class CH5 fly ash reduced the expansion to 0.009% from 0.027% of the control sample containing Britinia Sand at six months. In the same way expansion reduced to 0.013% from 0.030% of the control sample at one year. The reduction in the expansion as a result of ternary blend is 66.67% and 56.67% of the control sample at six months and one year respectively. The ternary blend was successful to keep the expansion limit far below the prescribed ASTM limit of 0.04% at one year. The increased efficacy of the blend may be due to the lower permeability of concrete with filler action of highly fine silica fume coupled with the higher alkali binding capacity with decreased  $\text{CaO/SiO}_2$  ratio upon the addition of more  $\text{SiO}_2$  in the form of silica fume.

#### **4.2.8.2 Ternary blend of fly ash and slag**

Like in the case of sulphate attack, there is no record of study of the ternary blend consisting of fly ash and slag against ASR. Therefore, this is also an unprecedented study for this sort of blend against ASR. The result of the ternary blend of fly ash, slag and GU cement



( $\text{Na}_2\text{O}_e=1.02\%$ ) with varied level of replacement has been shown in Figure 4.24.



**Figure 4.24: Effect of ternary blend of fly ash and slag on expansion of concrete prism with Spratt aggregate**

The 26-week expansion result of control sample prepared by Christidis 2006 using the similar Spratt aggregate is also shown in the same figure.

The results show that the blend containing 15 % slag and 15% fly ash CH5 provided the highest expansion of all the ternary blends with the expansion value of 0.038% at 26 week whereas the blend containing of 20 % slag and 40% of fly ash CH5 provided the lowest expansion of -0.007% at the same period. The expansion of blend consisting of 20% slag and 20% fly ash CH5, and 20% slag and 30% fly ash CH5 were 0.001% and -0.003%, respectively at the same period. The expansion of all the blends is quite lower than the control sample prepared using the same Spratt aggregate (0.163%). The expansion trend observed in this study is analogous to the trend observed elsewhere in the studies with the

binary blend of either fly ash or slag with GU cement. Literature review shows that ASR resistance of concrete prism increase with increase in the replacement level of both fly ash and slag in the form of binary blend. As in the case of binary blend, when both fly ash and slag are used in the form of ternary blend, efficacy of ASR resistance increases with increase in the total amount of both SCMs. The main reason behind the increased efficacy with the increase in the fly ash and slag may be due to dilution effect and alkali binding characteristics of SCMs. Though the fly ash CH5 has  $\text{Na}_2\text{O}_e$  content of 2.16% (two times more than  $\text{Na}_2\text{O}_e$  of cement i.e., 1.02%), it may contribute far less  $\text{Na}_2\text{O}_e$  in the pore solution. According to Hobbs (Hobbs 1988), fly ash and slag contributes 17% (one sixth) of their  $\text{Na}_2\text{O}_e$  in the pore solution. However, many investigation results (Shehata and Thomas 2006, Duchense and Berube 1994) do not agree with the above estimate. According to the study by Shehata and Thomas 2006, alkali release of fly ash depends upon the  $\text{Na}_2\text{O}_e$  and CaO content of fly ash. Duchense and Berube 1994 had also observed difference in available alkali with different types of fly ashes. Addition of fly ash produces the C-S-H gel capable to binding more alkali (Shehata et al 1999). Addition of SCMs causes reduction of the alkalinity in the pore solution due to incorporation of more alkalinity in the secondary C-S-H gel (negative contribution) (Duchense and Berube 1994).

The lower amount of expansion of ternary blends containing silica fume and fly ash (Figure 4.23) or slag and fly ash (Figure 4.24) suggests that silica fume and slag could be the viable option for the development of ternary blend with fly ash to combat ASR. Study results of various authors show that use of slag or silica fume with fly ash enhances the properties of the concrete (Thomas et al 1999, Radomski et al, 2007, Dongxu et al 2000).

