INVESTIGATION OF ACTIVATION IN HIGH VOLUME FLY ASH CONCRETE

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Dedicated to

MY PARENTS

Abstract

Supplementary cementitious materials (SCMs) like fly ash are increasingly being used as cement replacement in concrete due to environmental, economical, and concrete quality-related concerns. With demonstrated enhancement to overall durability while improving workability and reducing the water demand, the use of lower priced fly ash results in economical production of high performance concrete. The use of fly ash in concrete is currently restricted to low volumes of cement replacement.

In this work, strength gain in concrete mixtures with 60%, 70% and 80% replacement of cement by weight with very low calcium fly ash was investigated. Additionally, hydraulic and pozzolanic reactions were investigated in 70% fly ash mixture using thermogravimetric analysis and iso-thermal calorimetry. The pozzolanic reaction was observed to initiate at 14 days of age and stopped at 56 days due to complete depletion of $Ca(OH)_2$ in the system. Lime activation was investigated for the 70% fly ash mixture using both quick lime and hydrated lime. Hydrated lime was used to increase the alkalinity of the system and quick lime to provide additional $Ca(OH)_2$ for the fly ash pozzolanic reaction. Strength development, hydraulic reaction of cement and pozzolanic reactions in the hydrating lime-fly ash-cement systems were monitored at $25^{O}C$ curing temperature. The test results indicated that hydrated lime was not effective in enhancing strength nor influence the pozzolanic reaction. Notable changes in the very early strength and strength gain at later ages were recorded in quick lime activated system. Addition of quick lime was observed to significantly contribute to early reactivity with the first few hours. Quicklime was observed to contribute additional $Ca(OH)_2$, which allowed pozzolanic reaction to continue even after the lime contributed by cement hydration was depleted. The influence of curing temperature on compressive strength, chemically bound water content, $Ca(OH)_2$ content and heat generated in the quick lime activated fly ash were investigated for curing at $40^{O}C$. Test results confirm that curing at higher temperature increases the rate of early strength gain while producing lower long term strength in both fly ash systems with and without quick lime. The main findings of the experimental investigation, which are of relevance to hydration in lime-fly ash-cement system are: (a) the initiation of pozzolanic reaction was found not to be influenced by the $Ca(OH)_2$ content of the system; (b) the initiation and the initial rate of the pozzolanic reaction are controlled by the temperature. Increasing the temperature was found to accelerate the initiation and the rate of pozzoloanic reaction.

Nomenclature

C………………Cement

F………………Fly Ash

H………………H_2O

CaO……………Quick Lime

$Ca(OH)_2$……....Hydrated Lime

CH……………..Calcium Hydroxide

HL……………..Hydrated Lime

QL……………..Quick Lime

C-S-H…………Calcium silicate hydrate

The following abbreviations are also used:

W/C	Ratio of Water to Cementitious material by weight
TGA	Thermogravimetric Analysis
XRF	X-Ray Fluorescence
UPV	Ultra sonic Pulse Velocity
SCM	supplementary cementitious material
OPC	Ordinary Portland cement
Control	Concrete with 100% cement as cementitious material

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Chapter-1

Introduction

As sustainability moves to the forefront as a major initiative for the construction industry and the society as a whole, emphasis on producing concrete with alternate cement or with increased volume fractions of supplementary cementitious materials (SCM) and industrial by products such as fly ash, and slag, has grown rapidly. This interest in reducing cement consumption is driven by the consideration that cement production is associated with a significant volume of Carbon dioxide and is the second largest source of anthropogenic carbon in the atmosphere. However, as concrete is the second largest material consumed by human beings in the world next to water, the continuous production of concrete is required to ensure the development of infrastructure to support growth. This has therefore generated significant interest in ensuring the continued production of concrete with less quantum usage of cement.

Use of mineral admixtures or supplementary cementitious materials (SCM) at low levels of cement substitution has been shown to improve specific aspects of concrete performance. Blended cements, which are essentially binary blends of cement and SCMs, are available commercially. The use of fly ash in concrete is particularly attractive for use as cement replacement since it allows for beneficial utilization of waste material which is generated in large quantities. Fly ash used in moderate quantities as cement replacement can significantly enhance the properties of concrete. There is increasing interest among researchers to replace higher amounts of Portland cement with fly ash.

The current annual worldwide production of fly ash is approximately 500 million tonnes, but only approximately 20% is being used by the cement and concrete industry (Mehta, 1999). Since the demand and consumption of Portland cement is increasing, it is becoming imperative for the cement and concrete industry to start utilizing more fly ash to meet these demands rather than increase Portland cement production (Malhotra and Mehta, 2002). Concrete made with fly ash substitution of cement often displays slow hydration that is accompanied by slow setting, low early age strength and even low final. This effect is more pronounced as the level of fly ash replacement is increased. The low reactivity of fly ash is a major hindrance to the development of concrete consisting of large volumes of fly ash. In concrete containing fly ash significant proportion of fly ash remain unreacted even after significant time. It is increasingly becoming evident that the solution lies in activating the fly ash to enhance its reactivity thereby maximizing the maximum potential of the cementing action provided by fly ash hydration to be harnessed. Effective use of high volume fly ash as cement replacement therefore requires development of appropriate methods of activation, which enhance the reactivity of fly ash.

In this thesis, high volume cement replacement with fly ash is investigated. The objectives of the work reported here is not just to test high volume cement replacement with fly ash, but to, develop an understanding of the role of fly ash in the contributing to strength gain. Compressive strength gain with 70% cement replacement is investigated. Finally, the use of lime activation in enhancing the strength gain in high volume fly ash concrete is explored.

1.1 Objectives

The objectives of the work presented here are:

1. To investigate the hydration of fly ash in high volume to strength gain at different ages in fly ash blended cement
2. To explore the role activation in enhancing the strength gain in high volume fly ash concrete.
3. To investigate influence of temperature and lime activation on the hydration in high volume fly ash concrete.

1.2 Organization of thesis

This thesis is organized in four chapters. Description of content of each chapter is given below.

Chapter 2

A review of literature on the characteristics and performance of fly ash in concrete is presented. The specifications, composition, reactions and performance characteristics of fly ash under various conditions are summarized. Methods of activation and the effect of different activators on early as well as later ages of concrete proportioned with fly are reviewed.

Chapter 3

Details of the experimental program to investigate high volume fly ash concrete are presented in this chapter. The materials and test methods used in the experimental test program are described.

Chapter 4

Results strength gain and hydration in high volume fly ash concrete are presented. The strength gain is related with the progress of hydration determined using thermogravimetric analysis. Inferences are drawn from analysis of the data and observations in relation to the reported work and available literature.

Chapter 5

Results from lime and temperature activation of high volume fly ash concrete are presented in this chapter. An understanding of the role of lime and temperature in promoting the pozzolanic reaction in fly ash is developed using information from isothermal calorimetry, thermogravimetric analysis and compressive strength measurements.

Chapter 2

Literature Review

2.1 Introduction

The ash extracted from flue gasses in a thermal power plant using electrostatic precipitator is classified as pulverized flue ash (PVA) by IS 3812 (Part-1). Fly ash typically consists of fine particles with low unburnt carbon, less loss of ignition and exhibits pozzolanic activity. The pozzolanic property of fly ash makes it suitable as material for cement replacement. In India, during 2010-2012 about 131.09 million tonnes of fly ash was generated and about 73.13 million tonnes fly ash utilised for various purposes including cement industry.

Strength contribution of fly ash in a cement mix varies widely, depending on the physical and chemical properties of the ash and the general characteristics of the cement in which it is used. Fly ash contains heterogeneous combinations of amorphous (glassy) and crystalline phases. The largest fraction of fly ash consists of glassy spheres of two types: solid and hollow (cenospheres). These glassy spheres usually make up 60 to 90% of the total mass of fly ash, with the remaining fraction of fly consisting of a variety of crystalline phases. The composition of these glasses is dependent on the composition of pulverized coal and temperature at which it is burned. The shape, fineness, particle size distribution and density of fly ash particles influence the properties of freshly mixed, unhardened concrete and the strength development hardened concrete.

Concrete containing fly ash can achieve properties that are not achievable through the use of hydraulic cement alone. Fly ash has been shown to reduce the water demand and produce higher workability in fresh concrete. The products of reaction of fly ash partially fill in the spaces initially occupied by mixing water that were not filled by the hydration products of the cement, thereby reducing the concrete permeability to water and aggressive chemicals (Manmohan and Mehta 1981). The reduced permeability and the reduction of the free lime content in hydrated cement has been shown to improve the performance in alkali-silica reactivity. The reaction rate of fly ash is slower, as compared to hydraulic cement, which reduces the amount of early heat generation and the detrimental early temperature rise in massive structures. The low reactivity of fly ash also affects the strength gain in concrete.

Extensive research has been done to improve the understanding of the chemical reactions involved when fly ash is blended with cement for use in concrete. Strength enhancement characteristics of fly ash vary widely, depending on the physical and chemical properties of the fly ash and the general characteristics of the cement in which it is used. In general, the finer the fly ash, the lower the loss on ignition (LOI) and the greater the concrete's long-term compressive strength. Increased fineness also lowers the water demand and increases resistance to sulfate attack in concrete. LOI, an indicator of carbon content and fineness are controlled using beneficiation processes. Depending on the size, density, and distribution of particles containing carbon, the LOI can be increased, decreased, or unchanged by this technique.

The chemical and phase compositions of fly ash play a vital role in determining its reactivity and are typically used for characterizing fly ash. While the designation and the exact chemical requirements may vary, both ASTM and IS 3812 use the chemical composition reported in terms of oxides for characterizing fly ash. The amounts of the four principal constituents vary widely as shown in the Table 2.1 below. The Silica content of fly can be present in crystalline and glassy phases that remain after the combustion of the pulverized coal are a result of materials with high melting points and incombustibility.

Table 2.1 Typical composition of fly ash

Fly ash components	**Mass (%)**
SiO_2	35 to 62
Al_2O_3	10 to 30
CaO	1 to 35
Fe_2O_3	4 to 20

The sum of the first three constituents (SiO_2, Al_2O_3, and Fe_2O_3) must exceed 70% for a fly ash to be classified as an ASTM C 618 Class F fly ash; whereas their sum must only exceed 50% to be classified as an ASTM C 618 Class C fly ash. Class C fly ashes generally contain more than 20% of material reported as CaO; therefore, the sum of the SiO_2, Al_2O_3, and Fe_2O_3 may be significantly less than the 70% Class F minimum limit. As per IS 3812 The sum of the first three constituents must more than 70% and CaO must be less than 10% for a fly ash to be classified as Silicious fly ash; whereas the ratio must be more than 50% and CaO more than 10% treated as a Calcareous C fly ash. The main contributor to the pozzolanic reaction in concrete is the siliceous glass from the fly ash because it is the amorphous silica that combines with lime and water to form calcium silicate hydrate (C-S-H).

Fly ash reacts in concrete with the hydraulic cement in the following ways

1. Solutions of calcium and alkali hydroxide, which are released into the pore structure of the paste, combine with the reactive silica particles of fly ash, forming a cementing medium;
2. Heat generated by hydration of hydraulic cement helps initiate the pozzolanic reaction and contributes to the rate of the reaction.

Acknowledged advantages of using fly ash used in concrete are listed below:

1. Reduction of water requirement for a given slump
2. Reduction in heat of hydration and thus reduction of thermal cracks and improves soundness of concrete.
3. Improve workability, pumpability and finishability of concrete.
4. Converting released lime from hydration of OPC into additional binding material-contributing additional strength of concrete mass.
5. Reduces the permeability and adsorption of concrete due to the reaction between fly ash and lime.
6. Fly Ash generally exhibit less bleeding and segregation.
7. The addition of fly ash to concrete reduces the cost.
8. Use of fly ash in concrete environmental benefits and its became eco-friendly

2.2 Chemical activity of fly ash in hydraulic cement concrete

The principal products of the reactions of fly ash with calcium hydroxide and alkali in concrete is calcium silicate hydrates (C-S-H) and calcium aluminate hydrates which are the same as that of the hydration of Portland cement. The morphology of class F fly ash reaction production is suggested to be more gel like and denser than that from Portland cement (Idorn, 1983). The reaction of fly ash depends largely on breakdown and dissolution of the glassy structure by the hydroxide ions and the heat generated during the early hydration of the hydraulic cement fraction. Fly ash continues to consume $Ca(OH)_2$ to form additional C-S-H, as long as $Ca(OH)_2$ is present in the pore fluid of the cement paste and as long as there is available mixing water filling space that the C-S-H can occupy; at $W/C < 0.4$ by mass, there will be more space available before all cementitious material react (Philleo 1991). Regourd et al. (1983) state that a very small, immediate chemical reaction also takes place when fly ash is mixed with water, preferentially releasing calcium and aluminium ions to solution. This reaction is limited, however, until additional alkali or calcium hydroxide or sulfates are available for reaction. Idorn (1984) has suggested that, in general, fly-ash reaction with Portland cement in modern concrete is a two-stage reaction. Initially and during the early curing, the primary reaction is with alkali hydroxides and, subsequently, the main reaction is with $Ca(OH)_2$.

The effectiveness of the use of fly ash in concrete depends on the following factors.

1. The chemical and phase composition of the fly ash and of the hydraulic cement;
2. The alkali-hydroxide concentration of the reaction system;
3. The morphology of the fly ash particles;
4. The fineness of the fly ash and of the hydraulic cement;
5. The development of heat during the early phases of the hydration process; and
6. The reduction in mixing water requirements when using fly ash.

2.3 Determination of Reactivity of fly ash in cement paste

The hydration of fly ash- cement binder includes the hydration of cement clinker and pozzolanic reaction of fly ash. $Ca(OH)_2$ is released during the hydration of cement clinker and activates the pozzolanic reaction of fly ash, where it will be observed. Baert et al. (2008) determined $Ca(OH)_2$ and chemically bound water for fly ash cement paste by using Thermogravimetry analysis and they reported depletion of calcium hydroxide during the pozzolanic reaction is noticeable from 7-14 days. Before the age of 7 days, more water is chemically bound per gram cement when fly ash is present. Wang et al. (2004) identified that fly ash has the ability to promote the cement hydration. Takemoto (1980) observed the hydrolysis of clinker minerals is accelerated by alkalis, which are present in the fly ash. Pane et al. (2005) observed unique correlations between the amount of chemically bound water and hydration heat of a binder, the chemically bound water and $Ca(OH)_2$ content and reactivity degree of a fly ash, its soluble silica content and its fineness. According to Neville (1995), pozzolanic reaction starts after one week or more and he explained of this delay could be that glass materials in fly ash is only broken down when the pH value of the pore water is at least 13.2 and also rate of solubility of the glass network is dependent on the temperature and so is the rate of pH development. In the incubation period particles of fly ash behave as crystallization centres of hydration products precipitation for $Ca(OH)_2$ and reaction products organising from the cement hydration C-S-H. Marsh (1988) replaced 30 and 50% cement replaced with fly ash and he reported initially the reaction of fly ash with calcium hydroxide is very low. With increasing the age fly ash reacts with calcium hydroxide and finally C-S-H can change to $C_3S_2H_3$. The hydrate formed from this direct action, binds probably more water per unit mass than does the hydrate formed from the pozzolanic reaction.

Baert et al.(2008) determined hydration of fly ash cement paste by using Isothermal Calorimeter and they reported rate of hydration of the pastes clearly exhibits a third hydration peak. This could well be due to the conversion of ettingite, which has been enhanced by the presence of fly ash, to monosulphate. In the first 18 hours, the rate of heat release by the hydration of cement is diminished in the presence of fly ash. After that cement hydration is accelerated. According to Rahhal et al. (2004), the effect of fly ash incorporation into Portland cements hydration reactions; correspond to a delayed appearance of the second peak caused by the clinker reaction, on calorimetric curves and a reduced intensity of the heat dissipation rate compared to the plain Portland cement. In the first hours immediately after mixing, the total amount of heat evolved was greater than for the plain Portland cement. Nocun et al.(2001) identified that in some cements, there is also third peak attributed to transformations in aluminates hydrated phase. It can generally attributed from excess of tricalcium aluminate and replacement sulphoaluminate phase(AFt) by monosulphoaluminate(AFm).

2.4 Compressive strength and rate of strength gain

The strength at a given age as well as the rate of strength gain of fly ash concrete are affected by the characteristics such as particle size, free lime and pozzolanicity of the particular fly ash, the cement with which it is used, and the proportions of each used in the concrete (EPRI CS-3314). As compared to the concrete without fly ash proportioned for equivalent 28-day compressive strength, concrete containing a Class F fly ash may develop lower strength at 7 days or less when tested at room temperature (Abdun-Nur 1961).

After the rate of strength gain of hydraulic cement slows, the continued pozzolanic reaction of fly ash provides strength gain at later ages if the concrete is kept moist; therefore, concrete containing fly ash with equivalent or lower strength at early ages may have equivalent or higher strength at later ages than concrete without fly ash. This strength gain continues with time and results in higher later-age strengths than can be achieved by using additional cement (Berry and Malhotra 1980). Lane and Best (1982) have reported strength increases of 50% at 1 year for concrete containing fly ash, as compared with 30% for concrete without fly ash using 28-day strengths as references. Mather et al (1965) reported that concrete containing fly ash at ages up to 10 years showing higher performance compared to concrete without fly ash.

Cook et al. (1981) reported that some of Class C fly ashes were as effective as Portland cement on an equivalent mass basis. Class C fly ashes may not show improved later age strength gain compared to class F Fly ashes. Naik et al (1995) replaced cement with fly ash with replacement levels of 15-70% and they reported that compressive strength of fly ash mixtures decreases with increasing amount of fly ash. 15 to 30% replacement of fly ash with cement mixture showed the best results when compared to high volume replacement level of cement with fly ash.

Fly ash from different sources exhibit large variations in physical properties and chemical and phase compositions. Efficiency factor is often used as a measure of the relative performance of fly ash compared with Portland cement. Efficiency factor is defined as the part of the fly ash in a pozzolanic concrete, which can be considered as an equivalent to Portland cement, having same properties as the concrete without fly ash. Papadakis et al. (2002) calculated efficacy factors for SCMs (silica fume, fly ash, natural pozzolans) and reported that efficiency factors are different depending on the property used for evaluation (strength, durability).When SCMs are used to replace cement, the strength is reduced first, but as times proceeds this gap is gradually eliminated and strength became higher than that of control for those SCMs with higher active silica content in comparison with cement. Efficiency factor of pulverised fly ashes is equivalent to Portland cement. The natural SCMs exhibit much lower effiency factors. Efficiency factor was correlated with the active silica content of SCM and an analytical relationship was found for artificial SCMs (fly ash, slag), This Analytical relationship cab be applied as a first approximation of efficiency value of the artificial SCM. This approach used for rapid prediction of the quantity, but most of the all the quantity of the SCM used in the concrete mix design.

2.5 High Volume Fly ash

Studies on compressive strength, tensile strength, flexural strength and modulus of elasticity have shown that 30% fly ash replacement of cement produces the best result (Naik et al. 1995). Similarly concrete mixtures proportioned at 25% cement replacement with fly ash, Class C fly ashes were shown to have lower demand of air-entrainning than Class F fly ash (Gebler et al. 1986). The abrasion resistance of Class C fly ash was generally superior to Class F fly ash. Tikalsky et al. (1985) observed the same trend but up to 35% cement replacement. This represents normal volume replacement of cement.

High volume fly ash concrete may be defined as having a fly ash content of 50% or greater by mass of cementitious materials. Some of the researches described more than 35% replacement of cement as a high volume fly ash concrete. Naik et al. (1995) reported concrete made with 50% class C fly ash exhibited lower shrinkage, lowest permeability value, higher abrasion resistance and very low chloride permeability. Naik et al. (1992) reported concrete made with 50% Class C fly ash shows higher abrasion resistance .Bilodeau and Malhotra (1992) observed lower abrasion resistance for concrete made with 55-60% class F fly ash. Ellis et al. (1991) reported that concrete made with Class F fly ash was more effective in reducing concrete permeability than concrete incorporating Class C fly ash. Some researchers have found reduction in sulphate resistance of concrete due to addition of class C fly ash. High volume fly ash concrete can be considered to represent concrete containing higher percentages of fly ash than normal for the intended application of the concrete. This has low w/cm content and is batched to a dry consistency. Several researchers have reported on development of High volume fly ash concrete of moderate to high slumps using high-range water-reducers and possessing suitable properties for commercial construction.

2.6 Activation of fly ash cementitious system

Fly ash as a cement replacement in concrete is very common and attractive because of its large availability, widespread familiarity with use in construction and the potential for high volume utilization. However, the use of fly ash is also accompanied by increased setting time and decreased early strength. As fly ash qualitatively is not equivalent to Portland cement, this reduction in strength occurs due to water-cement ratio.

