STRENGTH AND DURABILITY STUDIES ON SILICA FUME CONCRETE

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CERTIFICATE

This is to certify that thesis entitled **“Strength and Durability Studies on Silica Fume Concrete”** being submitted by Ms. Shweta Goyal to the Thapar University, Patiala, India, for the award of the degree of “**DOCTOR OF PHILOSOPHY** in Civil Engineering”, is a record of original bonafide research work carried out by her. Ms. Shweta Goyal has worked under our guidance and supervision.

To the best of our knowledge, the thesis has reached the requisite standard. The material contained in this thesis has not been submitted, in part or in full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

Concrete is the most widely used construction material utilized since time immortal. However, the environmental concerns necessitate a reduction in clinker usage in the construction industry that is possible only by the use of supplementary cementitious materials, called mineral admixtures in the making of concrete. These mineral admixtures, when introduced in the cement system, react with calcium hydroxide to form calcium-silicate-hydrate gel. Some of the examples of mineral admixtures are silica fume, fly ash, slag etc. Each of these mineral admixtures posses different properties. The objective of the present study is to investigate the synergistic effect of using a combination of silica fume and Indian fly ash. This study is necessary because silica fume is expansive in nature, and fly ash is cheap and abundantly available in India. Therefore, use of small proportion of silica fume along with large proportion of Indian fly ash, is expected to provide overall economy without compensating in the desirable properties of concrete.

The investigation is divided into two parts. In the first part, the concentration is on the strength aspects of the resultant concrete. The major objective of the first phase of the work is to choose the most suitable combination of silica fume and fly ash to improve strength characteristics of concrete. The investigation is carried out for a wide range of water-to-binder ratios and under variable curing regimes. Three different water-to-binder ratios ranging from high (0.45) to medium (0.35) and then to low (0.25) are used to ensure wide variation in strength. Under each water-to-binder ratio, eight mixes are prepared using various combinations of silica fume and fly ash. Out of the eight mixes, one mix is a control mix with no mineral admixture, three mixes are binary mixes having only one mineral admixture, that is, either silica fume or fly ash; and four mixes are the ternary mixes with different combinations of silica fume and fly ash.

Further, in order to study the minimum number of curing days required for each mix to reach a definite strength level, five different curing regimes are adopted in the study and its influence is studied in terms of strength development and water impermeability of concrete. The curing regimes vary from continuous water curing to continuous air curing. In between these two curing regimes, curing regime with water

curing for 7 days followed by air drying is investigated as it is the curing practice normally followed for OPC concrete. Fourth curing regime consists of water curing for 28 days followed by air drying, which is normally suggested in literature for mineral admixture concretes. Along with this, the effect of wet-dry cycles is also investigated by adopting the curing regime of 14 days of initial water curing followed by wet-dry cycles.

The effect of water-to-binder ratio, mineral admixtures and curing regimes is studied in terms of compressive strength development, tensile strength development and water impermeability of concrete. Compressive strength development studies are performed at the age of 1, 3, 7, 14, 28, 56 and 90 days for all five curing regimes. Tensile strength is studied through both split tensile test and flexure strength test, conducted at the age of 7, 28, 56 and 90 days. Water impermeability test is performed to check transport rate of water in concrete because it is known that most deterioration processes need aggressive fluids to penetrate through the capillary pore structure of the concrete and react, thereby causing destruction. This test is performed as per DIN 1048 guidelines, at the end of 90 days to see the ultimate transportation rate in various mixes under different curing regimes. Along with these tests, non-destructive tests, like, rebound hammer and ultrasonic pulse velocity tests are also performed on the specimens meant for compressive strength studies, prior to destructive compressive strength test. The objective of performing these tests is to develop a combined relationship between non-destructive parameters and compressive strength, for a wide range of compressive strength values. At the end, economics of the best ternary mix is compared with the binary mixes.

From the first phase, it is observed that the ternary mix with 5% silica fume, 15% fly ash and 80% cement is the most suitable mix in terms of strength development and overall economy of the system. For a given strength level, the system makes the concrete cheaper by nearly 15% than the corresponding concrete made by using only silica fume as a mineral admixture. From the combined compressive strength and water impermeability studies, it is obtained that for silica fume concrete and the best ternary combination, seven days of initial water curing is both necessary and sufficient to explore the pozzolanic activity and for reaching a desirable strength and durability level.