#### **4.2.9 Comparison of expansion between AMBT and concrete prism**

Result of expansion from AMBT (Figure 4.16) and concrete prism test (Figure 4.21) for the mix containing Britinia sand as reactive fine aggregate shows that the expansion of the mortar bar under AMBT test is 1.121% at 14 days whereas the expansion of the prism under concrete prism test is 0.027% at 39 weeks for cement for cement with alkalinity 0.89% raised to 1.25%. Under ASTM expansion limit of 0.10% for 14 days for the AMBT test, the expansion of mortar bar (1.121%) exceeded far more than the prescribed limit. When tested the same sand under concrete prism test using GU cement, the expansion is well within the ASTM limit of 0.04% for 1 year. This result clearly shows that the expansion of the mortar bar under AMBT test is overly conservative for this type of aggregate. From the result of the Figure 4.21 and Figure 4.16, it can be concluded that the Britinia sand is highly sensitive to alkalis. When there was continuous supply of higher concentrated alkali under AMBT test, the mortar bar expanded enormously. But when there was limited amount of alkalis with lower concentration under prism test prepared with GU cement (Figure 4.21), the expansion was very low. Therefore, for such type of aggregate, the result suggests that the AMBT test only can not be the reliable indicator. Prism test is also necessary. An experimental result (Thomas et al 2007) also shows that out of tested 91 samples prepared using seven different types of reactive aggregates, 29 samples had failed under AMBT test which had passed under concrete prism test.

## **Chapter 5**

### **Conclusions and Recommendations**

#### **5.1 Conclusions**

Based on the experimental results of this study carried out on five different types of SCMs with varied level of replacement of the General Use Portland cement, the following conclusion can be drawn.

1. Low calcium fly ash, silica fume and granulated blast furnace slag enhances the sulphate resistance of GU Portland cement. The efficacy of these SCMs increases with increase in the replacement level. The low calcium fly ash can meet ASTM limit for high sulphate resistance at the replacement level of 20% and above. Similar trend can be ascribed for silica fume with replacement level of 3% and above. In the context of slag, it can meet the ASTM limit for high sulphate resistance for the replacement level of 30% and above.
2. The sharp rate of increase in expansion beyond 78 for two blends containing 3% SF and 20% slag, provides insight into the mechanism by which these blends work against the sulphate attack. Permeability has been found to be the main cause of reduced expansion for the blend containing lower amount of these types of SCMs.
3. High calcium fly ashes were found to have low resistance to sulphate attack. However, no clear trend exists between the replacement level and sulphate susceptibility for the high calcium fly ash. Also the sulphate susceptibility of high calcium fly ash can not be predicted only with its calcium content without its mineralogy.

4. The addition of small amount of silica fume (about 5%) to the high calcium fly ashes/cement system produces blend of superb sulphate resistance. The reduced permeability is believed to be the main reason behind the high efficacy of such blend.
5. The addition of optimum amount of gypsum also enhances the performance of high calcium of high calcium fly ash by producing more ettringite at the early stage of hydration. However, the efficiency depends upon the chemical and a mineralogical composition of the fly ashes. It is therefore, essential to establish optimum gypsum content for each fly ash before using it in engineering application. Pre-blending of the gypsum with fly ash produces much better results than adding the gypsum to the mix ingredients as an additive.
6. Ternary blend of fly ash and slag also seems to be viable option for better sulphate resistance. However, no clear trend between expansion and replacement level for such blend was established in this study.
7. Some reactive aggregates are very much sensitive to alkali levels and their reactivity can not be determined from AMBT alone. Concrete prisms of field data are needed to assess the reactivity of such aggregates.
8. In the AMBT test, permeability is a considerable factor for the expansion of the mortar bars.
9. For some aggregates, expansion of concrete prism is not sensitive to alkali levels after the level of alkalinity crosses a certain threshold value.
10. Expansion trend of high alkali high calcium fly ash is very much different than that of fly ashes of low and moderate alkali contents.

11. Like in the sulphate attack, ternary blend of silica fume or slag with high calcium fly ash is effective in combating ASR. However, the amount of SCM (slag or silica fume) should be sufficient to get their full potential in preventing ASR.

## **5.2 Recommendations for Further Studies**

1. Ternary blend of slag with high calcium fly ash have been found to be effective in combating ASR and, to some extent, sulphate attack. More research work is needed in this area to study the efficacy of such blends with aggregates of varied reactivity.
2.  $\text{SO}_3$  optimization approach has also been found to be one of viable options in preventing sulphate attack with some types of high calcium fly ashes. More research work and feasibility studies are needed in this area
3. As the present study focused on ternary blend with 20% fly ash, it is recommended to carryout study in the development of ternary blend with 40% fly ash so that higher amount of fly ashes can be accommodated in concrete applications

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## Appendix A: Sulphate attack data