To improve the properties of fly ash researchers have used of the methods like thermal, mechanical and chemical activation to achieve enhanced reactivity from fly ash action to compensate the loss of early strength.

Thermal Activation: properties of fly ash are improved by increasing the curing temperature.

Mechanical activation: At low to medium cement replacement, grinding Portland cement clinker and mineral additives to relatedly higher fineness yields the desired early strength. Grinding efficiency, however reduces with higher fineness due to agglomeration tendency of cement.

Chemical Activation: fly ash concrete properties are increases by activate the intergrinding chemicals with Portland cement clinker and mineral additives and adding chemical reagents at the time of mixing concrete.

The efficiency however, of some of these methods is debatable since a number of them are too energy demanding, while others fail in simple cost-benefit analysis. Different methods, such as fine grinding, elevated temperature curing and use of chemical activators, have been explored to overcome these shortcomings. After comparative studies, it has been found that the use of chemical activator is the most effective and efficient technique to activate the potential pozzolanic reactivity of coal fly ashes and to improve the performance of the fly ash in concrete. The addition of chemical activator(s) can significantly enhance the rate pozzolanic reactions between fly ash and lime, and hence increase the strength development rate and ultimate strength of hardened concrete containing fly ash. Chemical activator(s) can be easily added into concrete mixtures during the concrete mixing process.

2.6.1 Activation using Hydrated Lime

Huang and Cheng (1986) activated hydrated lime to fly ash and they reported the addition of hydrated lime accelerate the reaction degree of fly ash at both early and later ages. This acceleration effect would be minimal unless curing takes place at higher than the room temperature. Gray and Lin (1972).reported that both the rate of strength gain and the ultimate strength of lime-treated fly ash are highly dependent on the curing temperature. The interaction between fly ash and $Ca(OH)_2$ has attracted the attention of several researchers. They all seem to agree that the quality and quantity of calcium hydroxide that is present in the matrix of a fly ash cement system is crucial for the future performance of these systems. In the early 1980s, Takemoto and Uchikawa (1980) suggested that the rate of CH consumption in mixtures of CH and fly ash increases notably with increasing CH content in the initial mixture. They attributed this phenomenon to an increase in available calcium ions, due to the increase in CH surface relative to the fly ash surface. Biernacki et al. (2001) while confirming the results of the aforementioned authors demonstrated that since fly ash hydration is the only reaction that consumes CH and since the C/S ratio does not change appreciably, the rate of ash hydration increases too with CH/fly ash ratio. Ma and Brown (1997) hydrothermally treated both types of fly ash with $Ca(OH)_2$. They observed that C–S–H formation was more extensive when CH was added in high-lime fly ashes. In contrast, mild hydrothermal treatment of low-lime ash in the presence of $Ca(OH)_2$ did not appear to accelerate the formation of any of the cementing phases.

2.6.2 Activation using Quick Lime

Shi (2001) concluded that cement made with quick lime shows significantly higher strength than the cement made with hydrated lime at all ages of hydration. The influence of quick lime was more pronounced during the early stage of hydration and remained constant after the first month of hardening process. Antiohos et al. (2008) used quick lime as fly ash replacement in cement-fly ash blends and reported fly ash cement pastes had a positive influence mainly on strength development. The reaction rate of high Calcium fly ash and fly ash with quick lime resulted in a notable acceleration of the fly ash degree of reaction throughout the curing period. It was concluded that apart from physical effect of lime and the creation of CH bonds among fly ash particles, the solubility of SiO_2 is also increased leading to a greater release of soluble silica in to hydrating matrix. Antiohos et al. (2003 part-1) used quick lime to activated class C fly ash and they reported that Quicklime in fly ash Concrete is effective, inexpensive and it improves the both early and later age strengths. In case of high calcium ashes addition of lime must be limited to small percentages. Small percentage of lime fully employed the available amorphous silica from the fly ashes to form additional C-S-H. These observations formulated by Brown (1997) that in the presence of $Ca(OH)_2$, the solubility of SiO_2 leading to a greater release of soluble silica in to hydrating matrix. This accounts for the improved strengths of activated lime fly ashes at lateral ages during the early stages of hydration, added lime works alternatively to enhance the strength of the system. Anitohos et al. (2003) proposed that quick lime addition and its subsequent formation to $Ca(OH)_2$ result in a higher basicity inside the matrix. The pH increase leads to the corrosion of the densified outer layer of fly ash particles leaving more active cores exposed for reacting forming additional hydration products. An additional explanation for the improved early age strengths observed in lime-activated fly ash systems is the formation of flocs inside the matrix due to lime hydration. Pandian and Balasubramonian (1999) noted that these flocs reduce the effective voids, and hence the inter connectivity of the pores, leading to a denser microstructure.

2.6.3 Activation using Chemical Reagents

Some of the researchers identified pozzolanic reaction is initiated when the pH and of the pore solution is beyond 13.2 or 13.3. pH value can be applied to express the pozzolanic activity of fly ash. A fall of pH usually indicates the occurrence of reaction of fly ash. The lower the pH is, the higher the degree of reaction in fly ash. For increasing the pH value of concrete, Shi (1996) added Na_2SO_4 and $CaCl_2.2H_2O$ to hydrated lime blended with fly ash paste and reported that both Na_2SO_4 and $CaCl_2.2H_2O$ are effective in activating the reaction of fly ash and increasing strength concrete containing fly ash. Na_2SO_4 is more effective at early ages and $CaCl_2.2H_2O$ at later ages. In Na_2S0_4 activated pastes, all fly ash particles in the pastes were covered by coagulated gel and needles, which were interlocked. $CaCl_2$ activated pastes appeared to be less dense than the Na_2S0_4 activated pastes, but most spaces between fly ash particles were filled by foil-like gel and hexagonal. The addition of activator changed the other hydration products. In addition to C-S-H, ettringite (AFt) and monosulphoaluminate (AFm) were detected in the pastes.

When Na_2S0_4 was added, strong AFt diffraction peaks were formed at initial days and diminished slightly with time. Very weak AFm diffraction peaks were appear at initial days, and diminished with time and disappeared at lateral days. The early pozzolanic reaction between lime and fly ash depends upon the dissolution of fly ash. The addition of Na_2S0_4 to lime-fly ash pastes increases the alkalinity of the solution and the dissolution of fly ash at initial stages, which accelerates the pozzolanic reaction between lime and fly ash. At the same time, a large amount of AFt is also formed due to the added $S0_4^{2-}$. The accelerated initial pozzolanic reaction and the formation of AFt induce high early strength of the lime-fly ash paste. As time proceeds, pozzolanic reaction continues and pastes become stronger.

In the $CaCl_2$ activated pastes, AFm were formed at initial days and it disappear lateral ages. The addition of $CaCl_2$ inhibits the solubility of $Ca(OH)_2$ and hence decreases the p^H of pore solution due to the common ion effect, which decreases the dissolution of fly ash, but favours the formation of a solid solution of $Ca_4Al_2[(SO_4^{2-})_X(Cl^-)_Y(OH^-)_{2-2X-Y}].nH_2O$ (X<1 and Y<2). This solid solution increases the dissolution of fly ash particles and the pozzolanic reaction, which enhances the strength of fly ash cement and concrete. As time proceeded, the intensity of these diffraction peaks increased significantly and the portion of SO_4^{2-}, Cl^- and OH^- changed with time. Weak AFt diffraction peaks appeared at early ages, but disappeared at lateral ages.

Fraay et al. (1989) added the alumina and silica from the firm chain existing in the ash surface. Aimin and sarkar (1991) added 3-5% gypsum in to cement system with class F fly ash and observed a distinct increase in the strength of new blend. They attributed that fact to the reaction between the sulfate ions the alumina of the ash, which eventually led to the dissociation of glass structure and finally to a denser microstructure. Poon et al. (2001) used anhydrite to achieve a greater reaction degree in cement mortars with high fly ash replacement. Fan et al. (1999) added a small quantity of Na_2Sio_3 in to the fly ash – $Ca(OH)_2$ blend. They reported the effect of Na_2Sio_3, which formed NaOH in the pore solution it, will increase the pH of fly ash concrete.

2.7 Temperature Role in fly ash concrete

Fly ash is totally temperature sensitive. Pozzolonic reaction starts after glass particles are broken down in fly ash. Glass particles break down on increasing curing temperature. Maltais et al. (1997) replaced weight of cement with 10, 20 and 30% of fly ash and cured specimens at 20°C and 40°C. They reported that fly ash does not react during the first days of curing. ,The elevation of the curing temperature contributes to reduce the long term compressive strength. Curing at 20°C contributed higher long term compressive strength of fly ash mixtures. According to many studies, the negative effect of high curing temperature is directly related to microstructure of OPC cement paste. Alexanderson (1972) suggested that the influence of high curing temperature was related to the significant difference between the thermal expansion coefficients of various phases present in the cement. The increase in the volume of water and air due to rise in temperature is prevented by the rigid Skelton of the hardening cement pastes.

An elevation of the curing temperature on the long term compressive strength of most fly ash mortars can probably be explained by the fact that the pozzolanic reaction is, like most chemical reactions, significantly influenced by the temperature (Xu 1993, Bijen et al. (1995), and Fraay 1989). According to Fraay et al. (1989) temperature sensitivity of the fly ash hydration process can be explained by considering that the dissolution of fly ash particles is directly affected by the pH level of the pore water solution. These authors showed that the OH^- ion concentration increases significantly with temperature. Berry and Malhotra (1987) reported that once pozzolanic reaction has been initiated by heat, it will carry on even if temperature is reduced. Zhang et al. (2000) reported that the pH value decreases with increasing amount of fly ash content and elevated temperature increases the pH of high volume fly ash concrete by increasing the OH^- ions concentration in the system.

Chapter-3

Materials and Experimental Program

3.1 Introduction

This section presents the details of materials and experimental methods used in the study. The types of specimens, mix proportions and test methods employed are presented.

3.1.2 Cement

In the present investigation, commercially available 53 Grade ordinary Portland cement was supplied by Bharathi Cement with Specific Gravity of 3.15 and Fineness of 325 m^2/kg was used for all concrete mixtures. Oxide composition of cement was determined by using X-ray fluorescence (XRF) are listed in Table 3.1 and The chemical composition, chemical and physical properties of the cement are are listed in Tables 3.1, 3.2 and 3.3, respectively.

Table 3.1 Oxide composition of OPC 53 grade cement

Test	**Unit**	**Results**
CaO	% by mass	71.326
SiO_2	% by mass	16.15
Al_2O_3	% by mass	3.104
Fe_2O_3	% by mass	5.525
MgO	% by mass	0.723
K_2O	% by mass	0.717
Na_2O	% by mass	0
SO_3	% by mass	2.053

Table 3.2 Chemical properties of OPC 53 grade cement as per IS: 12269-1987

Test conducted	**Unit of Measurement**	**RESULT**	**Requirement as per IS: 12269-1987**
Lime saturation factor	% by mass	0.9	0.8-1.02
Total loss on ignition	% by mass	0.8	Max 4
Insoluble residue	% by mass	0.25	Max 2
Magnesia (MgO)	% by mass	1.1	Max 6
Tricalcium Aluminate (C_3A)	% by mass	7	Not specified
Sulphuric anhydrideSO_3 (%)	% by mass	1.5	Max 3
Chloride (%)	% by mass	0.002	Max 0.1

Table 3.3 Physical properties of OPC 53 grade cement as per IS: 12269-1987

TEST PARAMETERS	Unit of Measurement	RESULTS	Requirements as per IS:12269-1987
Normal consistency	%	30	
fineness	m^2/kg	325	Min 225
initial setting	minutes	150	Min 30
final setting	minutes	260	Max 600
soundness			
Le-Chatilier	mm	1	Max 10
autoclave	%	0.03	Max 0.8
compressive strength			
1 day	MPa	20	Not specified
3 day	MPa	39	27
7 days	MPa	49	37
28 days	MPa	70	53

3.1.3 Fly Ash

Fly ash conforming to the requirements of IS 3812 and IS 1727 (1967) supplied by DIRK with Specific gravity of 2.5 and fineness of 320 m^2/kg was used as a supplementary cementitious material in concrete mixtures. The chemical properties of fly ash was determined by using X-ray fluorescence (XRF) are listed in Table 3.4 and Physical properties are listed in Table 3.5.

Table 3.4 Chemical properties of fly ash as per IS: 3812

Test	Unit	Results	Requirement As Per IS: 3812
SiO_2	% by mass	58.14	35 min
Al_2O_3	% by mass	28.39	Not specified
Fe_2O_3	% by mass	5.733	Not specified
SiO_2+Al_2O_3+Fe_2O_3	% by mass	92.26	70 min
CaO	% by mass	1.871	Not specified
MgO	% by mass	0.506	5 max
SO_3	% by mass	0	2.75 max
Na_2O	% by mass	0	1.5 max
Total chlorides	% by mass	0.05	0.05 max
Loss of Ignition	% by mass	2.5	12

Table 3.5 Physical properties of fly ash as per IS: 3812

Test	Unit	Results	Requirement As Per IS: 3812
lime reactivity	MPa	5	4.5 min
Fineness	m^2/kg	320	320
compressive strength as a percentage of cement mortar cubes	%	85%	more than 80%
Soundness as per autoclave	%	0.01	max

3.1.4 Lime

Two different limes are used as activated components in all concrete mixtures as mentioned below.

3.1.4.1 Hydrated Lime

75% Purity of reagent grade $Ca(OH)_2$ supplied by SISCO Research laboratories was used.

3.1.4.2 Quick Lime

95% Purity of reagent grade CaO supplied by SISCO Research laboratories was used.

3.1.5 Aggregates

Locally available river sand with a specific gravity of 2.67 and fineness modulus of 2.83 was used as fine aggregate and crushed granite of specific gravity of 2.63 was used as coarse aggregate. Two different classes of coarse aggregate fractions were used: 10-4.75 mm and 20-10 mm. The aggregate properties are listed in Tables 3.6, 3.7 and Particle size distribution of fine aggregates shown in Figure 3.1.

Table 3.6 Gradation of Fine aggregates

Sieve Size(mm)	% passing	Standard grading limits IS: 383 - 1970
10 mm	100	100
4.75 mm	99.4	90-100
2.36 mm	95.2	75-100
1.18 mm	77.8	55-90
600 micron	35.1	35-59
300 micron	8.6	08-30
150 micron	0.8	0-10

Table3.7 Combined grading of coarse aggregates

Coarse Aggregates Fraction			Combined grading	As per is:383-1970
sieve size(mm)	**20mm**	**10mm**		
40	100	100	100	100
20	96.54	100	98.27	95-100
10	0.1	74.9	37.50	25-55
4.75	0	3.4	1.7	0-10

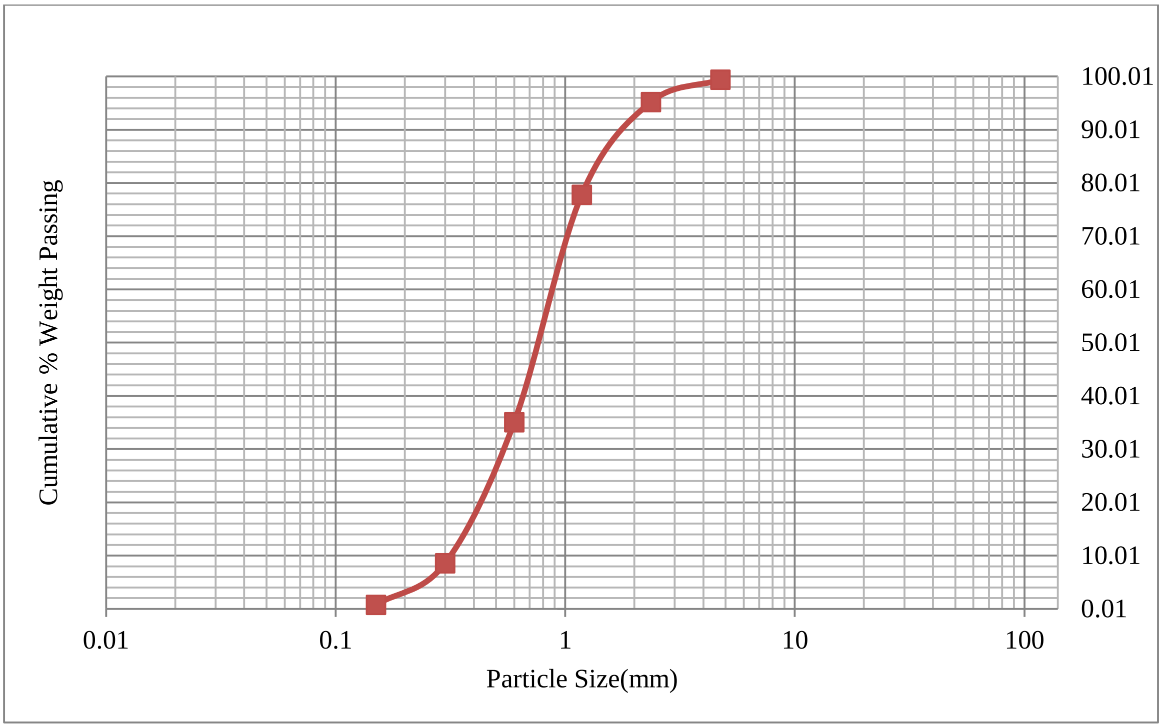

Figure 3.1 Particle size distribution of Fine aggregates

3.2 Experimental program and Mix Proportions

Concrete mix design for the mix design procedure given in IS: 10262 was followed with minor modification for M35 grade. For a target mean strength of 43 MPa, two different water/cement ratios equal to 0.43 and 0.50 were considered (from Fig 2, curve E IS 10262-1982 for 53G). Taking into considerations, the minimum requirements for cement content in kg/m^3 of concrete for M35 as per IS 456-2000 as 300 kg/m^3, cement content was fixed at 340 kg/m^3. Using this, the water content was determined. In the concrete mixture fine aggregate were taken as 40% of the total aggregate volume fraction. The weights of fine and coarse aggregate were then calculated considering the specific gravities of coarse and fine aggregate.

The Concrete mixtures were produced at a constant water/Cement ratio of 0.43 and at a water/cement ratio of 0.50.In case of 0.43 Water/Cement ratio, one control mixture and three different mixtures with different levels of cement replacement were prepared. The control mixture contained no fly ash. Concrete mixtures labelled M1, M2 and M3 were produced with varying level of cement replacement corresponding to 80%, 70% and 60% of weight of cement. In case of 0.50 Water/cement ratios, one control (no fly ash) mixture and one 70% cement replacement with fly ash mixture was prepared. Mixtures labelled as C2, M4. The design mixtures are presented in Table 3.8 and the final batch weights of the different mixes for one cubic meter of concrete are presented in Table 3.9.

Table 3.8 Design mixture proportions

Name of The Mix	Cement Content (%)	Fly ash Content (%)
C1	100	0
M1	20	80
M2	30	70
M3	40	60
C2	100	0
M4	30	70

Table 3.9 Summary of weight proportion of the various mixes

Materials(kg/m^3)	C1	M1	M2	M3	C2	M4
OPC 53 grade cement	340	68	102	136	340	68
Fly ash(pozzocrete 60)	0	272	238	204	0	272
Water/Cement Ratio	0.43	0.43	0.43	0.43	0.50	0.50
20 mm aggregates	573	573	573	573	573	573
10mm aggregates	573	573	573	573	573	573
Fine aggregates(river sand)	767	767	767	767	767	767
Water	146	146	146	146	170	170
Density (kg/m^3)	2398	2398	2398	2398	2359	2359

3.2.1 Casting and Curing of Specimens

IS standard 150mm Cubes were cast from each mixture to evaluate compressive strength gain. Concrete was prepared using a drum mixer with a capacity of 4 litres. The ingredients were put into the mixer in the decreasing order of their sizes staring from 20mm aggregate to cement. Dry mixing of the aggregates and cement was done for two minutes and then water was added gradually in the rotating mixer and allowed to mix for 15 minutes. During the mixing process, the walls and bottom of mixer were scraped well to avoid sticking of mortar. After mixing, the slump was checked and noted down to ascertain the effects of differently proportioned blends on workability of concrete. Finally the fresh concrete was placed in oiled moulds and compacted properly in three layers, each layer being tamped 35 times using a tamping rod.

After the initial setting of concrete, the surface of the specimen was finished smooth using a trowel. Immediately after casting, all specimens were covered with plastic covers to minimize moisture loss. The specimens were stored at room temperature about 25°C. Specimens were demoulded 24 hours after casting and kept in curing water tank as shown in Figure 3.2(c).