Results of the experimental investigation are further used to develop a mathematical model for the relationship between compressive strength (20 MPa to 112 MPa) and tensile strengths (split tensile strength and flexure strength) of concrete. Two general models relating tensile strengths of concrete with compressive strength, water-to-binder ratio, concrete age and initial water curing regime are proposed. These models are validated with the data available in literature (having the compressive strengths ranging from 1 MPa to 118 MPa) using appropriate statistical tools to demonstrate the reliability and applicability of the proposed models. Predictability of the proposed models are found to be much superior vis-à-vis other existing models.

In the second phase of the study, the chemical resistance of concrete is investigated. It is because the deterioration of concrete due to aggressive environments is an issue of major concern throughout the world and the chemical resistance of concrete decides the service life and hence overall economy of the system. The chemical resistance of concrete is studied in terms of acid attack, sulfate attack and chloride ingress. For studying the chemical resistance, the mixes that are found to be performing best in the binary and ternary combination are chosen and are subjected to aggressive chemicals for a duration of nearly one year.

To study the acid attack, three mixes under each water-to-binder ratio are subjected to aggressive chemical environment simulated by 1% sulfuric acid, 1% hydrochloric acid and 1% nitric acid, taken separately. The deterioration process is analyzed periodically up to 48 weeks by studying compressive strength loss and weight loss of the specimens. It is observed that, generally, the use of ternary mixes with 5% silica fume and 15% fly ash is best in resisting any type of acid attack. Also, reduction in water-to-binder ratio helps in making the concrete impermeable and thus reducing the attack. Comparing the usefulness of mass loss study and strength loss study, it is found that the mass loss is a surface phenomenon and thus, does not represent the overall characteristic of concrete. Therefore, studying mass loss alone cannot be taken as a reliable index in judging the efficiency against acidic media. It is also observed that the courses of action of sulfuric acid attack and hydrochloric acid attack are quite different due to the solubility of reaction products formed.

Sulfate attack on concrete is studied on four mixes for three water-to-binder ratios. These include the control mix, two binary mixes with silica fume and the best ternary mix. The test solutions for studying sulfate attack include 5% sodium sulfate and 5% magnesium sulfate, taken separately. The maximum exposure duration is kept at 12 monthly cycles of wetting and drying. The deterioration process is analyzed by progressive strength loss and weight loss of the specimens, along with visual observations and measurement of ultrasonic pulse velocity. It is observed that lowering the water-to-binder ratio or the use of combination of silica fume and fly ash tend to improve the performance of concrete in sodium sulfate exposure by resisting the compressive strength loss to the barest minimum value. However, in magnesium sulfate exposure, the use of mineral admixtures tends to aggravate the sulfate attack. Different mechanisms of sodium sulfate and magnesium sulfate attack are proposed based on the observations in the present study and from the literature available.

For studying the chloride penetration mechanism, five mixes are chosen for each water-to-binder ratio, which include one control mix, three binary mixes with different percentages of silica fume or fly ash and the best ternary mix. The major objective of studying the chloride ingress is to obtain chloride penetration profiles for mixes with various binary and ternary combinations; and to develop a relationship between free and total chlorides in order to judge the performance of the mix under chloride exposure. The study is carried out with 5% sodium chloride and 5% calcium chloride solutions. The desired solution is ponded on the concrete specimens for a period of 1 year and then a core is drilled out from the centre of the specimen. The core is further cut into thin slices along the depth and then, the slices are further powdered and titrated in order to obtain total chloride and free chloride content at different depths. It is found that lowering the water-to-binder ratio reduces both total and free chloride content at a given depth. The use of mineral admixtures increases the chloride binding capacity of concrete thus reducing the amount of chlorides available for corrosion of steel reinforcement. For both sodium chloride and calcium chloride exposures, ternary mixes are found to perform better than the binary mixes containing either silica fume or fly ash, thus leading to the conclusion that the ternary mixes are best in resisting chloride ingress in concrete.