Legend

Measurement to be taken

Broken

**Table A1: Expansion result of mortar bars containing different SCMs at 5% sodium sulphate solution**

Mix	Expansion (week)													
	1	2	3	4	8	12	13	15	26	39	52	78	104	
CONTROL (REDO)	0.013	0.018	0.026	0.029	0.045	0.073	0.084	0.115	0.306	0.647	1.568			
CONTROL	0.006	0.020	0.024	0.031	0.047	0.071	0.081	0.119	-	-	-	-	-	
20% Fly Ash CH2	0.012	0.024	0.030	0.034	0.045	0.064	0.074	0.095	-	-	-	-	-	
20% Fly Ash CH1 (Redo)	0.017	0.026	0.031	0.033	0.046	0.066	0.092	0.119	0.222	0.600				
20% Fly Ash CH1	0.025	0.030	0.034	0.040	0.108	0.160	0.195	0.286	-	-	-	-	-	
20% Fly Ash CH1 (Redo)	0.020	0.028	0.034	0.039	0.093	0.132	-	-						
40% Fly Ash CH2	0.013	0.022	0.026	0.030	0.039	0.050	0.053	0.059	0.119	0.197	0.329	0.711		
40% Fly Ash CH1	0.016	0.025	0.032	0.045	0.100	0.219	0.289							
0.10 Gyp/20 Fly Ash CH1	0.016	0.023	0.027	0.032	0.058	0.099	0.126	0.185	0.467	1.000	2.000			
0.25 Gyp /20 Fly Ash CH1	0.015	0.023	0.029	0.035	0.093	0.179	0.213	0.285	0.546					
0.5 Gyp /20 Fly Ash CH1	0.021	0.027	0.035	0.043	0.102	0.177	0.211	0.304	10.000					
0.75 Gyp /20 Fly Ash CH1	0.013	0.021	0.029	0.037	0.086	0.190	0.227	0.297	0.641					
1 Gyp / 20 Fly Ash CH1 (Redo)	0.012	0.022	0.027	0.029	0.052	-	-	0.118	0.369					
1 Gyp /20 Fly Ash CH1	0.011	0.018	0.023	0.025	0.043	0.093	0.118	0.153	0.529	1.000				
2 Gyp /20 Fly Ash CH1	0.021	0.028	0.037	0.058	0.131	0.231	0.276	0.434	1.000					
3 Gyp /20 Fly Ash CH1	0.016	0.022	0.025	0.030	0.053	0.133	0.173	0.243	0.806					
4 Gyp /20 Fly Ash CH1	0.016	0.022	0.028	0.030	0.062	0.135	0.167	0.218	0.844	-				
8 Gyp /20 Fly Ash CH1	0.013	0.025	0.034	0.045	0.093	0.171	0.207	0.286	0.858					
12 Gyp /20 Fly Ash CH1	0.014	0.032	0.037	0.050	0.105	0.185	0.223	0.296	0.637					
16 Gyp /20 Fly Ash CH1	0.024	0.043	0.048	0.063	0.115	0.173	0.202	0.231	0.435	0.657	1.054			
20 Gyp /20 Fly Ash CH1	0.025	0.039	0.056	0.070	0.140	0.217	0.248	0.301	0.522	0.898				
0.25 Gyp /20 PB Fly Ash CH1	0.015	0.021	0.026	0.029	0.080	0.155	0.194	0.266						
0.5 Gyp /20 PB Fly Ash CH1	0.014	0.025	0.030	0.039	0.078	0.134	0.166	0.227						
0.75 Gyp /20 PB Fly Ash CH1	0.015	0.024	0.029	0.035	0.083	0.137	0.167	0.198	0.626					