Figure 3.2 Preparation and curing of sample: (a) 150mm cube mould; (b) specimen after demolding; (c) Specimens being cured.

3.3 Test Methods

An experimental program was designed to study strength development in fly ash concrete mixture proportions. Each concrete mixture was evaluated with respect to Slump, compressive strength, Ultrasonic Pulse velocity. Additionally Thermogrvimetric analysis (TGA) and Isothermal Calorimeter

3.3.1 Slump

Slump was used to find the Workability of fresh concrete where the nominal maximum size of aggregate does not exceed 38 mm. slump cone was used to find the slump of the concrete as per the requirements of IS 1199-1959.

3.3.1.1 Procedure

Figure 3.3 Slump measurement on fresh concrete

Oil was applied on the base plate and interior surface of the slump cone. After that, Slump cone was tighted with base plate with screws and finally kept on the levelled surface. Immediately slump cone was filled with fresh concrete approximately one-quarter of height of the cone, each layer was tampered with the tampered rod 25 times. After compacting the top layer, mould and the base plate was cleaned with the clothes. Slump cone was Unscrewed from the base plate and removed immediately from the concrete by raising it slowly and carefully in a vertical direction. Finally slump cone of the base plate kept reverse position, height between the top of the mould and highest point of the concrete was measured with the scale. This height indicated the slump of the concrete. Slump measurement of fresh concrete as shown in Figure 3.3.

3.3.2 Ultrasonic Pulse Velocity

UPV was used to measure the quality of concrete in terms Homogeneity of concrete, Presence of cracks, voids and other imperfections, changes in concrete Structure with time and velocity Co-related to strength as per the requirements of IS 13311 (part-1):1992.

3.3.2.1 Procedure

Transducers are connected to the sockets marked “TRANS” and “REC”, before switching on the ‘V’ meter. Concrete surface was cleaned with the clothes. Grease was applied on the transudures surface and pressed it hard onto the surface of the concrete. Transducers are holded surface of the concrete until a consistent reading was appeared on the display. This reading was indicated the travel time of the pulse wave measured in microsecond and length was measured with vernier calliper in millimetres. The ratio of length to travel time indicates the pulse velocity. Concrete quality was depending upon the pulse velocity as shown in table 3.10 and set up was shown in figure 3.4.

Table 3.10 Concrete quality grading

S.No	Pulse velocity(km/s)	Concrete Quality Grading
1.	Above 4.5 km/s	Excellent
2.	3.5 km/s to 4.5 km/s	Good
3.	3.0 km/s to 3.5 km/s	Medium
4.	Below 3.0 km/s	Doubtful

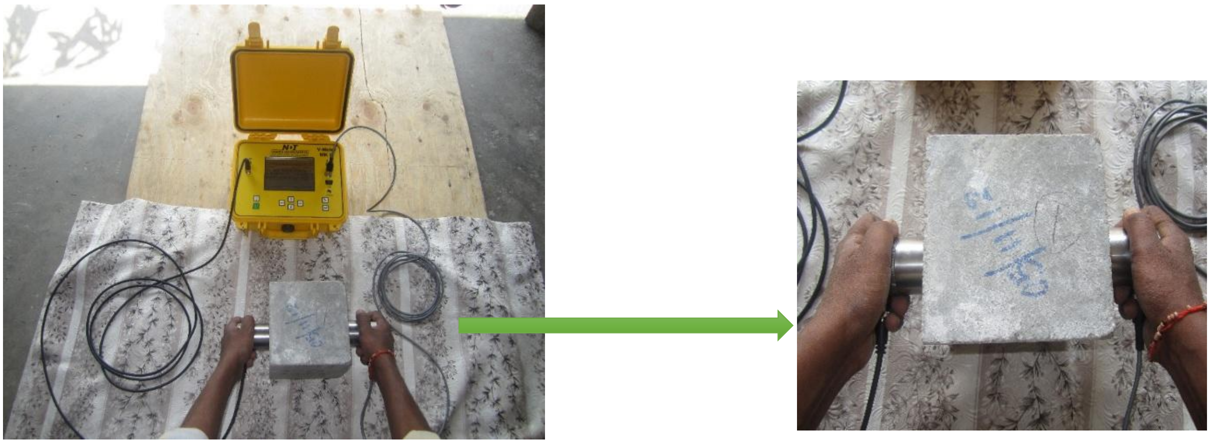

Figure 3.4 ultrasonic pulse velocity setup for measuring the ultrasonic pulse velocity in Concrete.

3.3.3 Compression Strength Testing

2000kN digital compressive testing machine was used for determine the compressive strength of hardened concrete as per the requirements of IS 516-1959.

3.3.3.1 Procedure

Before starting the test the weight of the sample was recorded. The plates of the machine were cleaned and specimen was kept centrally between the two plates as shown in Figure 3.5(a). Load was applied gradually on the specimen at a pace rate of 5.15kN/s up to failure. Once the sample was failed, the failure pattern was recorded as shown in Figure 3.5(b) and the compressive strength was calculated from the maximum load recorded in the test.

Figure 3.5(a) 2000 kN digital compressive testing machine

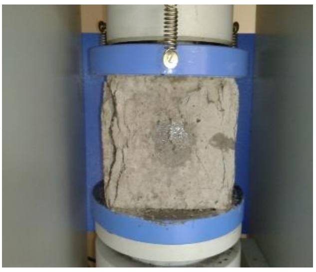

Figure 3.5(b) Failure pattern of the concrete cube

3.3.4 Thermogravemetric Analysis

Thermo-gravimetric analysis (TGA) was performed on cement samples at different ages. TGA was used to determine the evaporable water content, the non-evaporable water content and the $Ca(OH)_2$ contents of hydrating cementitious materials at different ages after casting. The temperature profile prescribed consisted of initially ramping the temperature from the ambient to 100 deg C at the rate of 10C/min. The samples were held at 100 deg C for 4 hours before ramping the temperature at 10degC/min to 1000 deg C. The sample was held at 1000degC for 1 hour. Following is the profile for TGA used in the experiment.

3.3.4.1 Methodology

TGA Samples Were Prepared of Cement and Fly Ash in the Same Proportion and Same W/C ratio as it was in the Concrete Mixes. After preparation, samples were kept in 1.5 ml air tight vials. At the time of testing, samples were crushed in to the powder form at inert atmosphere, sample was sieved with 1018 micros sieve and retained sample was used for testing.

Samples was taken in to crucibles with the weight between 10-15 mg. Samples were heated with the ramping of 10^{o}C/min from initial temperature to 105^{o}C and 10^{o}C/min from 105^{o}C to1000^{o}C.samples were held 240 minutes at 105^{o}C and 60 minutes at1000^{o}C. TGA experiment profile shows in figure 3.6.

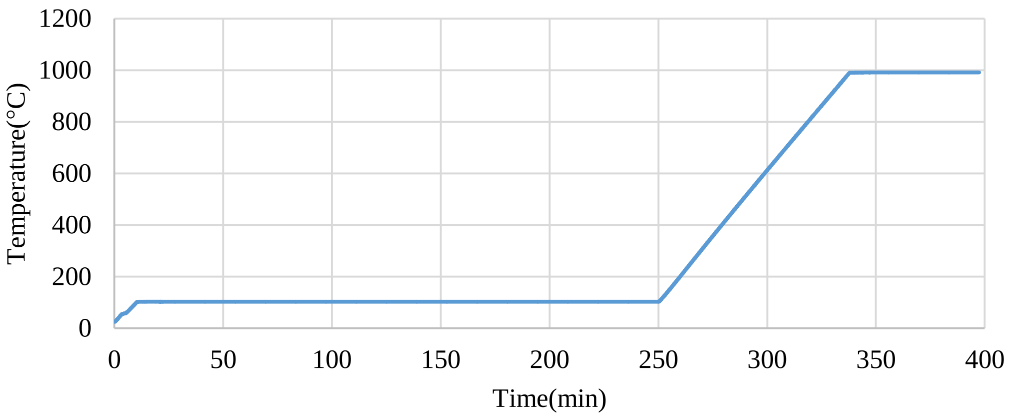

Figure 3.6 TGA program in the experiments

3.3.4.2 Principle

Thermogravimetric analysis depends on measuring the dynamic weight loss from a sample as it heated at a controlled rate. Derivative thermogravimetric (DTG) curve is often calculated to better identify the changes as shown in Figure 3.7.

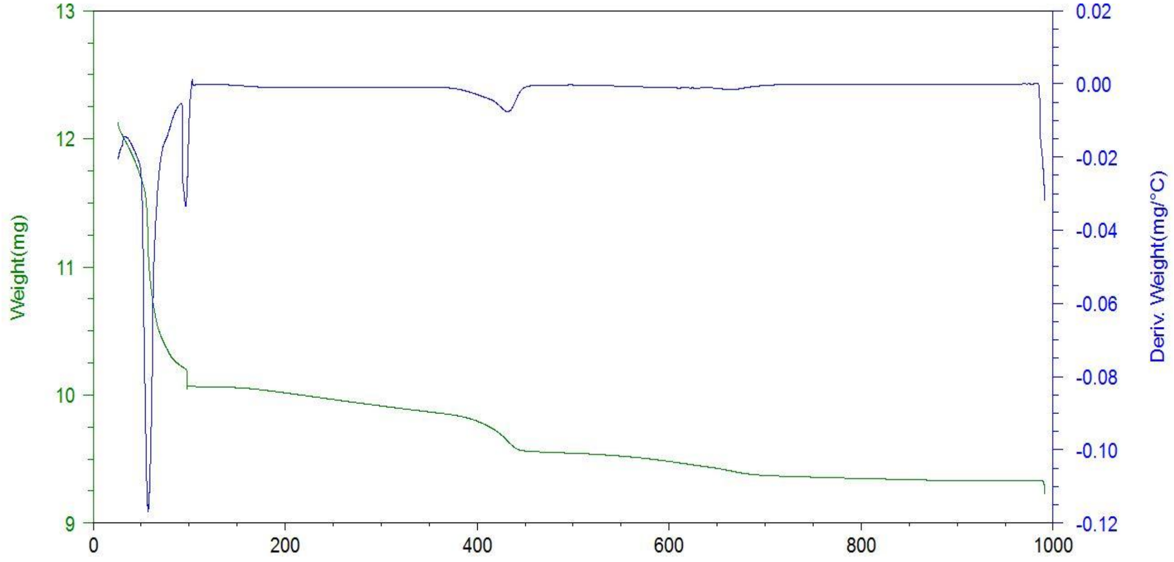

Figure 3.7 shows an example of TGA and DTG curves of a cement fly ash lime pastes

From 25 to 415°C: part of bound water in C-S-H escapes as shown in figure 3.7

From the thermogravimetric curve, weight loss due to dehydration of calcium hydroxide occurs in the region of 380 and 520° C minus the ignition loss of powder to the binder weight as shown in Figure 3.8 and the chemical reaction is:

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

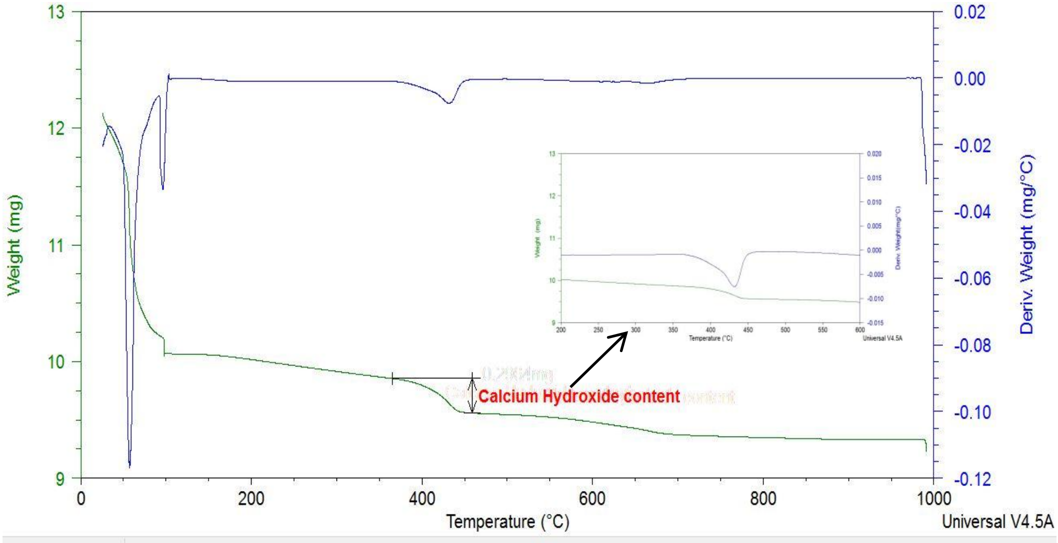

Figure 3.8 Identification of Calcium Hydroxide content

Non Evaporable water or chemically bound water defined as the loss of mass between 105 to 1000°C minus the ignition loss of powder to the binder weight as shown in Figure 3.9

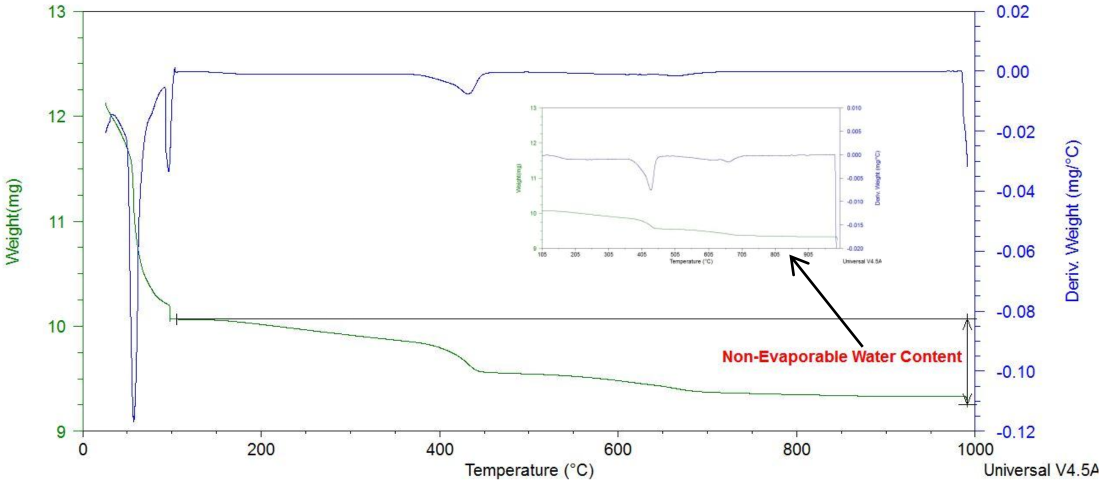

Figure 3.9 Identification of Non Evaporable Water Content

3.3.5. Isothermal Calorimetry

3.5.5.1. Principle

Iso-thermal Calorimetry is one of the techniques used to follow the hydration process by monitoring the rate of heat release. Since hydration is an exothermic reaction, rate of heat release provides a measure of reaction kinetics. Additionally, the extent of reaction can be determined from the total heat evolution. The advantage of this technique is that the determination of hydration process at different temperature from 5^{O}C to 90^{O}C can be followed continuously at different water/cement ratios in situ without the need for drying the samples.

3.5.5.2. Procedure

The heat released from cementitious paste samples at 25°C and 40^{o}C were determined using an isothermal calorimeter TAM Air (shown in Figure 3.10). The equipment consists of 16 parallel twin type measurement channels maintained at a constant temperature: one from the sample, the other for the reference vessel. The reference vessel is used to reduce the signal to noise ratio and to correct measurement and temperature artefacts. 20ml ampoules are used for both the sample and the reference container. Heat is conducted from the sample to the reference sample (silica with same thermal mass as the hydrating sample) and hence the hydration is effectively isothermal. Calorimeter provides for continuous measurements of the early stage of hydration where the heat flow is relatively high.

Paste samples were prepared from the cementitous material using the same proportions of materials by weight as used in the concrete mixtures. Cement, fly ash and lime are referred to as cementitious materials. After preparation, samples were kept in 20 ml air tight ampoules and introduced into the calorimeter. Measurements of heat flow were performed at 0ne second intervals up to 7 days after mixing. The typical rate of heat evolution for a hydrating cement shows several periods as shown in Figure 3.11.

Figure 3.10 Isothermal Calorimeter

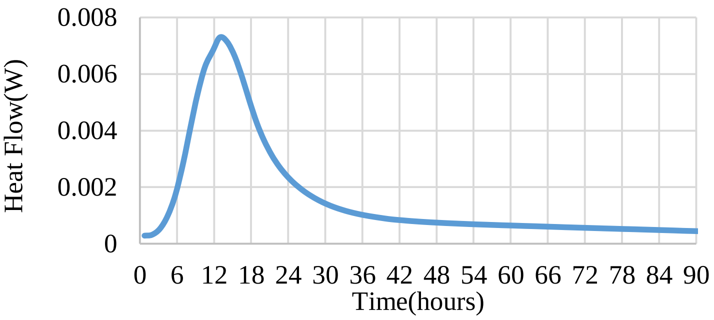

Figure 3.11 Typical rate of heat evolution for hydrating cement

Chapter-4

High Volume Fly ash Concrete

4.1 Introduction

Fly ash has often been used as a cement replacement to improve specific aspects of concrete performance. While fly ash has been shown to improve durability aspects such as reducing the potential for restrained shrinkage and thermal cracking and alkali silica expansion, its low reactivity is a major hindrance to the development of concrete consisting of large volumes of fly ash. Fly ash essentially relies on pozzolanic reaction to contribute to strength development. Successful production of high volume fly ash replacement therefore requires an understanding of the reactivity and the reactions of fly ash in cement system.

In this chapter the potential of high volume cement replacement with fly ash is investigated. Concrete mixtures with 60%, 70% and 80% cement replacement with fly ash were evaluated for strength gain. The extent of hydration reaction and the rate and extent of pozzoloanic reaction in the fly ash concrete was evaluated using thermo-gravimetric (TG) analysis.

4.2 Experimental Results

An experimental program was developed to evaluate fly ash concrete mixture proportions with water to cementitious material ratios equal to 0.43 and 0.50 w/c at cement replacement levels equal to 60%, 70% and 80% by weight with fly ash. Each concrete mixture was evaluated with respect to slump, Ultrasonic pulse velocity and compressive strength. Additionally, Thermogravimetry analysis was performed using cement paste samples for 70% cement replacement fly ash.

4.2.1 Concrete with 0.43 w/c ratio

4.2.1.1 Slump

The slump of all four concrete mixtures measured immediately after mixing is shown in Table 4.1. The beneficial effect of fly ash in improving workability is evident in the increased slump value obtained on increasing the fly ash content.

Table 4.1 slump values of the concrete mixtures

Mix proportions	Slump(mm)
Control	40
80% F+20% C	90
70% F+30%C	70
60% F+40%C	60

The improvements of fly ash have been documented in the literature (Lane, 1983). The volume of cement plus fly ash normally exceeds that of cement without fly ash; fly ash has lower density resulting in a larger volume of fly ash for an equivalent mass of cement replacement. This results in an increase in the paste volume of concrete with improved plasticity and better cohesiveness. The volume of fines from fly ash also compensate for deficient aggregate fines.

4.2.1.2 Ultrasonic Pulse Velocity

Ultrasonic pulse velocity (UPV) was measured at 1, 3, 7, 14, 28, 56 and 90 days of age. Pulse velocity for propagation of ultrasonic waves was obtained for both compression (P-wave) and shear waves (S-wave) and the values are listed in Tables 4.2 and 4.3, respectively and shown in figures 4.1 and 4.2, respectively. The UPV from concrete with fly ash for both P and S waves were consistently lower than the corresponding value obtained from the control mixture and the difference increased with an increase in the fly ash content. For all mixtures the S-wave velocities are consistently lower than P-wave velocities at any age.