**Table A1: Expansion result of mortar bars containing different SCMs at 5% sodium sulphate solution (continued)**

Mix	Expansion (week)												
	1	2	3	4	8	12	13	15	26	39	52	78	104
1 Gyp /20 PB Fly Ash CH1	0.007	0.018	0.023	0.036	0.100	0.197	0.243	0.359					
3 Gyp /20 PB Fly Ash CH1	0.014	0.026	0.034	0.050	0.101	0.162	0.190	0.251	0.748				
4 Gyp /20 PB Fly Ash CH1	0.024	0.035	0.037	0.049	0.093	0.156	0.181	0.232	0.612				
8 Gyp /20 PB Fly Ash CH1	0.010	0.018	0.026	0.030	0.057	0.109	0.135	0.163	0.397				
10 Gyp /20 PB Fly Ash CH1	0.018	0.027	0.038	0.041	0.079	0.124	0.156	0.183	0.343	0.536	0.940		
12 Gyp /20 PB Fly Ash CH1	0.018	0.031	0.040	0.046	0.087	0.135	0.135	0.170	0.321	0.492	0.783		
14 Gyp /20 PB Fly Ash CH1	0.017	0.025	0.037	0.042	0.067	0.053	0.062	0.068	0.106	0.193	0.349		
15 Gyp /20 PB Fly Ash CH1	0.018	0.023	0.038	0.042	0.049	0.061	0.069	0.080	0.147	0.235	0.504		
16 Gyp /20 PB Fly Ash CH1	0.018	0.026	0.039	0.052	0.113	0.181	0.220	0.261	0.484				
40 Gyp /20 PB Fly Ash CH1	0.025	0.033	0.052	0.085	0.182	0.282	0.330	0.403	0.694	1.073	1.412		
40 Gyp /20 PB Fly Ash CH1	0.021	0.036	0.058	0.098	0.222	0.366	0.426	0.526	0.971	1.379			
88 Gyp /20 PB Fly Ash CH1	0.037	0.071	0.132	0.184	0.403	0.640	0.702	0.814	1.288	1.680	2.059		
3% SF	0.018	0.023	0.026	0.028	0.033	0.038	0.041	0.043	0.053	0.067	0.086	0.217	0.604
5% SF	0.009	0.014	0.015	0.018	0.019	0.023	0.025	0.030	0.036	0.041	0.048	0.074	0.147
3 SF/ 20% Fly Ash CH1	0.009	0.016	0.022	0.023	0.026	0.031	0.033	0.035	0.044	0.068	0.113	0.241	0.443
5 SF 20% Fly Ash CH1	0.006	0.011	0.015	0.015	0.020	0.023	0.026	0.024	0.027	0.029	0.040	0.048	0.058
0.10 Gyp /20 Fly Ash CH2	0.014	0.017	0.028	0.032	0.064	0.124	0.149	0.213	0.467				
0.25 Gyp /20 Fly Ash CH2	0.015	0.022	0.030	0.030	0.034	0.067	0.082	0.107	0.256				
0.5 Gyp /20 Fly Ash CH2	0.014	0.020	0.027	0.025	0.035	0.060	0.077	0.098	0.248				
0.75 Gyp /20 Fly Ash CH2	0.021	0.029	0.038	0.035	0.042	0.052	0.063	0.075	0.130	0.273	0.557		
1 Gyp /20 Fly Ash CH2	0.013	0.025	0.030	0.031	0.049	0.076	0.102	0.123	0.326	1.163	Broken		
0.25 Gyp /20 PB Fly Ash CH2	0.011	0.017	0.020	0.031	0.050	0.087	0.098	0.126	0.307				
0.5 Gyp /20 PB Fly Ash CH2	0.010	0.018	0.020	0.030	0.051	0.084	0.097	0.126	0.264	0.579			
0.75 Gyp /20 PB Fly Ash CH2	0.020	0.023	0.023	0.031	0.048	0.075	0.086	0.111	0.227	0.475			
1 Gyp /20 PB Fly Ash CH2	0.014	0.023	0.025	0.031	0.050	0.088	0.108	0.138	0.312	0.471			
8 Gyp /20 PB Fly Ash CH2	0.015	0.028	0.030	0.030	0.040	0.054	0.062	0.083	0.143	0.269			
10 Gyp /20 PB Fly Ash CH2	0.011	0.021	0.025	0.027	0.036	0.054	0.074	0.087	0.183	0.388			
12 Gyp /20 PB Fly Ash CH2	0.017	0.026	0.030	0.032	0.042	0.053	0.068	0.077	0.133	0.223			
14 Gyp /20 PB Fly Ash CH2	0.014	0.019	0.024	0.027	0.033	0.047	0.050	0.054	0.081	0.123			



**Table A1: Expansion result of mortar bars containing different SCMs at 5% sodium sulphate solution (continued)**

Mix	Expansion (week)												
	1	2	3	4	8	12	13	15	26	39	52	78	104
16/20 PB Fly Ash CH2	0.015	0.021	0.027	0.027	0.035	0.049	0.053	0.054	0.067	0.097			
20/20 PB Fly Ash CH2	0.018	0.027	0.032	0.034	0.041	0.056	0.057	0.064	0.099	0.144			
0.25 HEMI Gyp /20 Fly Ash CH2	0.017	0.026	0.029	0.034	0.071	0.129	0.157	0.211	0.610				
0.5 HEMI Gyp /20 Fly Ash CH2	0.011	0.017	0.021	0.028	0.048	0.097	0.100	0.143	0.407				
0.75 HEMI Gyp /20 Fly Ash CH2	0.013	0.017	0.021	0.024	0.030	0.054	0.059	0.075	0.181	0.452	0.618		
1 HEMI Gyp /20 Fly Ash CH2	0.018	0.022	0.031	0.032	0.042	0.061	0.067	0.079	0.154	0.326			
0.25 HEMI Gyp /20 Fly Ash CH1	0.014	0.026	0.029	0.044	0.117	0.240	0.316	0.397					
0.5 HEMI Gyp /20 Fly Ash CH1	0.009	0.020	0.025	0.032	0.082	0.155	0.211	0.264					
0.75 HEMI Gyp /20 Fly Ash CH1	0.017	0.021	0.027	0.030	0.086	0.173	0.217	0.300	0.730				
1 HEMI Gyp /20 Fly Ash CH1	0.013	0.023	0.031	0.038	0.103	0.202	0.242	0.334	0.626				
20% Slag	0.015	0.021	0.024	0.027	0.034	0.043	0.043	0.051	0.069	0.113	0.209	0.367	0.883
30% Slag	0.007	0.007	0.012	0.011	0.015	0.022	0.032	0.033	0.043	0.053			
40% Slag	0.006	0.010	0.013	0.015	0.021	0.028	0.027	0.031	0.037	0.040	0.054	0.072	0.140
20% Slag/20% Fly Ash CH1	0.014	0.021	0.025	0.024	0.038	0.054	0.073	0.097	0.271				
30% Slag/20% Fly Ash CH1	0.011	0.017	0.021	0.026	0.037	0.041	0.053	0.059	0.181	0.247			
15% Slag/15% Fly Ash CH1	0.010	0.013	0.018	0.021	0.026	0.041	0.041	0.042	0.053	0.068			
20% Slag/40% Fly Ash CH1	0.016	0.020	0.024	0.026	0.036	0.044	0.048	0.051	0.060	0.067			
20% Slag/40% Fly Ash CH1 (Redo)	0.019	0.025											
40% Slag/20% HW	0.012	0.018											
20% Fly Ash F	0.015	0.022	0.026	0.030	0.040	0.046	0.049	0.051	0.056	0.068	0.094	0.134	0.218
40% Fly Ash F	0.013	0.018	0.021	0.025	0.029	0.034	0.036	0.039	0.042	0.050	0.057	0.061	0.070