Table 4.2 Pulse velocities of concrete

Age(days)	P-wave velocity(km/sec)			
	Control	80% F+20% C	70% F+30%C	60% F+40%C
1	3.915	2.487	2.712	2.830
3	4.086	2.769	3.260	3.281
7	4.196	2.845	3.342	3.794
14	4.329	3.182	3.624	4.089
28	4.534	3.624	4.104	4.205
56	4.765	4.223	4.372	4.450
90	4.855	4.428	4.512	4.691

Table 4.3 Shear velocities of concrete

Age(days)	Shear wave velocity(km/sec)			
	Control	**80% F+20% C**	**70% F+30%C**	**60% F+40%C**
1	3.652	2.102	2.198	2.293
3	3.852	2.152	2.304	2.516
7	3.965	2.220	2.488	2.581
14	4.105	2.286	2.617	3.540
28	4.202	2.856	3.182	3.713
56	4.438	3.544	3.852	4.023
90	4.689	3.961	4.215	4.301

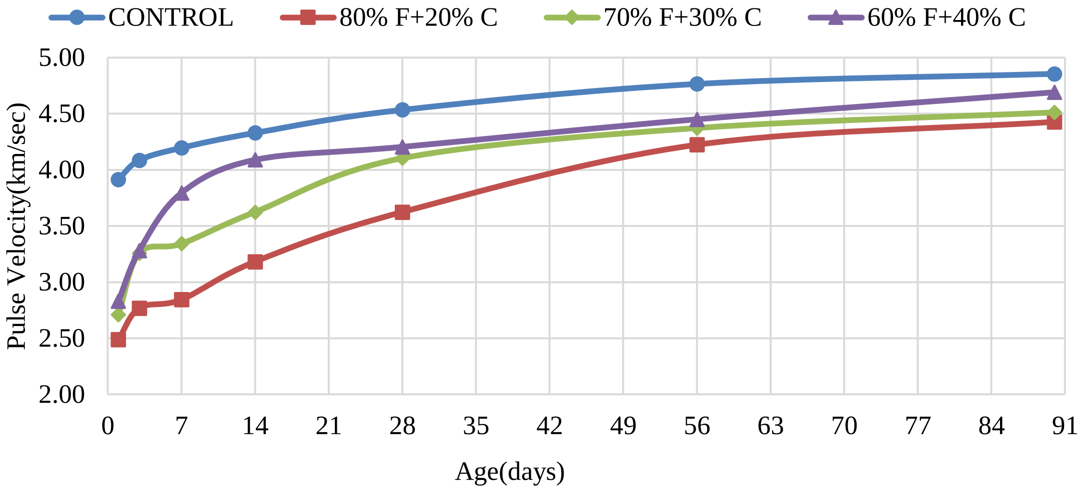

Figure 4.1 Pulse wave velocities of concrete with age

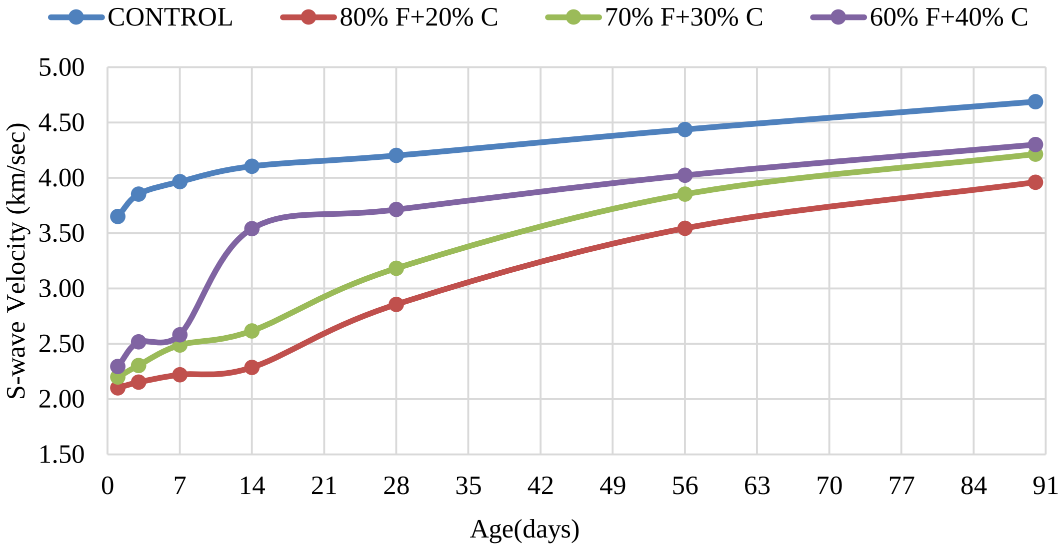

Figure 4.2 Shear wave velocities of concrete with age

P and S-wave velocities of control mixture were higher than 3.5 km/sec indicating good quality concrete as per IS 13311(part-1):1992. The fly ash mixtures attained pulse velocities in the range of 3.5 to 4.0 km/s at 56 days. For the control mixture, the initial values of P and S-wave velocities at 1 day are significantly higher than the fly ash mixtures. Further, the total increase in wave velocity values up to 90 days is a small percentage of the one day values. The P and S-wave velocities in fly ash mixtures are start from a low value at one day and exhibit a rapid increase up to 14 days, followed by a steady increase up to 90 days. The fly ash mixtures exhibit a significant increase relative to the one-day value; the total increases in in wave velocities are approximately 80% of the one day values.

Pulse velocity is indicative of the stiffness of the material which is reflected in the elastic modulus. The results obtained indicate, that for control mixture, there is a significant increase in the modulus within the first day. There is a smaller percentage increase in modulus after the first day up to 90 days. With progressing hydration, the change in the modulus of fly ash mixtures is significant when compared to the one day value. The results of the pulse velocity indicate that the contribution of the products of hydration influence the strength and modulus development differently.

4.2.1.3 Compressive strength

The average compressive strength obtained from three samples are listed in Table 4.4 and shown in Figure 4.3. The compressive strengths were determined at 1, 3, 7,14,28,56 and 90 days of age. The compressive strength of the control mix exceeded the mean target strength of 43 MPa for M35 grade concrete at 28 days of age. The compressive strength obtained from all mixtures were lower than the control mix at all ages. None of the fly ash mixtures attained the characteristic strength even after 90 days.

Table 4.4 Compressive strength of samples at different age

Age(days)	**Compressive strength of samples(MPa)**			
	Control	**80% F+20% C**	**70% F+30%C**	**60% F+40%C**
1	19.86	2.27	3.25	6.42
3	27.67	3.81	7.54	9.69
7	38.27	5.18	8.63	12.13
14	43.84	8.32	12.17	16.50
28	48.64	11.05	17.61	18.81
56	56.84	17.07	20.54	27.93
90	64.12	22.58	26.53	31.46

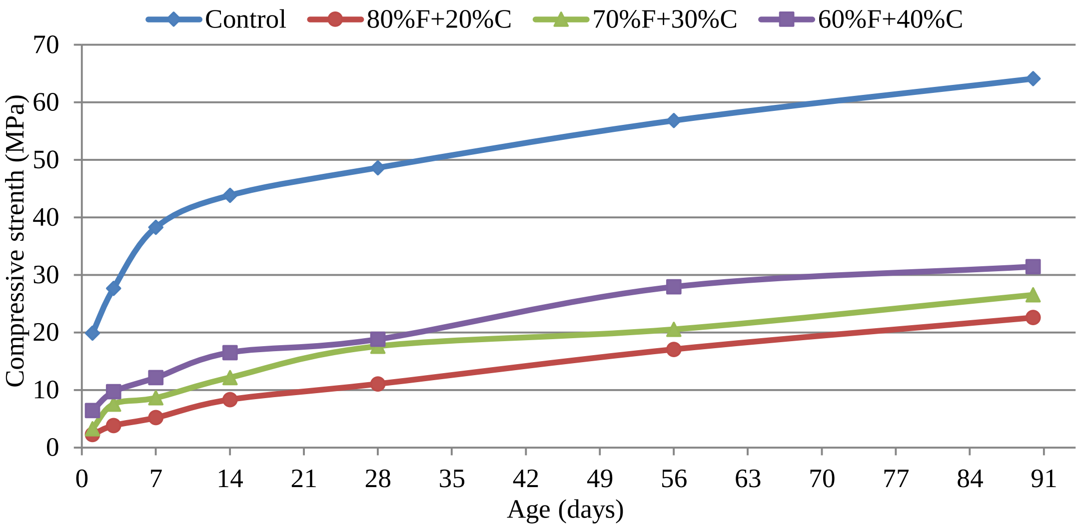

Figure 4.3 Variation of compressive strength for different mix proportions with age

To better understand the rate of strength gain and the efficiency of the supplementary cementitious material, the compressive strength of each mix at any given age was normalized with respect to the compressive strength of the control mixture and are listed in Table 4.5. The results indicate that at 14 days of age, the compressive strengths of all mixtures with cement replacement were roughly proportional to the weight percentage of cement in the cementitious binder. After fourteen days, the compressive strengths of all fly ash mixtures were higher than the compressive strength obtained as a proportion of cement in the mixture. This indicates that the initial gain in strength could be attributed to cement alone and the pozzolanic reaction started at 14 days. The fly ash does make a noticeable contribution to strength gain in the system at a later age. The composition of fly ash suggests very little lime in the material to support hydraulic activity. Therefore, the contribution to strength gain from the fly ash appears to be from the pozzolanic reaction, which would depend upon the lime released by cement hydration.

Table 4.5 Compressive strength at different ages as a percentage of control mix strength

Age(days)	**Compressive strength of samples(MPa)**			
	Control	**80% F+20% C**	**70% F+30%C**	**60% F+40%C**
1	100	11.4	16.4	32.3
3	100	13.8	27.3	35.0
7	100	13.5	22.6	31.7
14	100	19.0	27.8	37.6
28	100	22.7	36.2	38.7
56	100	30.0	36.1	49.1
90	100	35.2	41.4	49.1

4.2.1.4 Thermogravimetric Analysis

The variation in the $Ca(OH)_2$ content as a percentage of the cementitious binder with age is shown in Figure 4.5. It can be seen that for the control mixture, the $Ca(OH)_2$ content rapidly increases up to 7 days of age following which there is a steady decrease in the rate, which reaches an asymptotic value at 28 days. These findings correlate well with the measured increase in compressive strength; the rapid increase in the $Ca(OH)_2$ content coincides with the rapid increase in strength. The slowdown in the rate of strength gain after the first 7 days corresponds with the observed decrease in the rate of $Ca(OH)_2$.addition. The observations from TGA further indicate that strength gain produced by the hydraulic reaction of cement results in production of $Ca(OH)_2$.

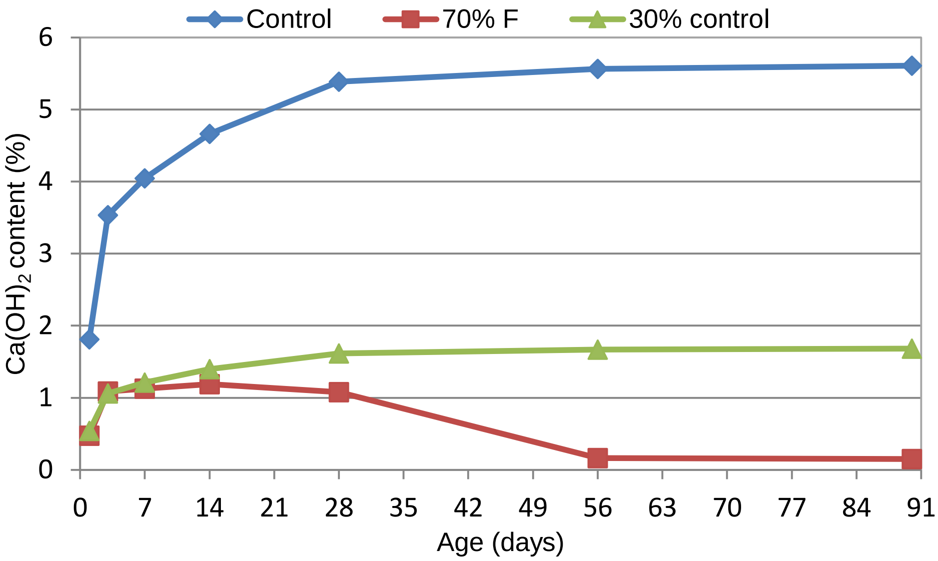

Figure 4.4 Calcium Hydroxide content for control and fly ash mixtures with age.

For the mixture with 70% cement replacement with fly ash, there is an initial increase in the $Ca(OH)_2$ content up to 7 days followed by depletion. The $Ca(OH)_2$ content obtained by scaling the control mixture is also shown in the Figure 4.4 for comparison. Up to 7 days of age, the $Ca(OH)_2$ content of the fly ash mixture appears to match the value obtained by scaling the $Ca(OH)_2$ content of control mixture to 30% of its value. This indicates that in fly ash-cement mixture, up to 14 days of age, $Ca(OH)_2$ is contributed only by the hydraulic activity of cement and that there is no consumption of lime up this age. After 7 days, the lime content started to decrease and it deviates from the contribution obtained from cement alone. This indicates that the pozzolanic reaction started after 7 day. There is complete depletion of lime in the fly ash mix at 56 days of age, which suggests there is insufficient lime to completely react with the available reactive silica in fly ash.

The non-evaporable water content as a percentage of the cementitious binder is shown in figure 4.5. For both mixtures, the chemically bound water increases steadily up to 14 days of age following which, the bound water content asymptotically increases to a constant value at 28 days. Up to 7 days of age, the chemically bound water content of the fly ash mixture appears to match the value obtained by scaling the chemically bound water content of control mixture to 30%. This indicates that up to 7 days, the chemically bound water content of the fly ash mixture is contributed only by the hydraulic activity of cement. After 7 days, the bound water in the fly ash mixture is higher when compared to 30 % control mixture. This indicates that the consumption of lime in the system coincides with additional contribution from fly ash hydration to the bound water in the system. Hence, fly ash contributes products of hydration after 7 days of age.

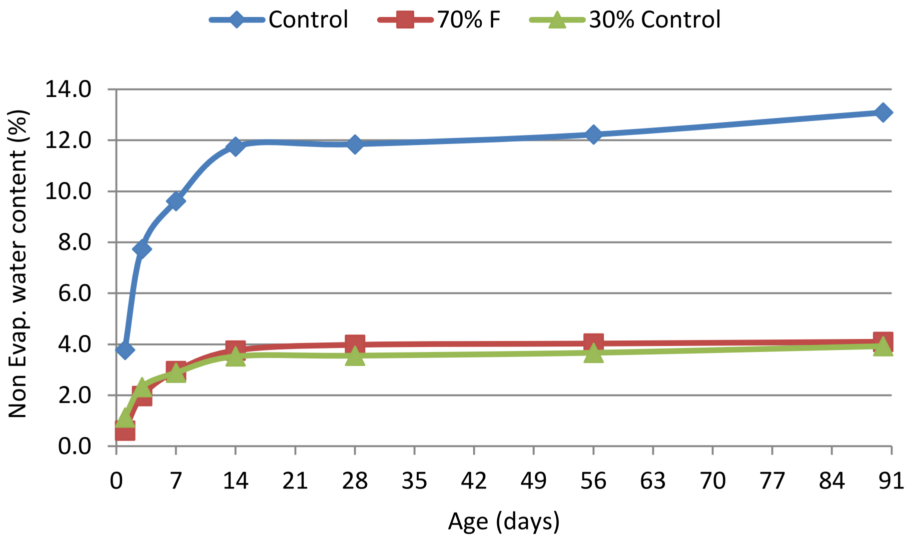

Figure 4.5 Non Evaporable Water content for control and fly ash mixtures with age

4.2.2 Concrete with 0.50 w/c ratio

4.2.2.1 Slump

The workability of mixtures indicated by slump measurements are shown in Table 4.6. The results are in agreement with those obtained for the 0.43 w/c concrete wherein higher slump was obtained from concrete containing fly ash in the binder.

Table 4.6 slump values of the concrete mixtures

Mix proportions	Slump(mm)
Control	90
70% F+30% C	196

4.2.2.2 Ultrasonic Pulse Velocity

P and S-wave velocities measured at the ages of 1, 3, 7, 14, 28, 56 and 90 days are listed in Table 4.7 and plotted in Figures 4.6 and 4.7. Consistent with the findings for 0.43 w/c ratio, the P and S-wave velocities of concrete obtained from fly ash mixture was lower than the control mix at all ages. For both mixtures, the S-wave velocities were smaller than the P-wave velocities at all ages. At one day of age both P and S-wave velocities in Fly ash mixture were significantly lower than the corresponding wave velocities in control mixture. Both P and S-wave velocities increased at a more rapid rate with age in the fly ash mixture than the control mixture.

Table 4.7 Compressive strength, Pulse Velocity and shear velocities of the cement and fly ash mixtures

Age(days)	**Compressive strength (MPa)**		**P-wave Velocity (km/sec)**		**S-wave velocity (km/sec)**	
	Control	**70%F+30%C**	**Control**	**70%F+30%C**	**Control**	**70%F+30%C**
1	12.25	1.91	3.740	2.265	3.502	1.917
3	20.92	3.86	3.986	3.182	3.652	2.119
7	26.72	4.72	4.009	3.212	3.798	2.316
14	32.11	7.77	4.276	3.553	3.920	2.519
28	37.51	10.89	4.498	4.090	4.109	3.012
56	44.46	16.63	4.512	4.104	4.234	3.757
90	46.68	23.32	4.635	4.367	4.522	4.184

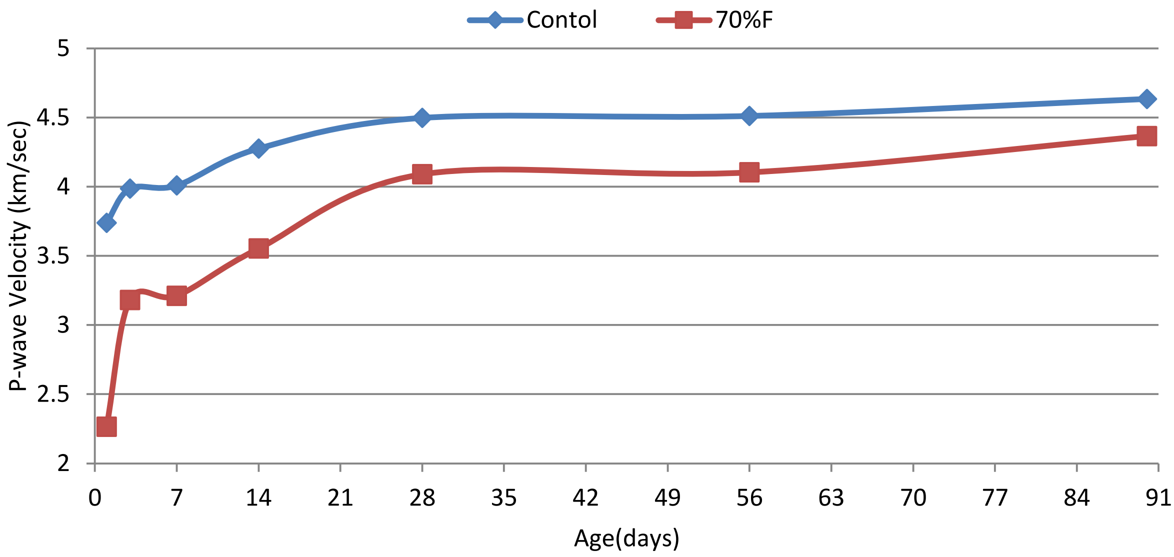

Figure 4.6 Pulse Velocities the Control and fly ash mixture with age

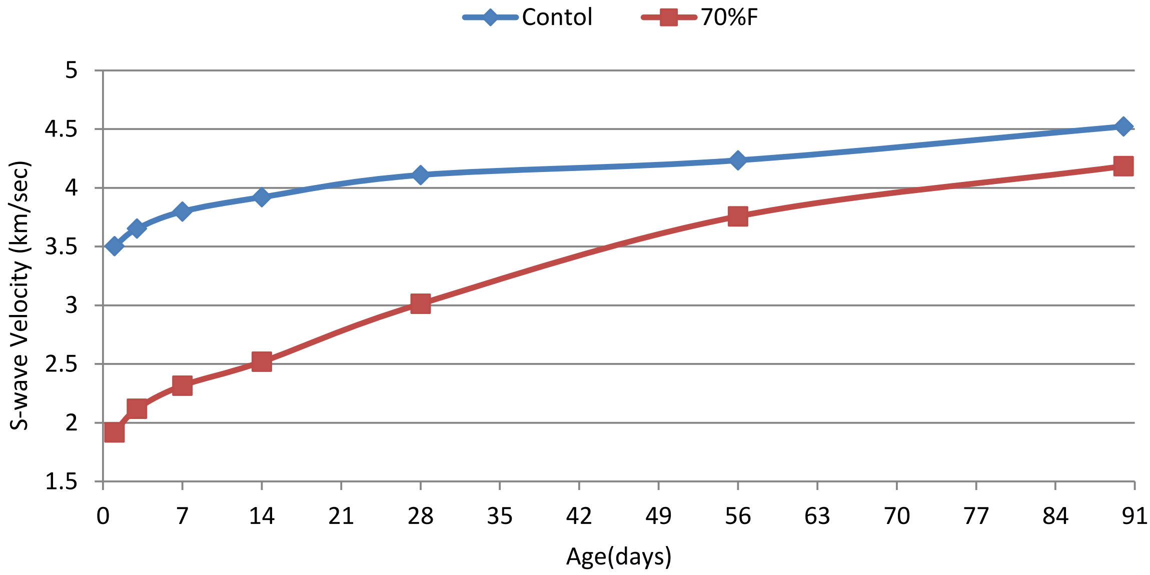

Figure 4.7 shear Velocities the Control and fly ash mixture with age

4.2.2.3 Compressive strength

The compressive strength of mixtures as a function of age are plotted in Figure 4.8. The compressive strength of the control mix exceeded the mean target strength of 43 MPa for M35 grade concrete by 56 days. The compressive strength obtained from fly ash mixtures was lower than the control mix at all ages. Fly ash mixture did not attain the target strength even after 90 days. A comparison of the strength gain obtained by the fly ash mixture with the scaled value of the compressive strength reveals that the fly ash mixture attains strengths higher than the 30% value of the control mixture only after 28 days.

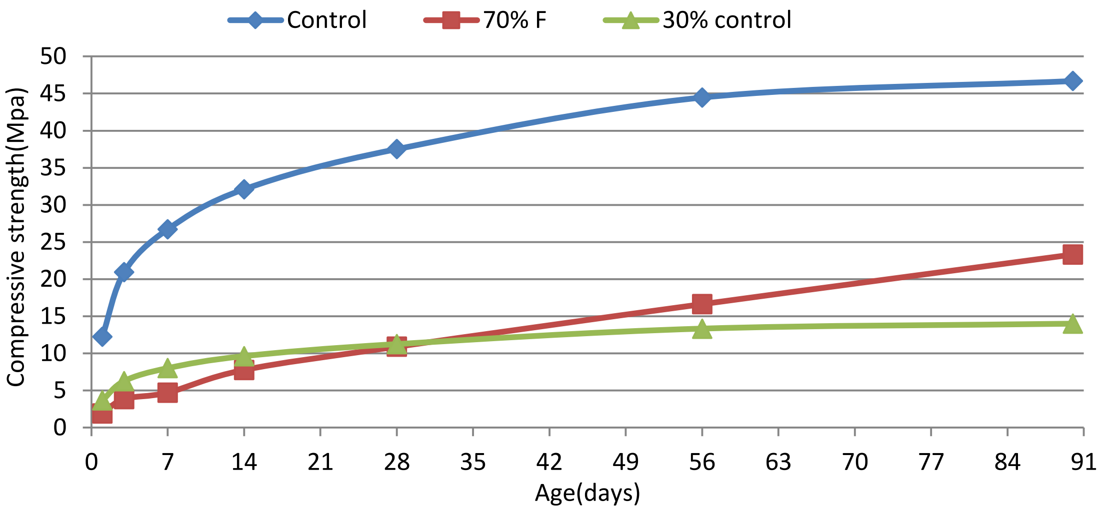

Figure 4.8 Compressive strength of the Control and 70% fly ash mixture with age

4.2.2.4 Thermogravimetric Analysis

The $Ca(OH)_2$ content as a percentage of the cementitious binder as a function of age is shown in Figure 4.9. It can be seen that in the control mixture, the $Ca(OH)_2$ content rapidly increases up to 7 days of age following which there is a steady increase up to an asymptotic value. These findings are in agreement with the measured increase in compressive strength; the rapid increase in the $Ca(OH)_2$ content coincides with the rapid increase in strength. The slowdown in the rate of strength gain after the first 7 days corresponds with the observed decrease in the rate of $Ca(OH)_2$.addition. A comparison of the $Ca(OH)_2$ content of the fly ash mixture with the 30% value of the control indicates that the hydraulic activity of cement alone contribute to lime in the system up to 7 days of age. Further, the consumption of lime is initiated at 7 days of age.

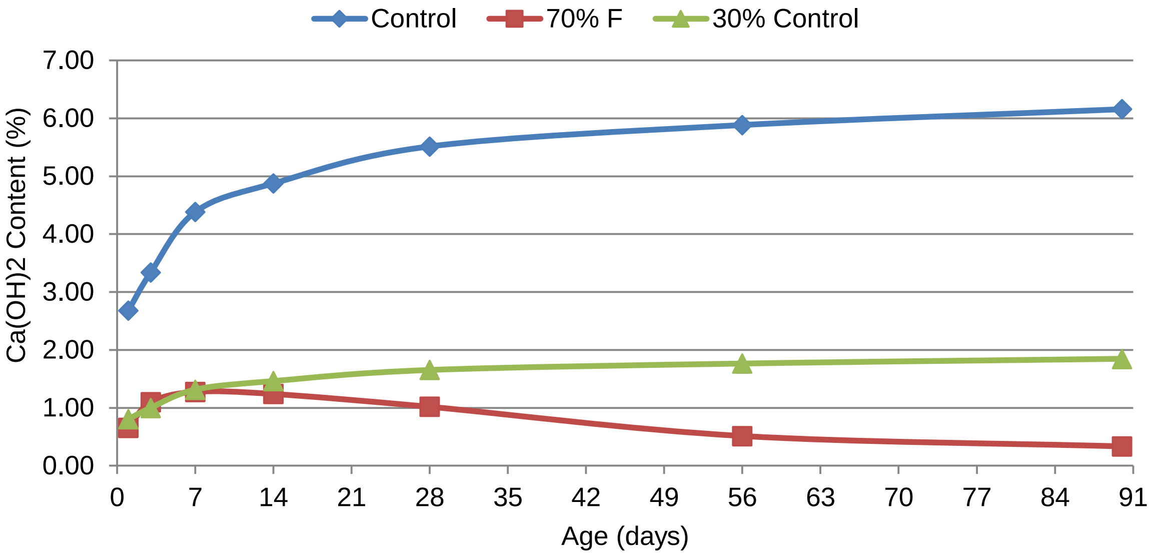

Figure 4.9 Calcium Hydroxide content for control and fly ash mixtures with age

The non-evaporable water content as a percentage of the cementitious binder is shown in figure 4.10. Up to 28 days of age, the chemically bound water content of the fly ash mixture is lower than the value obtained by scaling the chemically bound water content of control mixture to 30%. This indicates that up to 28 days, the water which is chemically bound in the products of hydration and $Ca(OH)_2$ in fly ash system is lower than the water bound in the control mixture per unit weight of the binder.

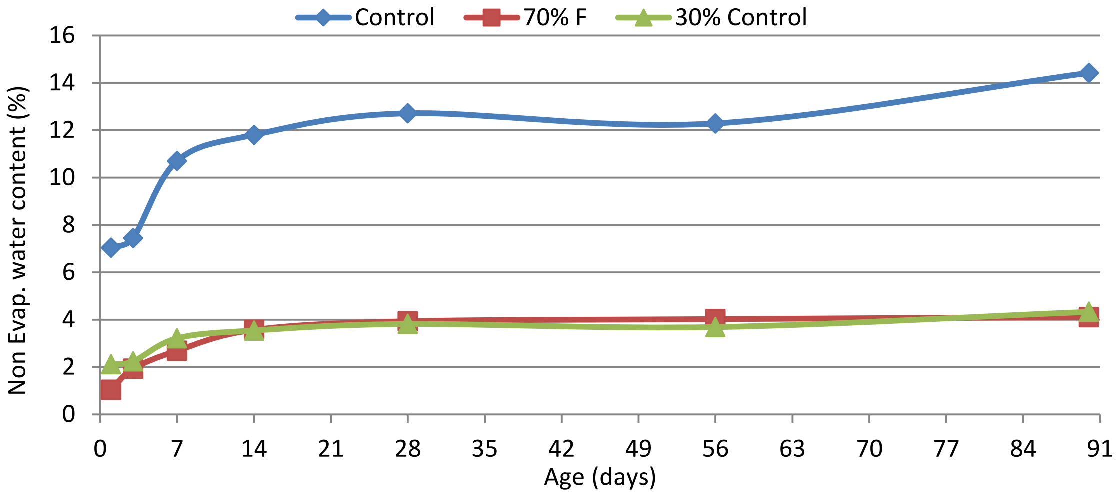

Figure 4.10 Non Evaporable Water content for control and fly ash mixtures with age

4.3 Discussion

A comparison of strength gain exhibited by concrete mixtures with w/c ratios equal to 0.50 and 0.43 is shown in Figure 4.11. For 0.43 and 0.5 w/c ratios, the strength of the fly ash mixture exceeds the scaled value obtained from control mixture at 14 and 28 days, respectively.

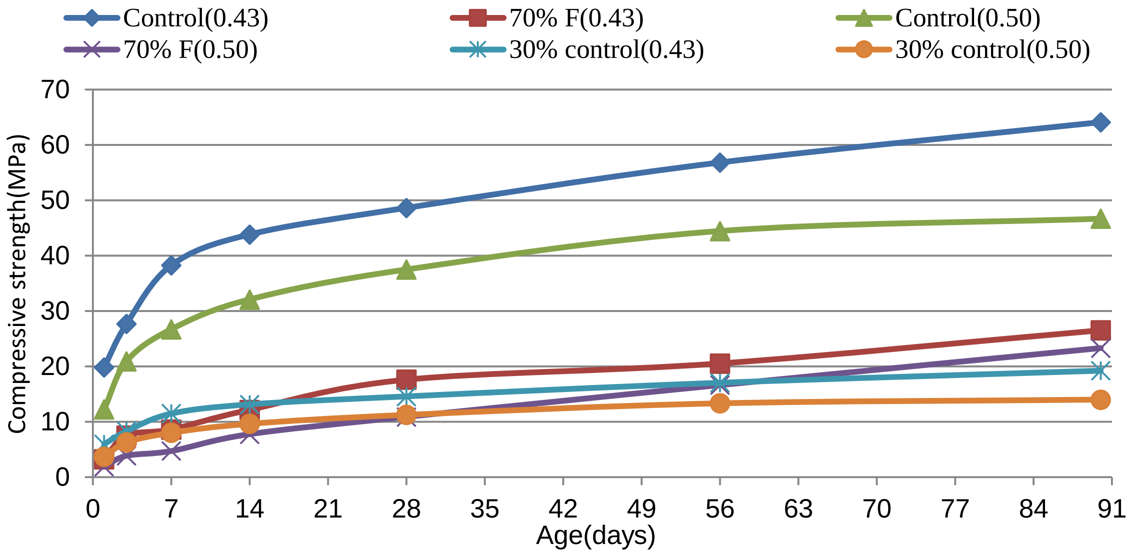

Figure 4.11 Comparison of Compressive strength of 0.43 and 0.50 w/c ratios

A comparison of the $Ca(OH)_2$ and non-evaporable water contents for the two w/c ratios are shown in Figures 4.12 and 4.13, respectively. The results indicate that the production and the initial consumption of lime in fly ash systems are not affected by the w/c ratio. Since the hydration of cement is the only source of $Ca(OH)_2$, the results suggest that the release of lime is controlled only by the weight of cement in the binder and are independent of the water in the system. Similarly, the consumption of lime in fly ash systems by the pozzolanic reaction is identical in both 0.43 and 0.5 w/c ratio mixes. Since the pozzolanic reaction contributes to $Ca(OH)_2$ consumption, the pozzolanic reaction appears not to be influenced by the water content or the concentration of fly ash in the mix.

The non-evaporable water content in the control and fly ash system are also not affected by the w/c ratio but are dependent on the binder as shown in Figure 4.13. The results of the fly ash system indicate that the extent of hydration and the products of hydration as a percentage of total binder content are identical at both w/c ratios evaluated in this study. The strength of the concrete mixture are however dependent on the water content; higher strengths are obtained for lower w/c ratio. Therefore while the extent of hydration in the control and fly ash mixture for w/c ratio equal to 0.43 are identical respectively to the extent of hydration in the control and fly ash mixture at w/c ratio 0.5, strength depends on the volume of the hydration products in a unit volume, which is controlled by the water content. Higher w/c ratio results in a more porous structure, which reduces the strength. A Comparison of strength development between control and fly ash mixture had previously shown that for higher w/c ratio, strength equivalent to cement system is produced at a later age. This implies that the strength of the products of fly ash hydration are more influenced by the water content than cement.

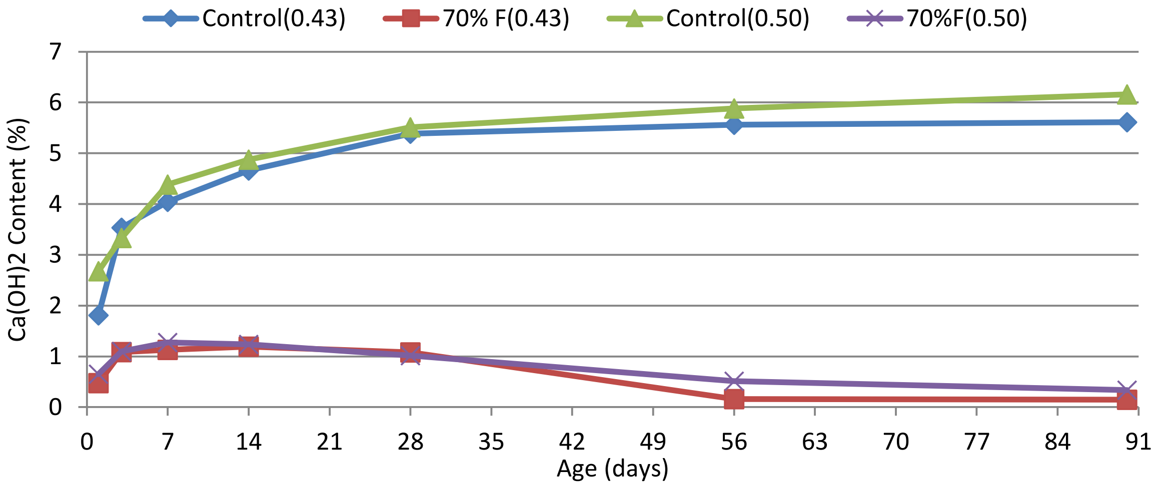

Figure 4.12 Comparison of Calcium hydroxide depletion of 0.43 and 0.50 w/c ratios

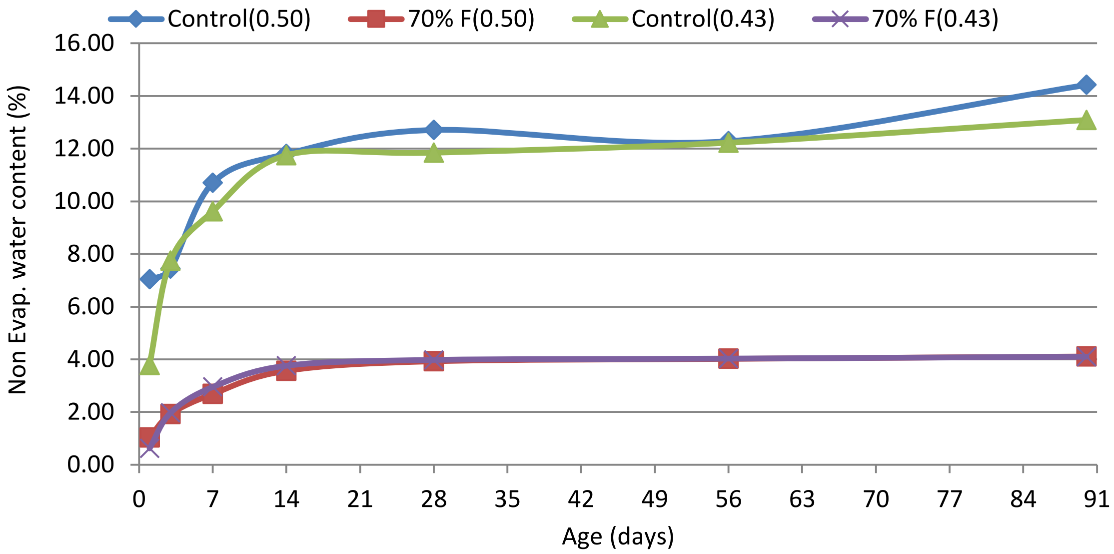

Figure 4.13 Comparison of chemical bound water content of 0.43 and 0.50 w/c ratios

4.4 Summary and Findings

Based on the results presented in this chapter the following conclusions can be drawn

1. Fly ash influences workability by increasing the slump.
2. The low Calcium Fly ash used in this study exhibits very low hydraulic activity. Its contribution to early age strength gain is very small. In cement-fly ash system, the pozzolaonic activity is totally dependent on the lime produced by the hydraulic reaction of cement. The rate of production of lime for given binder content from hydraulic activity of cement depends only on the cement content of the binder and is not influenced by the water content of the mixture. The pozzolanic reaction commences at 7 days of age when the lime content reaches a threshold value as a percentage of the binder content in the mixture. The lime content at which pozzolanic reaction starts is not influenced by the water content but is a fixed percentage of the total binder content.
3. Non Evaporable water content and production of lime as a percentage of the binder are not affected by the w/c ratio. At 70% cement replacement, there is a complete depletion of lime in the system by 90 days of age.
4. While the total strength gain is higher for the fly ash system with 0.43 w/c ratio when compared to w/c equal to 0.50, the rates of increase in the non-evaporable water content is identical in the two systems. This suggests that for the same extent of hydration, the

strength depends upon the water content which influences the distribution and packing of the products of hydration.

The available results suggest the possibility of using lime to activate the fly ash mixtures. From these 70% fly ash mixture taken as an activation purpose. This is investigated in the next chapter.

Chapter-5

Activation in High Volume Fly ash Concrete

5.1. Introduction

High volume replacement of cement with supplementary cementitious materials (SCM) has been shown to impact the strength gain and the final strength of concrete. Developing equivalent strength gain as cement is often called the efficiency of the SCM. Among all SCMs, fly ash at high replacement levels suffers from severe loss in strength. Researchers have tried mechanical, thermal and chemical methods of activation to achieve faster strength gain and higher ultimate strength from fly ash. The activation methods rely on grinding the fly ash to a smaller particle size, increasing temperature and using chemical activators to increase the reactivity and hence the rate of strength gain and ultimate strength.

The potential for contributing to overall strength depends upon the reactive silica content in the SCM. Grinding and thermal activation are ineffective when the chemical species present do not favour a reaction. The use of chemical activators has been very effective in activation of potential cementitious property of SCMs and pozzolanic reactivity of pozzolans. The use of lime, in particular, has been shown to be effective and efficient technique to activate the potential pozzolanic reactivity of coal fly ashes and to improve the properties of the fly ash concrete. The available information in the literature suggests that rate of ash hydration increases with addition of both lime (CaO) and hydrated lime ($Ca(OH)_2$). It has been shown that in the presence of $Ca(OH)_2$, there is an increase in the solubility of SiO_2 leading to a greater release of soluble silica into the hydrating matrix. The improvements to strength gain through accelerated hydration in the fly ash – $Ca(OH)_2$ system has been shown to be sensitive to temperature. Previous studies on lime activation have considered low volume cement replacements. In low-volume fly ash systems the influence of $Ca(OH)_2$ may be difficult to perceive since the cement hydration contributes significant quantity of $Ca(OH)_2$. In such systems the changes in pH on account of increase $Ca(OH)_2$ content on account of external activation using lime will be a smaller when compared to the contribution from cement in the system. Also in such systems the beneficial effect of activation may be offset by the significant presence of unreacted $Ca(OH)_2$, which weakens the system by increasing its porosity [Antiohos 2003].

In this study, lime and temperature activation has been studied in volume fly ash systems with 70% cement replacement with fly ash.Both quick lime and hydrated lime were evaluated. Quick lime contributes $Ca(OH)_2$ after a reaction with water which is exothermic without impacting the pH of the system. Hydrated lime on the other hand is expected to contribute additional Ca^{2+} ions and raise the p^H of the system. Therefore, the experimental program allows for evaluating the influence of $Ca(OH)_2$ content and p^H on the hydration of fly ash in cement-fly ash system.

Strength gain was monitored in concrete mixtures with different levels of lime dosage. The baseline concrete mixtures 70% of the fly ash was used for comparison. The fly ash in these mixtures was replaced with equal mass of lime at different proportions. Thermogravimentric analysis was performed on cement-fly ash paste samples with lime addition to study the rate of $Ca(OH)_2$ production and depletion in activated systems. Additionally isothermal calorimetry was performed to study the influence of lime on the early hydration. The results obtained from lime replacement were interpreted considering two effects: (a) reduction in the reactive silicain the mixture with the decreasing fly ash content; and (b) the gain in strength contributed by the activation provided by lime.