**Table A2: Expansion result of mortar bars containing different SCMs at lime solution**

MIX	Expansion (week)													
	1	2	3	4	8	12	13	15	26	39	52	78	104	
CONTROL (Redo)	0.004	0.004	0.005	0.008	0.011	0.012	0.013	0.013	0.016	0.016	0.021	0.027	0.031	
CONTROL	0.010	0.009	0.013	0.014	0.016	0.016	0.019	0.020	-	-	-	-	-	
20% Fly Ash CH2	0.004	0.011	0.013	0.012	0.013	0.017	0.013	0.016	-	-	-	-	-	
20% Fly Ash CH1	0.007	0.010	0.010	0.010	0.012	0.013	0.013	0.015	-	-	-	-	-	
20% Fly Ash CH1 (Redo)	0.006	0.007	0.008	0.009	0.010	0.011	0.011	0.013	0.016	0.017	0.024	0.025	0.034	
40% Fly Ash CH2	0.009	0.010	0.014	0.013	0.017	0.018	0.016	0.019	-	-	-	-	-	
40% Fly Ash CH1	0.014	0.017	0.015	0.015	0.019	0.019	0.022	0.021	0.029	0.027	0.027	0.039	0.035	
0.10 Gyp/20 Fly Ash CH1	0.003	0.003	0.003	0.003	0.008	0.007	0.006	0.006	0.015	0.015	0.021	0.021	0.033	
0.25 Gyp /20 Fly Ash CH1	0.004	0.007	0.007	0.006	0.008	0.010	0.010	0.011	0.016	0.021	0.025	0.031	0.034	
0.5 Gyp /20 Fly Ash CH1	0.003	0.006	0.004	0.004	0.011	0.013	0.013	0.014	0.014	0.015	0.012	0.018	0.030	
0.75 Gyp /20 Fly Ash CH1	0.007	0.009	0.010	0.011	0.012	0.013	0.013	0.014	0.017	0.022	0.023	0.030	0.034	
1 Gyp /20 Fly Ash CH1	0.003	0.003	0.005	0.007	0.003	0.077	0.015	0.014	0.011	0.012	0.012	0.016	0.014	
2 Gyp /20 Fly Ash CH1	0.002	0.004	0.004	0.005	0.005	0.003	0.008	0.009	0.010	0.008	0.008	0.015	0.014	
3 Gyp /20 Fly Ash CH1	-0.001	0.001	0.004	0.003	0.004	0.007	0.011	0.011	0.014	0.013	0.013	0.023	0.022	
4 Gyp /20 Fly Ash CH1	0.000	0.004	0.005	0.007	0.005	0.010	0.012	0.013	0.018	0.014	0.014	0.025	0.024	
8 Gyp /20 Fly Ash CH1	0.004	0.005	0.007	0.009	0.015	0.018	0.018	0.020	0.025	0.023	0.026	0.028	0.041	
12 Gyp /20 Fly Ash CH1	0.009	0.010	0.011	0.012	0.015	0.017	0.017	0.017	0.017	0.023	0.028	0.029	0.039	
16 Gyp /20 Fly Ash CH1	0.013	0.018	0.019	0.020	0.023	0.025	0.025	0.026	0.030	0.029	0.037	0.038	0.048	
20 Gyp /20 Fly Ash CH1	0.007	0.009	0.013	0.015	0.021	0.019	0.019	0.020	0.023	0.024	0.033	0.034	0.046	
0.25 Gyp /20 PB Fly Ash CH1	0.005	0.004	0.005	0.005	0.006	0.008	0.009	0.011	0.013	0.013	0.018	0.024	0.033	
0.5 Gyp /20 PB Fly Ash CH1	0.004	0.007	0.008	0.011	0.011	0.012	0.014	0.017	0.015	0.016	0.018	0.022	0.033	
0.75 Gyp /20 PB Fly Ash CH1	0.010	0.013	0.013	0.014	0.014	0.015	0.015	0.016	0.020	0.027	0.029	0.032	0.033	
1 Gyp /20 PB Fly Ash CH1	0.011	0.008	0.007	0.012	0.017	0.017	0.015	0.018	0.015	0.014	0.020	0.025	0.037	
2 Gyp /20 PB Fly Ash CH1	0.002	0.004	0.007	0.013	0.011	0.009	0.012	0.013	0.013	0.005	0.013	0.017	0.029	
3 Gyp /20 PB Fly Ash CH1	0.008	0.007	0.014	0.021	0.016	0.016	0.018	0.020	0.024	0.016	0.019	0.028	0.039	
4 Gyp /20 PB Fly Ash CH1	0.008	0.006	0.011	0.015	0.014	0.012	0.016	0.017	0.017	0.010	0.013	0.020	0.033	
8 Gyp /20 PB Fly Ash CH1	-0.002	0.002	0.004	0.003	0.003	0.005	0.005	0.006	0.015	0.009	0.021	0.022	0.029	