5.2. Experimental Program

The baseline concrete mixture with 70% cement replacement with fly ash was chosen to evaluate the influence of lime dosage to high volume fly ash system.The concrete mixture composition was taken identical to the 70% fly ash mix used in the previous Chapters. Both Hydrated lime and quick lime were evaluated in the test program. In all mixtures the cement content was kept constant equal to 30% of the total mass of the cementitious material in the mix. Concrete mixtures with different levels of fly ash replacement with equal weight of lime or hydrated lime were tested as shown in Tables 5.1 and 5.2. For each mix compressive strength was measured at 1, 3, 7, 14, 28, 56 and 90 days of age using 150mm cubes.

Table 5.1 Concrete mix designations for different hydrated lime replacement

Cement Content (%)	Fly ash Content (%)	Hydrated Lime content (%)	Designation
30	68	2	30C-68F-2HL
	66	4	30C-66F-4HL
	65	5	30C-65F-5HL
	66	4	30C-66F-6HL
	62	8	30C-62F-8HL

Table 5.2 Concrete mix designations for different Quick lime replacement

Cement Content (%)	Fly ash Content (%)	Hydrated Lime content (%)	Designation
30	65	5	30C-65F-5QL
	60	10	30C-60F-10QL

5.3 Experimental results

5.3.1 Lime activation in 0.43w/c ratio system

5.3.1.1 Slump

The slump of the concrete mixtures measured immediately after mixing are shown in Tables5.3 and 5.4. The effect of both hydrated lime and quicklime in reducing the workability is evident in the decreased slump value obtained on increasing the lime content. The results indicate that in both HL and QL systems the reduction in slump is disproportionately higher than the decrease in contribution from the reduced fly ash content which suggests very early reactivity in these systems which influences the slump.

Table 5.3 slump values of the hydrated lime activated 70% fly ash mixtures

Designation	Slump(mm)
Control	40
30C-70F	70
30C-68F-2HL	57
30C-66F-4HL	51
30C-65F-5HL	45
30C-66F-6HL	42
30C-62F-8HL	37

Table 5.4 slump values of the quick lime activated 70% fly ash mixtures

Designation	Slump(mm)
Control	40
70% F+30%C	70
30C-65F-5QL	42
30C-60F-10QL	38

5.3.1.2 Compressive strength

The compressive strength of hydrated lime activated mixtures are listed in Table 5.5 and shown in Figure 5.1. The compressive strengths obtained as the average of three specimens were measured at the ages of 1, 3, 7,14,28,56 and 90 days of age. All lime activated fly ash concrete mixtures showed lower strength compared to control mixture. None of the mixtures attained the characteristic strength even after 90 days. There appears to be a slight increase in strength gain on increase the HL content up to 5% beyond which there is a decrease in both the short and long-term gains in strength. The strength of 5% HL content matched the strength of the baseline fly ash mixture. The results indicate that hydrated lime has little or no influence on the performance of fly ash when cured at 25 deg Celsius.

Table 5.5 Compressive strength as a function of age in hydrated lime activated to 70% fly ash and 30% cement

Age(days)	**Compressive Strength of Samples (MPa)**						
	Control	**70%F+30%C**	**2%HL**	**4% HL**	**5% HL**	**6% HL**	**8%HL**
1	19.86	3.25	3.66	3.57	3.42	3.02	2.25
3	27.67	7.54	6.34	6.87	7.35	5.45	5.91
7	38.27	8.63	8.00	9.18	9.10	8.05	7.23
14	43.84	12.17	11.02	11.30	12.35	9.76	11.32
28	48.64	17.61	14.40	14.40	15.88	13.91	15.20
56	56.84	20.54	19.93	22.72	21.54	19.74	20.59
90	64.12	26.53	25.60	26.13	28.29	24.80	24.48

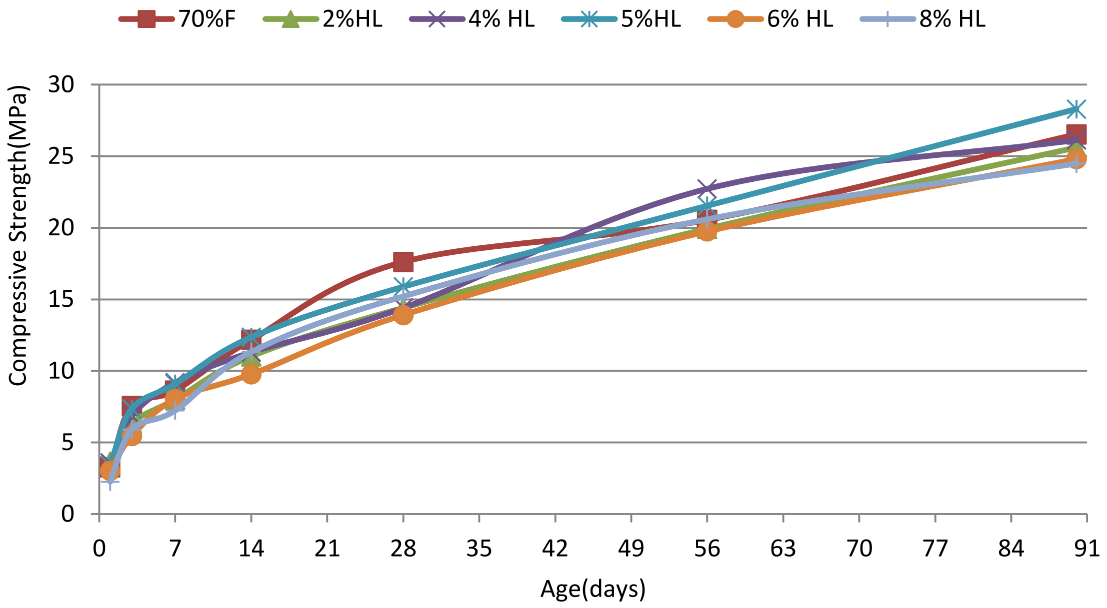

Figure 5.1 Variation of compressive strength for hydrated lime activated 70%fly ash mix with age

The compressive strength of quick lime activated fly ash mixtures are listed in Table 5.6 and shown in Figure 5.2. The compressive strengths were determined as the average of three specimens at the ages of 1, 3, 7, 14, 28, 56 and 90 days. Quick lime activated fly ash concrete mixtures showed lower strength compared to control mixture and higher strength compared to 70% fly ash mixture at all ages. The results of lime activation indicate a clear improvement in the strength from fly ash, particularly at one day and at later ages, which suggests that the quick lime contributes to an increase in reactivity of fly ash both very early and at later ages. The contribution from the increase in the reactivity of fly ash is higher than the loss in strength due to reduction in the reactive silica from fly ash replacement. On increasing the quick lime replacement beyond 5% there is a decrease in strength when compared to 5% replacement. This suggests the following possibilities: (a) the gain in strength from the increased reactivity of fly ash is offset by the loss in the amount of reactive silica between 5 and 10% replacement; or (b) there is an optimum dosage beyond which there is no gain in reactivity with increasing quick lime dosage.

Table 5.6 Compressive strength as a function of age in quick lime activated 70% fly ash system cured at a temperature of 25^{O}C

Age(days)	Compressive Strength of Samples (MPa)			
	Control	**70%F+30%C**	**5% QL**	**10%QL**
1	19.86	3.25	4.28	5.24
3	27.67	7.54	8.30	6.92
7	38.27	8.63	9.60	8.85
14	43.84	12.17	13.45	12.17
28	48.64	17.61	16.92	16.14
56	56.84	20.54	26.43	25.07
90	64.12	26.53	36.74	33.44

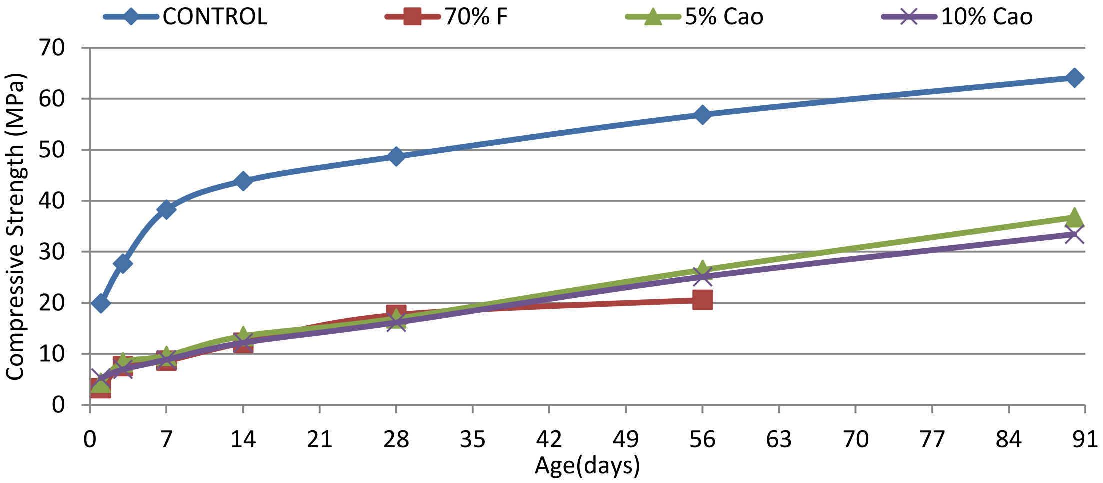

Figure 5.2 Variation of compressive strength for quick lime activated 70%fly ash mix with age

The strength results appear to be in agreement with findings reported in the literature where quicklime showed higher strength than hydrated lime at all ages [Shi 1996]. However, in contrast to the findings of Shi (1996) the difference between the quick lime and hydrated lime the difference was not more pronounced during the early ages and the difference continues to increase with time after the first month.

5.3.1.3 Thermogravimetric Analysis

The $Ca(OH)_2$ content as a percentage of the cementitious binder obtained from the TG analysis as a function of age is shown in Figure 5.3. The 30% scaled values of the control mixture (with no fly ash) is also plotted in the figure for comparison. It can be seen that for the control mixture, the hydraulic activity of cement results in continuous increase in the $Ca(OH)_2$ content up to 28 days of age following which there is a small change with age. Comparison of the 70% fly ash baseline mix with the scaled value of the control mix shows that the $Ca(OH)_2$ content of baseline mix matched the Ca(OH)2 content from hydraulic activity of cement. The deviation of $Ca(OH)_2$ content from the 30% scaled values suggests that the depletion of $Ca(OH)_2$ due to pozzolanic reaction is initiated at 7 days of age. In the quick lime activated systems the $Ca(OH)_2$ content of the lime activated systems are consistently higher at any age for higher dosage of quicklime. In case of quick lime activated fly ash systems, a notable increase in the $Ca(OH)_2$ content can be observed at one day of age; the $Ca(OH)_2$ contents at one day for the baseline, 5% and 10% lime activated systems were 0.47%, 1.44% and 2.82%, respectively. This indicates that the higher dosage of CaO results in a larger production of $Ca(OH)_2$ in the activated systems. In the lime activated systems the depletion of $Ca(OH)_2$ appears to be start at 7 days of age. This suggests that the initiation of the pozzolanic reaction is not influenced by the CaO dosage. The trends in the production and depletion of $Ca(OH)_2$ content are effectively parallel for the baseline the lime activated systems, which indicates that the production of $Ca(OH)_2$ from cement hydration and the subsequent consumption are not influenced by the $Ca(OH)_2$ content of the system. In the baseline fly ash mix also shows an almost complete depletion of $Ca(OH)_2$ in the system at 56 days, while there is continued decrease in the $Ca(OH)_2$ in the lime activated systems after 56 days.

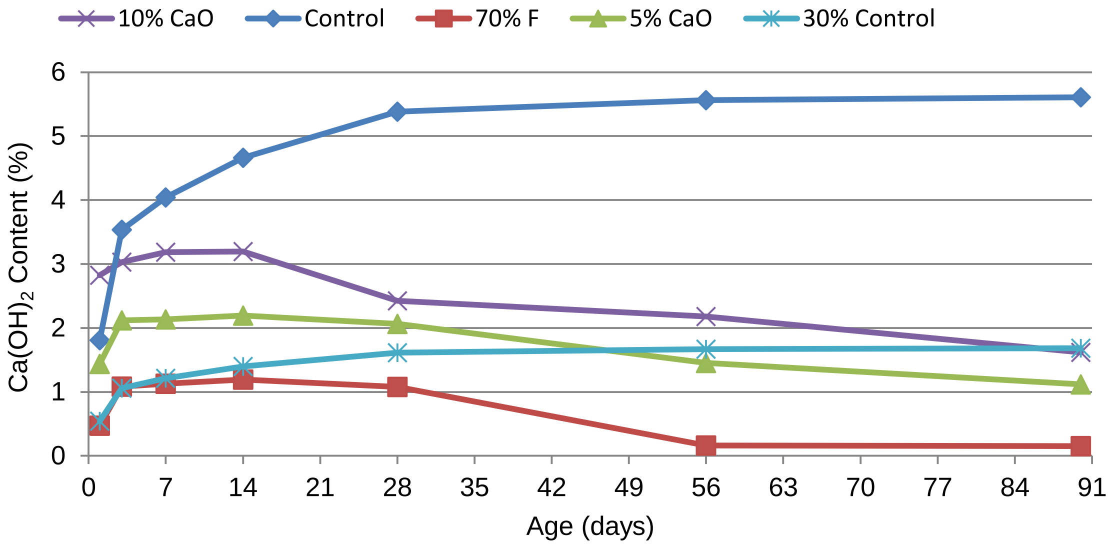

Figure 5.3 Calcium hydroxide content for quick lime activated 70% fly ash with ages at 25^{O}C

The results of the experimental program indicate that in-situ $Ca(OH)_2$ content in the binder does not significantly influence the rate of consumption of $Ca(OH)_2$. This is also in agreement with the rate of strength gain, which is similar in the baseline and the activated mixtures up to 28 days of age. While there is a complete depletion of $Ca(OH)_2$ in the baseline mixture by 56 days of age, a supply of lime is available in the lime activated systems. There is a continued consumption of lime after 56 days at a steady rate, which is essentially equal in both lime activated systems. This agrees well with the observed strength gain in lime activated systems, which exhibit a linear increase in strength with age at later ages.

The increase in the non-evaporable water content as a percentage of the cementitious binder of the mixtures with age is shown in Figure 5.4.Chemically bound water content increases monotonically which is the outcome of the progress of the hydration and the continuing accumulation of hydration products. The non-evaporable water contents of all the quick lime activated pastes are higher than the baseline 70% fly ash paste at all ages. In case of quick lime activated fly ash systems, a notable increase in the amount of combined water can be observed at one day of age; the non-evaporable water contents at one day for the baseline, 5% and 10% lime activated systems were 1.14%, 3.4% and 5.01%, respectively. The difference in the non-evaporable water content is higher than the difference in the $Ca(OH)_2$ content in the lime activated systems and baseline system at the same age. This suggests that there is significant early reactivity exhibited by the CaO activated system which contributes to reaction products. The increase in early reactivity exhibited in the lime activated systems is also reflected in the increased early strength gain in the quick lime activated systems. The one day strengths of the quicklime activated systems are higher than the baseline fly ash mixture. The non-evaoporable water content in the baseline mixture reaches an asymptotically constant value by 28 days which corresponds with the complete depletion of $Ca(OH)_2$ in the system. The lime activate systems show a continued increase in the non evaporable water content at a steady rate after 28 days, which corresponds well with the steady depletion of $Ca(OH)_2$ in the system and an almost linear increase in strength gain with age in these mixtures.

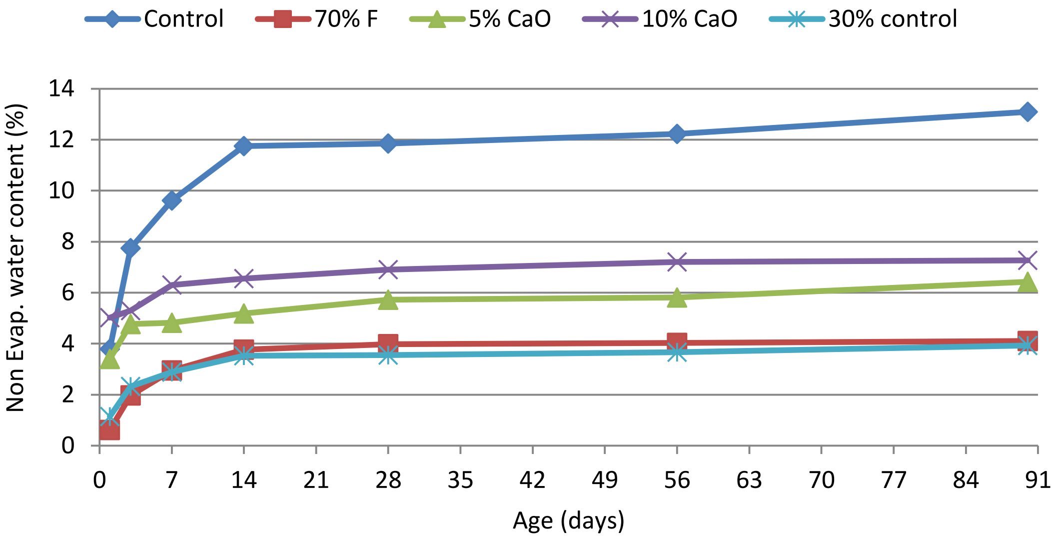

Figure 5.4 Non evaporable water content for quick lime activated 70% fly ash mix with age at 25^{O}C

5.3.1.4 Isothermal Calorimetry

The rate of heat release measured from the control, the baseline fly ash, the quick lime activated and hydrated lime activated cement paste samples is shown in Figure 5.5. In the quick lime activated systems, the early heat release from the exothermic reaction between CaO and water is evident in the first few minutes after mixing. Larger rate of heat release is noticed from the larger CaO dosage in the system. The lime activated mixtures exhibit higher early reactivity up to12 hours; the rate of reaction is significantly higher than even the control mixture in the first 6-8 hours. After the first 6-8 hours, the control mixture exhibits a faster rate of reaction of all mixtures and the subsequent rate of heat release is always higher than the lime activated systems. The peak in the rate of reaction occurs earlier in the case of lime activated systems. The lime activated system with 10% quick lime exhibits peak reactivity within the first 12 hours, which is earlier than the control mixture. The peak reactivity exhibited by the system with 5% quick lime coincides in time with the control mixture. The peak reactivity of the baseline fly ash system occurs at 18 hours when both the control and the lime activated systems are in the decelerating stage of the reaction. At 24 hours the rate of reaction in the baseline fly ash mixes is equal to the baseline fly ash mix, which is significantly lower than the control. This indicates that at one day of age, the reaction in all the fly ash mixtures (both activated and baseline) is driven by the hydraulic activity of cement alone.

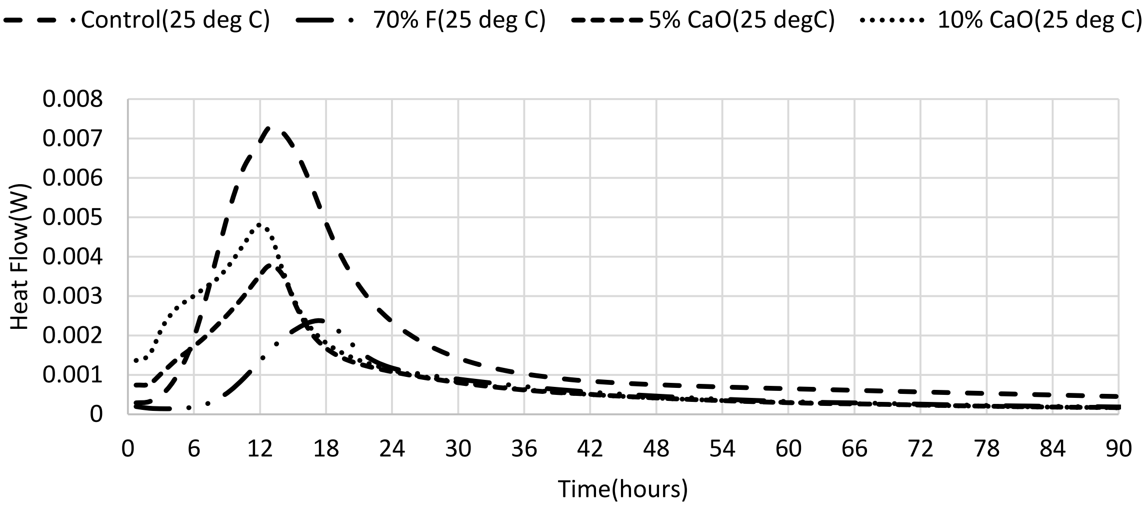

Figure 5.5 Heat flow at 25°C vs. time.