**Table A2: Expansion result of mortar bars containing different SCM's at lime solution (continued)**

MIX	Expansion (week)												
	1	2	3	4	8	12	13	15	26	39	52	78	104
10 Gyp /20 PB Fly Ash CH1	-	-	-	-	0.003	0.008	0.009	0.010	0.014	0.015	0.024	0.024	0.031
12 Gyp /20 PB Fly Ash CH1	-	-	0.006	0.008	0.011	0.012	0.012	0.013	0.014	0.018	0.031	0.029	0.031
14 Gyp /20 PB Fly Ash CH1	0.007	0.006	0.017	0.007	0.016	0.014	0.015	0.017	0.024	0.030	0.032		
15 Gyp /20 PB Fly Ash CH1	0.005	0.009	0.014	0.016	0.017	0.015	0.014	0.016	0.026	0.031	0.031		
16 Gyp /20 PB Fly Ash CH1	-	0.005	0.006	0.007	0.007	0.011	0.011	0.011	0.021	0.018	0.027	0.025	0.032
40 Gyp /20 PB Fly Ash CH1	0.002	0.002	0.001	0.000	0.007	0.005	0.006	0.006	0.018	0.024	0.030		
88 Gyp /20 PB Fly Ash CH1	0.025	0.047	0.072	0.079	0.106	0.109	0.111	0.112	0.118	0.123	0.124		
0.10/20 Fly Ash CH2	-	-	-	0.001	0.004	0.008	0.007	0.006	0.006	0.011	0.016	0.017	0.028
0.25/20 Fly Ash CH2	0.006	0.006	0.009	0.009	0.010	0.014	0.015	0.016	0.014	0.017	0.021	0.021	0.034
0.75/20 Fly Ash CH2	0.004	0.003	0.007	0.007	0.007	0.016	0.015	0.014	0.014	0.015	0.023	0.020	0.033
1/20 Fly Ash CH2	0.008	0.008	0.007	0.008	0.011	0.012	0.013	0.016	0.016	0.021	0.016	0.023	0.035
0.25/20 PB Fly Ash CH2	-0.003	0.001	-0.003	0.003	0.006	0.007	0.007	0.007	0.008	0.005	0.008	0.015	0.027
0.5/20 PB Fly Ash CH2	0.003	0.005	0.003	0.009	0.012	0.014	0.013	0.013	0.012	0.015	0.021	0.024	0.031
0.75/20 PB Fly Ash CH2	0.002	0.005	0.003	0.008	0.008	0.008	0.008	0.009	0.008	0.009	0.019	0.022	0.030
1/20 PB Fly Ash CH2	0.001	0.003	0.002	0.005	0.006	0.007	0.008	0.009	0.010	0.007	0.011		
8/20 PB Fly Ash CH2	0.006	0.007	0.009	0.009	0.010	0.015	0.015	0.024	0.026	0.030			
10/20 PB Fly Ash CH2	0.002	0.002	0.003	0.005	0.005	0.005	0.010	0.011	0.017	0.020			
12/20 PB Fly Ash CH2	0.009	0.011	0.012	0.008	0.011	0.012	0.021	0.022	0.027	0.029			
14/20 PB Fly Ash CH2	0.001	-0.001	0.003	0.003	0.009	0.012	0.015	0.014	0.019	0.024			
16/20 PB Fly Ash CH2	0.000	-0.001	0.001	0.002	0.009	0.012	0.015	0.015	0.020	0.023			
20/20 PB Fly Ash CH2	0.000	0.003	0.007	0.006	0.008	0.020	0.017	0.018	0.024	0.027			

## Appendix A1: RCPT data (sample cured at 35°C)

**Table A3: RCPT result of mortar cylinder prepared and cured simulating with sulphate samples**

SN	Mix	Total Charge passed (Coulombs)		
		1 day	Day at 20MPa 35C curing	56 Day
1	Control	10616*	10616*	6627
2	20 Fly Ash CH1	12554*	10556*	6988
3	3 SF	-	10336*	
4	5 SF	7151*	7151*	1376
5	5 SF/20 Fly Ash CH1	12398*	11558*	1291
6	3SF/Fly Ash CH1	13411*	10381*	2172
7	20% Fly Ash CH2	11501*	10689*	4714
8	15 Slag/15% Fly Ash CH1	-	10643*	3726
9	14% Gypsum /20 INT Fly Ash CH1	-	10498*	7557
10	16% Gyp / 20 INT Fly Ash CH2	-	10557*	
11	20% Slag	-	9559*	
12	30% Slag	-	9141*	
13	40% Slag	-	8694	
14	20% Slag/40% Fly Ash CH1	-		
15	20% Fly Ash F	-	10425*	
16	40% Fly Ash F	-		
17	40% Fly Ash CH1	-		
18	40% Fly Ash CH2	-		

Note: (\*) denotes the predicted total charge just before displaying overflow (OVF) status by RCPT testing machine

## Appendix B: Alkali-Silica Reaction Data

**Table B1: Expansion result of Concrete Prism for ASR test**

Description	% Expansion in Weeks										
	1	2	4	8	13	18	26	39	52	78	104
Control – Cement B alkalinity raised to 1.25% + Britinia sand	0.005	0.001	0.001	0.009	0.021	0.015	0.027	0.027	0.030		
Control – Cement B alkalinity raised to 1.40% + Britinia sand	-	-	-0.006	0.009	0.022	0.019	0.029	0.033	0.039		
Control –Cement E alkalinity raised to 1.25% + Britinia sand	-	0.003	-	0.011	0.018	0.014	0.018	0.028	0.034		
Control – Cement E alkalinity raised to 1.40% + Britinia sand	0.001	-	-	0.003	0.014	0.018	0.019	0.025			
30% Fly ash CH5/5% SF (Cement B alkalinity raised to 1.25%) + Britinia sand	-	-	-0.008	-0.005	0.003	0.002	0.009	0.010	0.013		
30% Fly Ash CH8 + 70% cement (Cement C alkalinity raised to 1.25%) + Britinia sand	-	-	0.009	0.037	0.087	0.106	0.156	0.178			
40% Fly Ash CH8 + 60% cement (Cement C alkalinity raised to 1.25%) + Britinia Sand	-	-	0.007	0.054	0.096	0.127	0.177	0.191			
50% Fly Ash CH8 + 50% cement (Cement C alkalinity raised to 1.25%) + Britinia sand	0.000	0.002	0.020	0.073	0.118	0.149	0.184	0.191			
60% Fly Ash CH8 + 40% cement (Cement C alkalinity raised to 1.25%) + Britinia sand	0.005	0.009	0.037	0.090	0.128	0.154	0.171	0.178			
30% Slag /20% Fly ash CH5 (Cement C alkalinity raised to 1.25%) natural sand and Spratt course Aggregate	-	-	-0.017	-0.018	-	-	-				
30% Slag /20% Fly ash CH5 (Cement D alkalinity raised to 1.25%) natural sand and Spratt course Aggregate (Redo)	-	-			-						
30% Slag /20% Fly ash CH5 (Cement D alkalinity raised to 1.25%) natural sand and Spratt course Agg. (Burlarp curing)	0.010	0.008	-0.007	-0.006	0.005	0.004	0.003				
	-	-									
	0.008	0.004	-0.003	-0.002	0.001	0.002	0.003				

**Table B1: Expansion result of Concrete Prism for ASR test (continued)**

Description	% Expansion in Weeks										
	1	2	4	8	13	18	26	39	52	78	104
15% Slag /15% Fly ash CH5 (Cement D alkalinity raised to 1.25%) natural sand and Spratt course Aggregate	- 0.012	- 0.013	-0.011	-0.010	0.001	0.011	0.033				
15% Slag /15% Fly ash CH5 (Cement D alkalinity raised to 1.25%) natural sand and Spratt course Aggregate (Redo)	- 0.007	- 0.004	-0.002	0.002	0.009	0.022	0.038				
15% Slag /15% Fly ash CH5 (Cement D alkalinity raised to 1.25%) natural sand and Spratt course Agg (Burlap Curing)	- 0.011	- 0.008	-0.005	-0.002	0.004	0.017	0.032				
20% Slag /20% Fly ash CH5 (Cement C alkalinity raised to 1.25%) natural sand and Spratt course Aggregate	- 0.015	- 0.015	-0.014	-0.015	-	0.006	0.001				
20% Slag /40% Fly ash CH5 (Cement C alkalinity raised to 1.25%) natural sand and Spratt course Aggregate	- 0.014	- 0.014	-0.013	-0.014	-	-	-				

**Table B2: Expansion result of accelerated mortar bar test**

Sn.	Description	% Expansion in days					
		3	7	10	14	28	
1	Control (Britinia Sand)	0.198	0.684	0.913	1.121	1.380	
2	Control (St. Mary Sand)	0.010	0.039	0.076	0.107	0.172	
3	Control (Jobe Sand)	0.414	0.736	0.848	0.931	1.150	
4	25% fly ash CH5/5% SF (Britinia Sand)	0.015	0.036	0.084	0.144	0.320	
5	25% fly ash CH5/5% SF (Jobe Sand)	0.020	0.077	0.132	0.190	0.369	
6	25% fly ash C16 (Jobe Sand)	0.006	0.018	0.025	0.042	0.148	
7	25% fly ash CH7 (Jobe Sand)	0.248	0.500	0.580	0.652	0.812	
8	15 Slag /15 Fly Ash CH5 (Spratt sand)	0.056	0.147	0.188	0.223	0.354	

## Appendix B1: RCPT data (sample cured at 80 °C)

**Table B3: RCPT result of mortar cylinder prepared and cured simulating with AMBT test samples**

Description	Total Charge Passed (Coulombs)		
	7 days	14 days	Expansion (%)
Control	8072	7417	0.931
5% SF	1902	1769	0.498
7% SF	607	700	0.231
10% SF	310	318	0.015
25% Fly ash CH5/5% SF	418	411	0.190
25% Fly ash C3/5% SF	400	333	0.082
25% Fly ash C4/5% SF	614	522	0.194
25% Fly ash C3	1285	980	0.437
20% Fly ash C3/3% SF	723	589	0.183
20 Fly ash C3/5% SF	465	419	0.120
25% Fly ash C3/3% SF	618	488	0.126
25% Fly ash C4/3% SF	912	788	0.360
25% fly ash C16	379	316	0.042
25% fly ash CH7	2479	1870	0.652