The rate of heat flow curves for the quick lime activated systems indicate the possibility of 2 distinct reactions in the first 12 hours. There is an early peak which occurs in the first few hours. This peak is more pronounced for higher quick lime content. The first peak is therefore clearly associated with CaO. The second peak, which occurs around 12 hours corresponds to the hydraulic reaction of cement. The heat released from the first reaction appears to accelerate the hydraulic reaction of cement in the fly ash system. The rate of reaction in the acceleration stage of the reaction is higher in quick lime activated samples and the peak occurs earlier in time than the control mixture.

The total heat obtained by integrating the rate of heat release for all the mixtures is shown in Figure 5.6. The total heat released indicates a larger extent of reaction in the 10% quick lime system when compared to the 5% quick lime and the baseline fly ash mixtures at two days after which there is essentially a constant difference between the three mixtures. After 2 days of age, the control system indicates a steady increase in the extent of hydration. There is a significantly faster increase in the extent of hydration in the control system when compared with the other systems. After 2 days the calorimetry data does not provide sufficient sensitivity to detect minute changes produced by the pozzolanic reaction and essentially indicates a steady rate of increase due to hydraulic activity of cement.

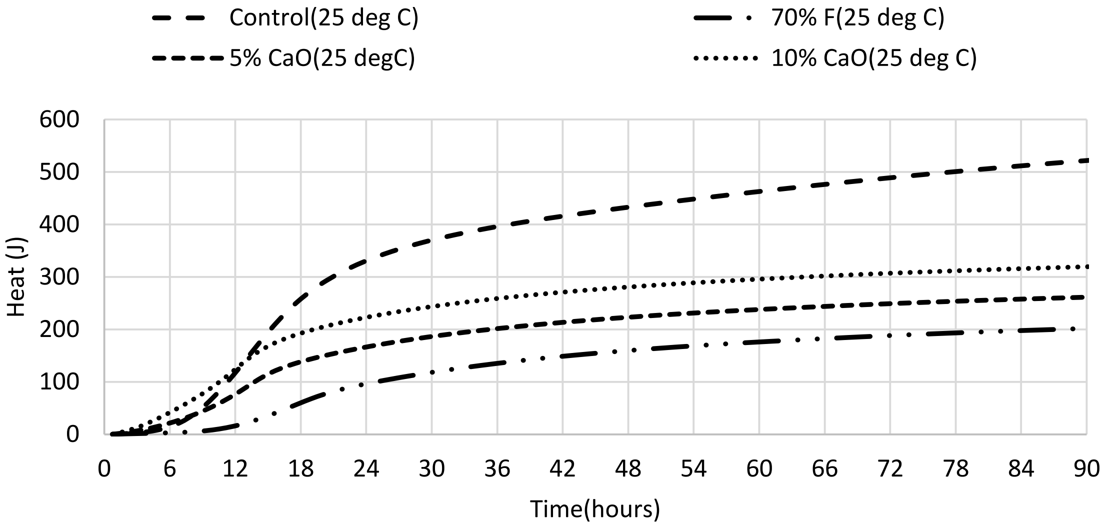

Figure 5.6 Cumulative heat vs. age for samples cured at 25^{O}C

The results of iso-thermal calorimetry indicate that quick lime activated systems exhibit a significantly higher early level of reactivity; quick lime enhances the early reactivity of fly ash. The heat released by the exothermic hydration reaction of CaO in water contributes to a faster onset of acceleration stage of in the hydration of cement. The results from isothermal carloimetry are in agreement with the observed slump and strength measurements. The initial exothermic reaction of quick lime with water accelerates the initial rate of hydration reaction in lime activated systems. The heat signature indicates an immediate effect of CaO addition which agrees with the reduction in slump with increasing CaO dosage. Further, the increased reactivity in the quick lime system in the first 12 hours, which increases on increasing the quicklime content agrees with the non-evaporable water content measurement in the cement binder and one day strength results. At one day, there was a significantly higher amount of non-evaporable water in the quick lime systems than the baseline fly ash system and the non evaporable water content increase on increasing the CaO content. At one day, the 10% quick lime mixture also exhibited a higher strength than the 5% quicklime and the baseline fly ash mixtures.

5.3.2 Quick Lime Activation at the temperature 40^{O}C

The influence of temperature on the strength gain and hydration was investigated in the lime activated system. The quick lime activated systems were selected for evaluation, since these systems showed improvements in strength at 25 deg C. In the experimental program, specimens were cured at 40 deg C until tested. Specimens were stored in an oven which was maintained at 40 deg C. Concrete cubes were wrapped in wet burlap which was kept moist by spraying water at a temperature of 40 deg C. The TGA samples were cast in sealed containers and kept in the oven until tested.

5.3.2.1 Compressive strength

The compressive strength of quick lime activated fly ash mixtures are listed in Table 5.7 and plotted in Figure 5.7. Compressive strength was measured at the ages of 1, 3, 7, 14, 28, 56 and 90 days and the average values of three specimens tested at each age are reported. The baseline fly ash mixture exhibited the lowest compressive strength of all mixtures evaluated. While the baseline fly ash and the control mixtures appear to reach an asymptotically constant value at 28 days the quicklime activated systems continue to show a steady linear increase with age after 28 days. Quick lime activated fly ash concrete mixtures showed lower strength compared to control mixture and higher strength compared to the baseline fly ash mixture at all ages. The results of lime activation indicate a clear improvement in the strength from fly ash, particularly in the later ages, which suggests that the quick lime contributes to an increase in reactivity of fly ash. The lime activated fly ash mixture exhibit a clear improvement in strength after 3 days when compared with the baseline fly ash mixture. At later ages the 10% quick lime mixture exhibits higher strength than the 5% quick lime mixture.

Table 5.7 Compressive strength as a function of age in quick lime activated to 70% fly ash system at40^{O}C

Age(days)	**Compressive Strength of Samples(MPa)**			
	Control	**70%F**	**5% CaO**	**10%CaO**
1	20.95	5.22	5.52	5.70
3	28.79	12.41	12.68	11.08
7	39.72	17.12	20.69	21.55
14	45.01	21.71	28.71	26.19
28	48.35	22.81	33.30	33.46
56	49.05	23.79	34.53	35.53
90	52.33	24.31	35.19	37.13

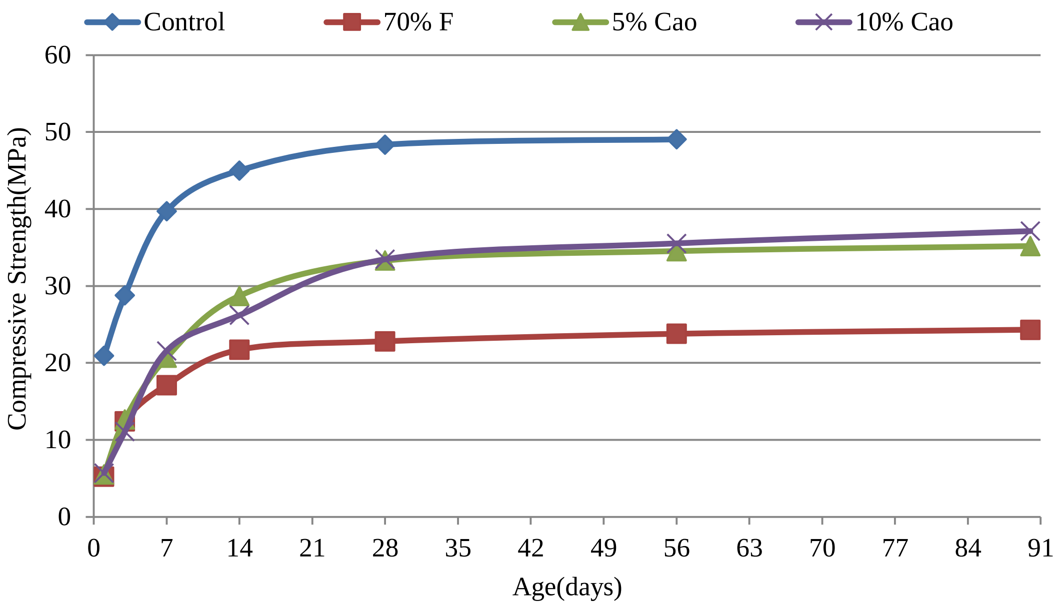

Figure 5.7 Variation of compressive strength for quick lime activated 70%fly ash mix with age at curing temperature 40ºC

While at one day the strengths of the quicklime activated are consistently higher than the baseline fly ash mixture, the improvement in strength in the quick lime system is only evident after 3 days. The influence of temperature on the compressive strength of fly ash concrete after three days can probably be explained by the fact that the strength gain comes from the pozzolanic reaction, which is significantly influenced by temperature. The pozzolanic reactivity is significantly enhanced in the presence of extra $Ca(OH)_2$ supplied by quick lime addition at a higher temperature.

5.3.2.2 Thermogravimetric Analysis

The $Ca(OH)_2$ content as a percentage of the cementitious binder obtained from as a function of age is shown in Figure 5.8. The 30% scaled values of the control mixture (with no fly ash) are also plotted in the figure for comparison. It can be seen that for the control mixture, the hydraulic activity of cement results in continuous increase in the $Ca(OH)_2$ content. Comparison of the 70% baseline fly ash mix with the scaled value of the control mix suggests that the depletion of $Ca(OH)_2$ due to pozzolanic reaction is initiated at 3 days of age. When compared with the baseline fly ash mixture the $Ca(OH)_2$ content of the lime activated systems are consistently higher at any age for higher dosage of quicklime. In case of quick lime activated fly ash systems, a notable increase in the $Ca(OH)_2$ content can be observed at one day of age; the $Ca(OH)_2$ contents at one day for the baseline, 5% and 10% lime activated systems were 0.68%, 1.73% and 2.37%, respectively. This indicates that the higher dosage of CaO results in a larger production of $Ca(OH)_2$ in the quick lime activated system. The trends in the production and depletion of $Ca(OH)_2$ content in the 5 and 10% quick lime systems are effectively similar, which indicates that the production of $Ca(OH)_2$ from cement hydration and the subsequent consumption are not influenced by the $Ca(OH)_2$ content of the system. The baseline fly ash mix also shows an almost complete depletion of $Ca(OH)_2$ in the system at 90 days.

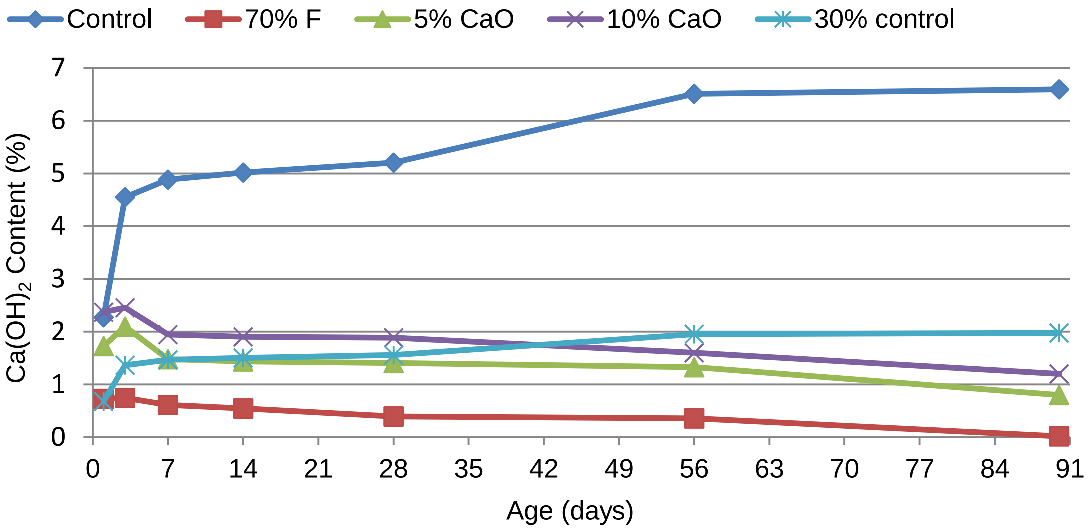

Figure 5.8 Calcium hydroxide content for quick lime activated 70% fly ash mix with age at 40°C

The results of the experimental program indicate that in-situ $Ca(OH)_2$ content does not significantly influence the rate of consumption of $Ca(OH)_2$. This is also in agreement with the rate of strength gain, which is similar in both the activated mixtures up to 28 days of age.

The increase in the non-evaporable water content as a percentage of the cementitious binder of the mixtures with age is shown in Figure 5.9. Chemically bound water content increases monotonically which is the outcome of the continuous progress of the hydration reaction and the continuing accumulation of hydration products. The non-evaporable water contents of all the quick lime activated pastes are higher than the baseline 70% fly ash paste at all ages. In case of quick lime activated fly ash systems, a notable increase in the amount of combined water can be observed at one day of age; the non-evaporable water contents at one day for the baseline, 5% and 10% lime activated systems were 1.57%, 4.79% and 5.13%, respectively. The difference in the non-evaporable water content is higher than the difference in the $Ca(OH)_2$ content in the lime activated systems and baseline system at the same age. This suggests that there is significant early reactivity exhibited by the CaO activated system which contributes to reaction products. The increase in early reactivity exhibited in the lime activated systems is also reflected in the increased early strength gain in the quick lime activated systems. The one day strengths of the quicklime activated systems are higher than the baseline fly ash mixture.

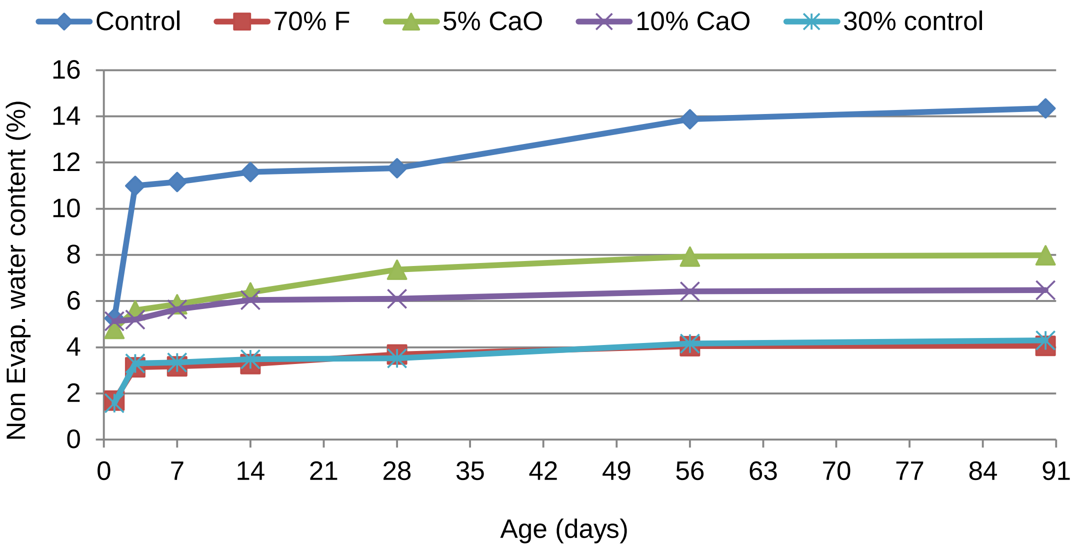

Figure 5.9 Non evaporable water content for quick lime activated 70% fly ash mix with age at 40°C

5.3.2.3 Isothermal Calorimetry

The rate of heat release measured from iso-thermal calorimetric measurements for samples cured at 40 deg C is shown in Figure 5.10. The heat of reaction obtained by integrating the rate of heat release for all the mixtures tested is shown in Figure 5.11. The rate of heat release indicates a significantly higher early reactivity in the lime activated systems when compared with the baseline fly ash system in the first 12 hours; the rate of reaction is significantly higher than even the control mixture in the first 6-8 hours. The peak in the rate of reaction also occurs earlier in the case of lime activated systems. The two peaks associated with the two reactions are clearly visible in the first few hours indicate 2 distinct reactions in the first 6 hours. The peak associated with exothermic reaction of CaO and water occurs in the first 2 hours. At 40deg C the reaction associated with CaO in the first few hours is significant when compared with the hydration reaction of cement. The heat released by the exothermic hydration reaction of CaO in water contributes to a faster onset of acceleration stage of cement hydration.

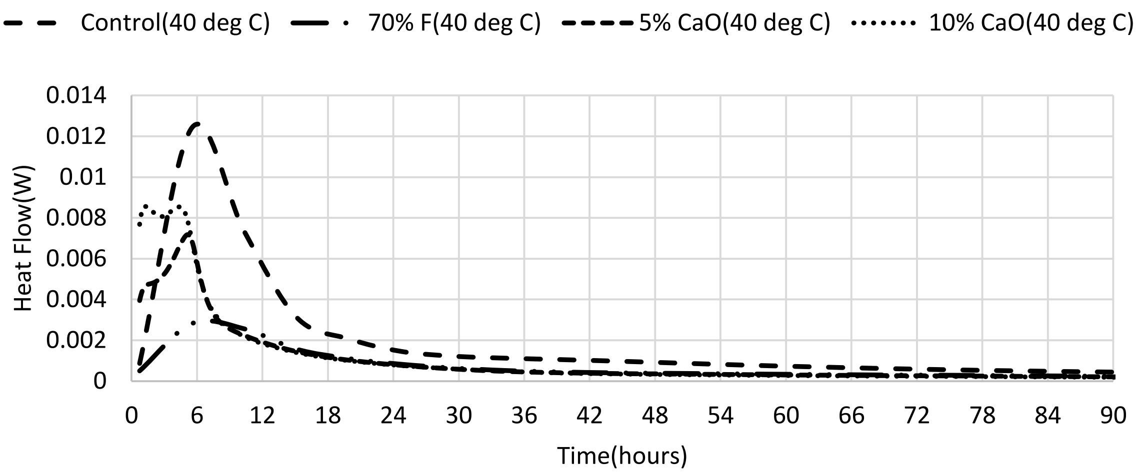

Figure 5.10 Heat flow at 40^{O}C vs. time.

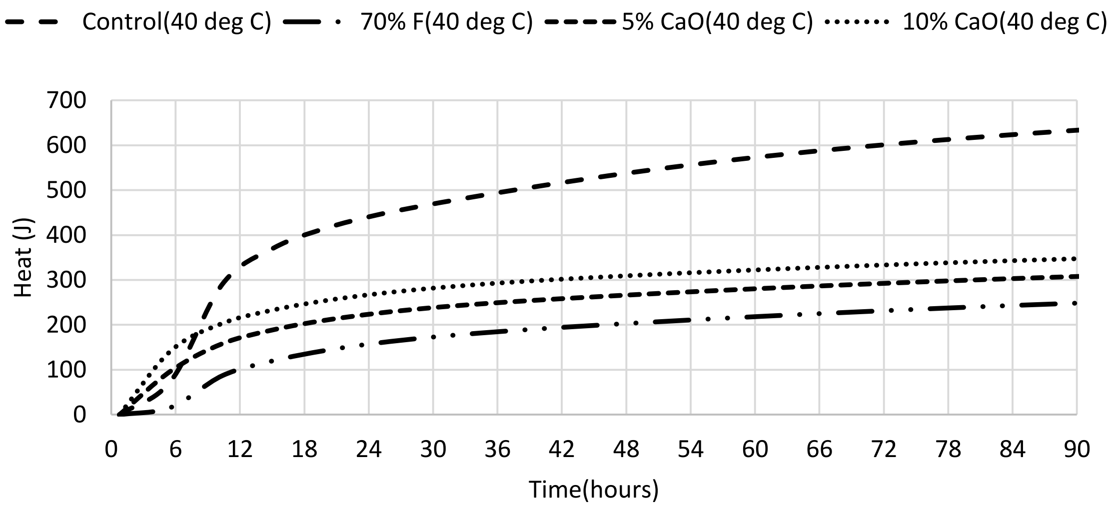

Figure 5.11 Cumulative heat vs. time at 40^{O}C

5.4 Discussion and Comparison of Results

Compressive strength gain in specimens cured at 25^{O}C and 40^{O}C is compared in Figure 5.12. Strength results indicate that higher temperature curing results in a more rapid gain of strength in the fly ash (both activated and baseline) systems but the final strengths are higher in the concrete cured at 25 deg C. These results are in conformity with the findings of other researchers who have shown that higher temperature results in faster early gain of strength but a lower ultimate strength.

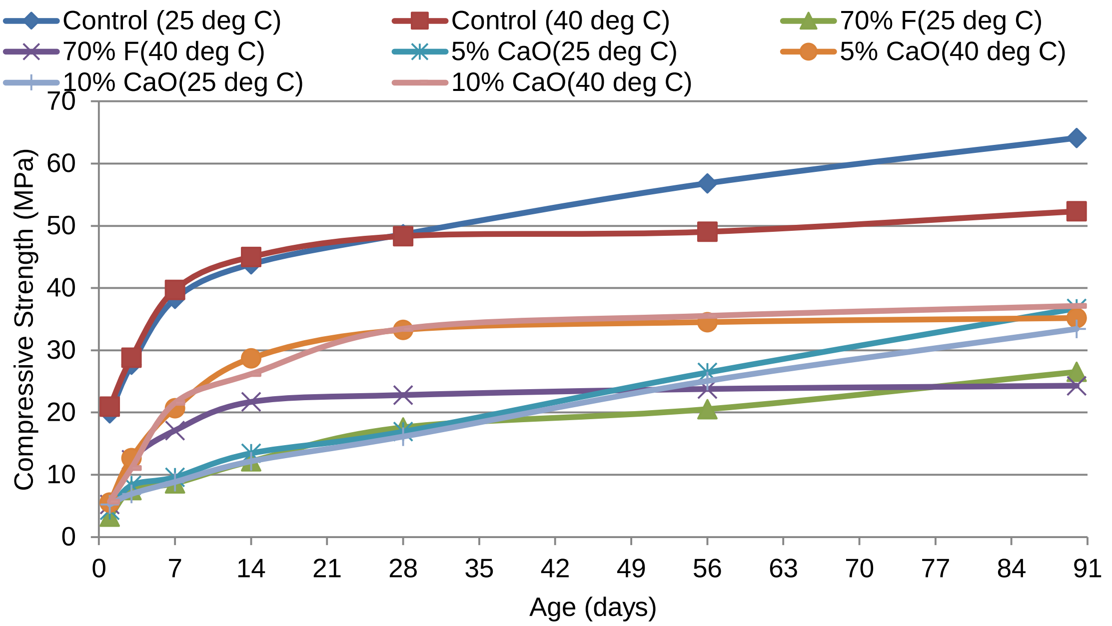

Figure 5.12 Comparison of compressive strength for quick lime activated mixtures at 25^{O}C and 40^{O}C with age.

Calcium hydroxide and non evaporable water content of mixtures cured at 25 and 40cdeg C are compared in Figures 5.13 and 5.14, respectively. Comparison of $Ca(OH)_2$ shows that there is a larger initial release of $Ca(OH)_2$ from cement hydration at 40 deg C when compared to 25 deg C curing, which contributes to a larger quantity of $Ca(OH)_2$ in the system in the first few days. There is also a faster initiation of pozzolanic reactivity at higher temperature. In all fly ash systems the $Ca(OH)_2$ content starts decreasing at 3 days when compared to 14 days for specimens cured at 25 deg C. The initial increase in the non-evaporable water content corresponds with the increase in the $Ca(OH)_2$ content produced by the hydraulic activity of cement. The decrease in $Ca(OH)_2$ content due to the pozzolanic activity of fly ash correlates well with the observed increase in the non-evaporable water content. There is also a faster initial rate of depletion of $Ca(OH)_2$ after the onset of pozzolanic reaction, which is observed at 40 deg C when compared with rate of depletion at 25 deg C. This indicates that the both the onset and the rate of pozzolanic reaction are accelerated by higher temperature.

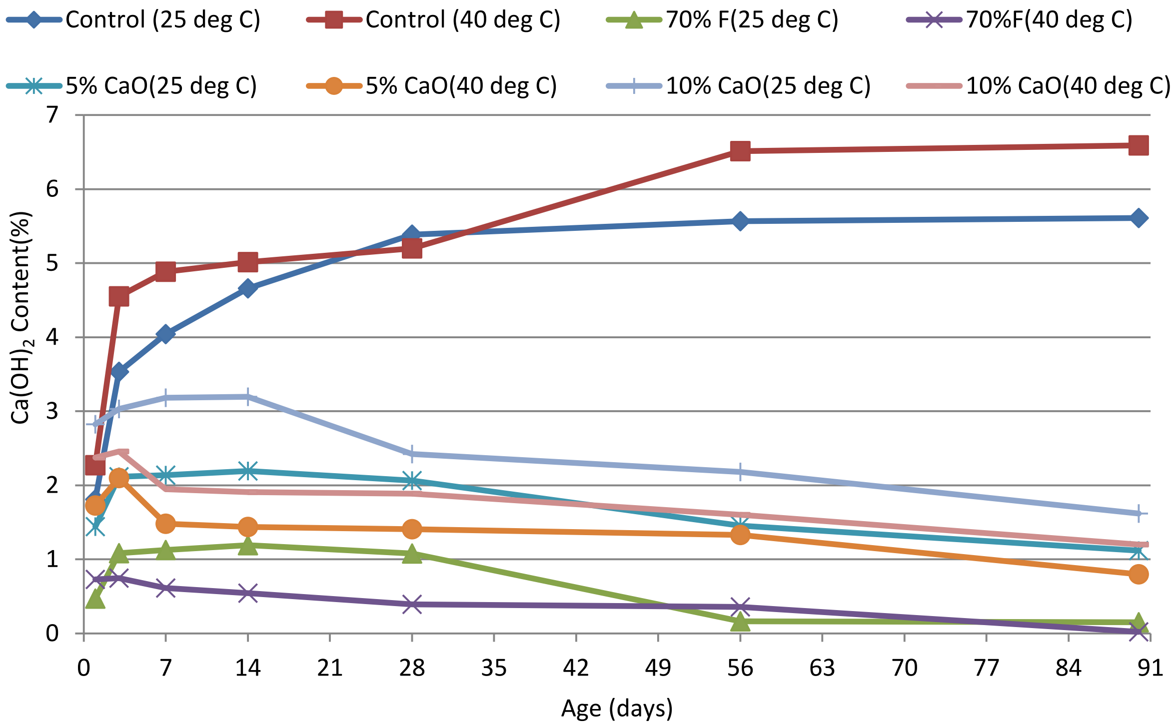

Figure 5.13 Comparison of Calcium hydroxide content for quick lime activated mixtures at 25°C and 40°C with age.

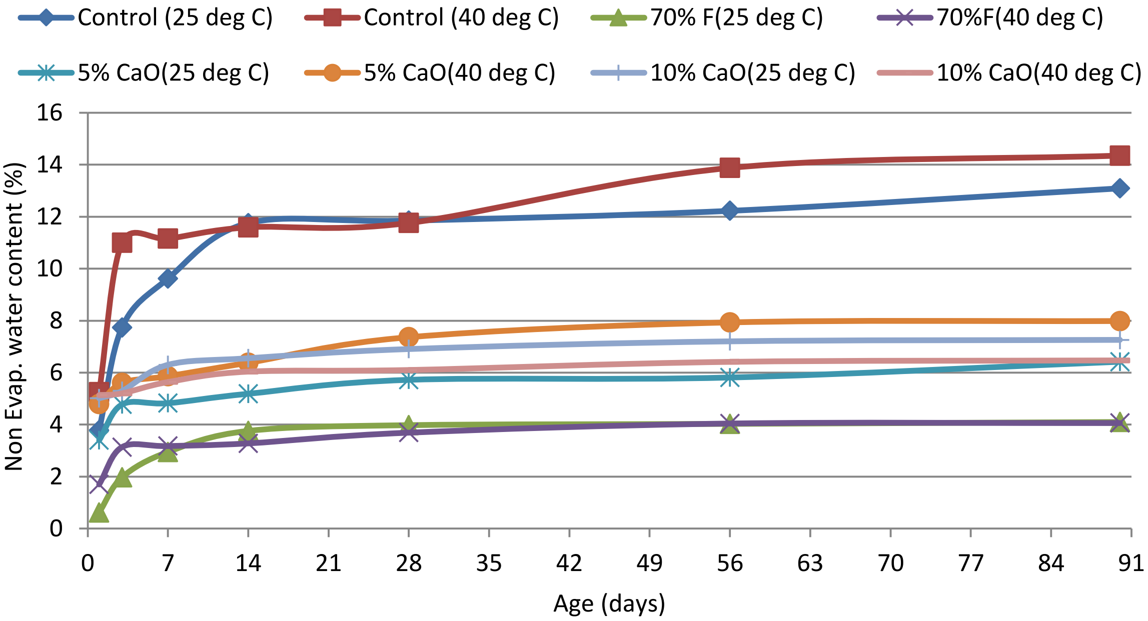

Figure 5.14 Comparison of Non evaporable water content for quick lime activated mixtures at 25°C and 40°C with age.

From iso-thermal calorimetry, a comparison of the heat flow measured from samples cured at 25 and 40 deg C, significantly higher levels of reactivity are observed in all specimens cured at 40 deg C. This correlates well with the observed strength gain; higher rates of strength gain are observed in the early ages in samples cured at 40 deg C. Therefore temperature enhances the early reactivity of cement in addition to faster onset of pozzolanic reaction. This is also confirmed by comparing the total heat at 19 and 100 hours as shown in Table 5.8. There is a larger extent of reaction at

Table5.8 Comparison of Heat at 25^{O}C and 40^{O}C with time

Designation	Heat (J)			
	25^{O}C		40^{O}C	
	10 hours	100 hours	10 hours	100 hours
Control	81	537	291	650
30C-70F	10	207	87	257
30C-65F-5QL	58	267	158	316
30C-60F-10QL	93	324	203	354

5.4.1 Evaluation of quick lime activation under outdoor curing

To evaluate the influence of varying temperature, concrete specimens with 5% quick lime were cast and after demolding were subjected to ambient temperature cycles. The specimens were wrapped in jute bags, which were kept moist by spraying water which was also stored in the same environment. The variation of temperature is shown plotted in Figure 5.15. The strength gain recorded from these specimens is shown plotted in Figure5.16. The results from 5% quick lime addition cured at 25 and 40 deg C are plotted in the same graph for comparison. It can be seen that strength gain in the specimens cured under ambient conditions was identical to the strength gain in specimens cured at 25 deg C, when the ambient temperature was equal to 25 deg C. However, the onset of higher temperature after 9 days results in a more rapid increase in strength in the ambient cured specimens, which is clearly evident from 14 days. From previous results it is known that at 25 deg C, the pozzolanic reactions are initiated at 14 days. The increase in rate of strength gain due to increase in ambient temperature after the 14 days could be attributed to an acceleration of both the hydraulic reaction of cement and of the pozzolanic reaction involving fly ash.

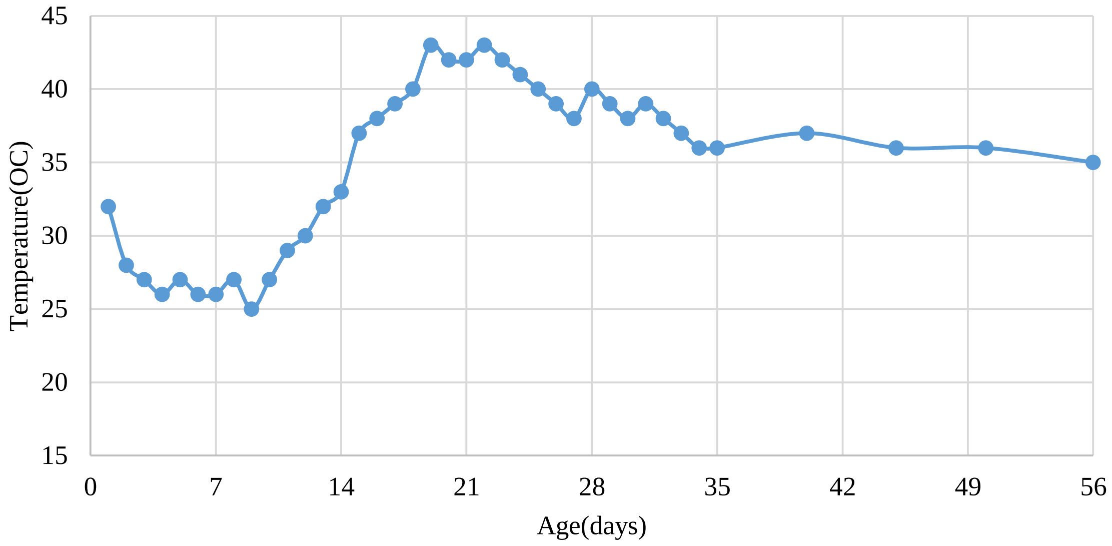

Figure 5.15 Variation of Temperature with age

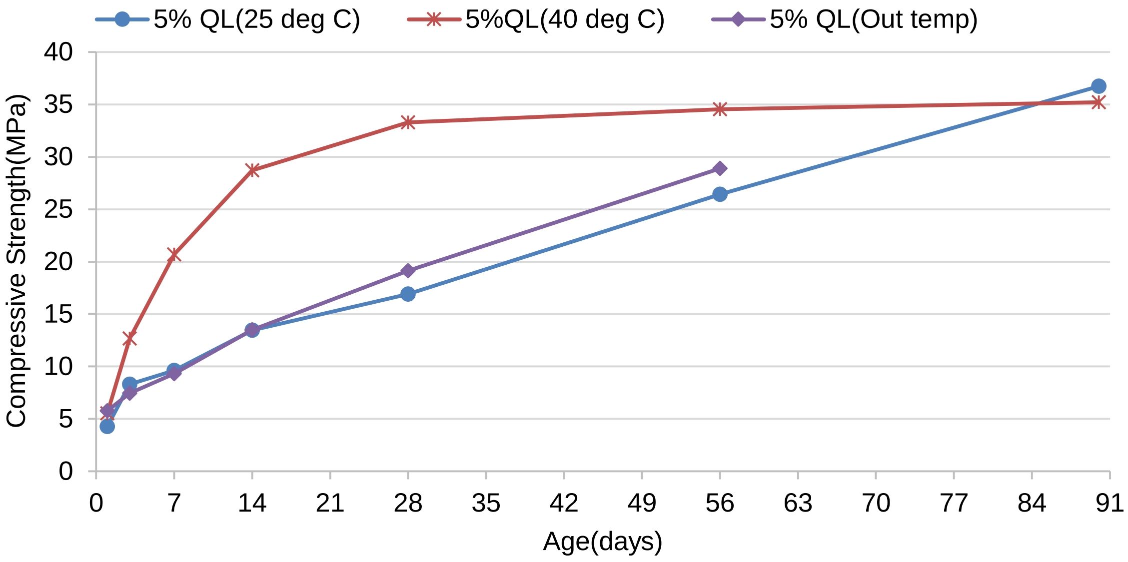

Figure 5.16 Strength gain in 5% lime activated fly ash concrete subjected to 25^{O}C, 40 ^{O}C and ambient temperature curing.

5.4 Summary and Findings

From the results of the experimental investigation of quick lime activated high volume fly ash system, the role of temperature and quick lime can now be defined. The general findings of this study, which are applicable for any temperature of curing are:

1. In high volume fly ash with 70% replacement of cement, there is a complete depletion of $Ca(OH)_2$ in the system, which essentially stops the pozzolanic reaction.

2. CaO contribute to increasing the $Ca(OH)_2$ content in the binder and to increasing the early reactivity of the cement-fly ash system. Quick lime activated systems exhibit higher strength at one day than the baseline fly ash mixture. This was consistently observed at both 25 and 40 degree Celsius curing.
3. The onset of pozzolanic reaction is not influenced by the $Ca(OH)_2$ content in the binder. It was observed that the depletion of $Ca(OH)_2$ in the binder initiated at the same time in base line fly ash mixture and the activated systems for both temperature of curing. The onset of pozzolanic reaction was however dependent on the temperature; the pozzolanic reaction was initiated earlier at higher temperature of curing.

CaO influences both the very early reactivity within the first 24 hours in the fly ash-cement system and also the pozzolanic reaction at later ages. At later ages, CaO contributes to continued pozzolanic reaction while in the baseline fly ash systems the pozzolanic reaction is stopped due to complete depletion of $Ca(OH)_2$. From the available data the following representation of the hydration process in the quicklime fly ash system can be developed.

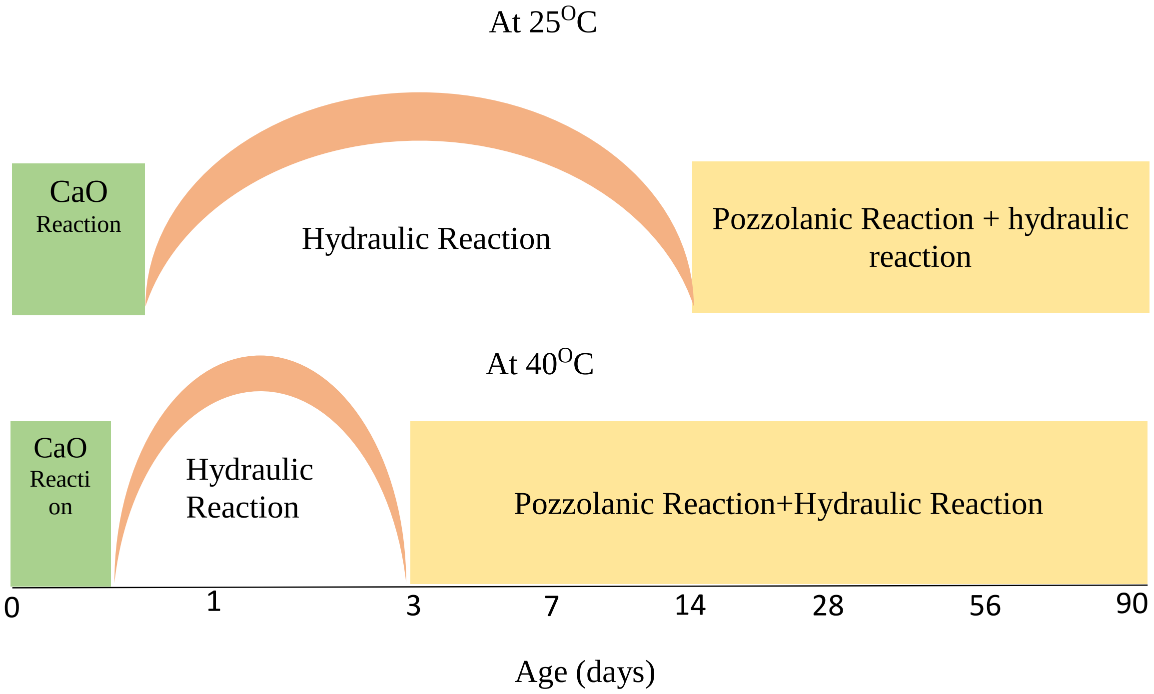

Figure 5.17 A schematic representation of hydration in fly-cement system with quick lime

5.5 Future Work

The results of this study show that there is sufficient promise in developing concrete with high volume fly ash. There are some findings which need further investigation and additional direction for developing approaches for objective evaluation and comparison of high volume fly ash with concrete using cement only are identified. The directions of future research which emerge from the work reported in this thesis are listed below.

1. An objective way of comparing fly ash concrete based on reactivity of fly ash and volume fractions needs to develop. Reactive silica controls in the fly ash determines its efficiency in strength gain. Similarly, when comparing with concrete mixtures based on substituting a given weight of cement with fly ash, the volume of fly ash in the resulting mixture would be higher than the volume of cement it replaces. Therefore in a unit volume of concrete containing fly which is replaces an equivalent weight of cement there would be a decrease in the cement and aggregate content when the batch weights of cement and aggregate are kept the same in both mixtures. Therefore, fly ash mixtures produced by replacing a given weight of cement with fly ash should be compared with a lower water to cement ratio mixture. Further, since some portion of fly ash is unreactive, it should be considered as a replacement of aggregate. An objective way of using the proportion of reactive silica to arrive at the true ratio of water to cementitious material for comparison with no fly ash concrete and a volumetric contribution of the non-reactive silica to the aggregate content in a unit volume of concrete is required for developing effective comparisons. An approach which considers the non-reactive silica from fly ash in the volume batching as contribution to aggregate is required.
2. Indications from isothermal calorimetry are that the CaO influences the setting behaviour of fly ash concrete, which needs to be investigated. Further, the enhanced reactivity of the fly ash cement system in the first few hours in the presence of fly ash needs further investigation. The exothermic heat release associated with reaction of CaO and water
3. The role of temperature in accelerating the onset of pozzolanic reaction needs further investigation through carefully controlled experiments at temperatures varying from 25 to 40 deg C.
4. The use of CaO does not influence the in-situ pH. Ca(OH)2 does influence the pH since it dissociates into Ca^{2+} and OH^- ions. However, the in-situ pH in the different mixtures

needs to be investigated. Further the combined use of high pH and temperature needs to be investigated by testing Ca(OH) activated mixes at higher temperature. The likely solution of combining CaO, which provides in-situ temperature rise and hydrated lime which would increase the pH needs be studied.

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