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MA	Mineral Admixtures
SP	Super-plasticizer
W/B	Water-to-binder ratio
SCM	Supplementary cementitious materials
FA	Fly ash
SF	Silica fume
f_c	Compressive strength
f_{cu}	Cube compressive strength
f_y	Cylinder compressive strength
f_{st}	Split tensile strength
f_r	Flexure strength
V	Ultrasonic pulse velocity
N	Rebound number
IAE	Integral absolute error
CH	Calcium hydroxide
WL	Weight loss
CSL	Compressive strength loss
RH	Relative humidity
$(O/P)_{avg.}$	Average of ratio of Observed and Predicted values

CHAPTER 1

INTRODUCTION

1.1. GENERAL

Concrete is the most important element of infrastructure development across the globe and a well-designed concrete can be a durable construction material. However, there is a growing concern about the environmental aspect of Portland cement, as the cement manufacturing industry is responsible for about 2.5% of total worldwide emission from industrial sources *(Aldea et al, 2000)*. Particularly, carbon dioxide emission has been a serious problem in the world due to the greenhouse effect. After the Rio-de Janeiro Earth Summit in 1992 and following the Kyoto Protocol in 1997, many countries have agreed to reduce the emission of carbon dioxide *(Ozer and Ozkul 2004).* These environmental concerns necessitate a reduction of clinker production in the cement industry that is possible only by using the cementitious materials, called the mineral admixtures or pozzolans (also known as supplementary cementing materials). According to ASTM C 595, a pozzolana is defined as 'a siliceous or siliceous and aluminous material, which in itself posses little or no cementation value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementitious properties' *(Papadakis and Tsimas 2002).* Thus, a pozzolanic material requires calcium hydroxide in order to form strength products. Portland cement contains calcium hydroxide as a hydration product.

Hydrated cement paste contains approximately 70% C-S-H, 20% calcium hydroxide, 7% of sulpho-aluminate and 3% of secondary phases. The calcium hydroxide, which appears as a results of the hydration, effect the quality of the concrete negatively by forming cavities because of its solubility in water and its low strength *(Oner et al 2005).* The use of mineral admixtures has a positive effect on quality of concrete by binding the calcium hydroxide *(Memon et al 2002; Papadakis and Tsimas 2002)*. The cement hydration reaction and pozzolanic reactions are as described below:

Cement Hydration Reaction:

$$\text{Cement } (C_3S\ ,C_2S)\ +\ H_2O\ \rightarrow\ \text{C-S-H gel} + Ca(OH)_2 \qquad \ldots(1.1)$$

Pozzolanic Reaction:

$$Ca(OH)_2\ +\ SiO_2\ \rightarrow\ \text{C-S-H gel} \qquad \ldots(1.2)$$

Therefore, when introduced in Portland cement paste, as a partial replacement of cement, pozzolanic material reacts with calcium hydroxide to form calcium-silicate-hydrate gel. Some of the common examples of pozzolans or mineral admixtures are grain granulated blast furnace slag (GGBS), fly ash (FA), silica fume (SF) etc. The brief comparison of these mineral admixtures with Portland cement in made in Table 1.1 *(Lewis et al 2003)* and their typical particle size distribution is shown in Fig. 1.1 *(Mindess 2006)*.

As can be seen from the Table, each of these mineral admixtures posses different properties. Therefore, when used with cement, they modify the composition of cement paste, influence the hydration and microstructure of the pastes and mortars and the strength and permeability characteristics of concrete.

There is a double environmental benefit from using mineral admixtures. Firstly, lower cement requirements leads to reduction in carbon dioxide generated by the production of cement. Therefore, the concrete made by using supplementary cementitious materials is more sustainable *(Harrison 2006)*. Secondly, the use of mineral admixtures utilizes a product that would ordinary be used for a landfill. The use of mineral admixtures is considered as the most effective means to deal with environment considerations and carbon dioxide emission and to use industrial by products judicially *(Bentur 2002)*. In ordinary concrete, fly ash is used primarily for economical reasons, as it is cheaper than Portland cement that they replace, but silica fime, being more expansive is not used. However, for very high strength concrete and low permeability, the use of silica fume becomes essential *(Mindess 2006)*.

1.2. ROLE OF SILICA FUME IN CONCRETE

Silica fume is the by-product during the manufacture of silicon or of various silicon alloys. Silica fume, which contains more than 80% to 85% of SiO_2 in amorphous form, is suitable to be used in cement and concrete industries. The typical particle size of silica fume is around 0.1-0.5 µm and the nitrogen BET surface is 20,000 m^3/kg. It is being used increasingly in the world as a mineral admixture to produce high performance concrete. Silica fume is light and has a low bulk density of 200 to 300 kg/m^3. It was first utilized in 1970's as an additive in concrete in Norway *(Sabir 1997).*

The action of silica fume in concrete is physiochemical. The physical phase of this action is in the refinement of void system of cement paste; particularly the transition zone due to its extremely small size. This physical action provides a denser, more homogenous and uniform paste. A replacement of 15% of cement mass by silica fume will add approximately 20,00,000 particles to each cement grain, in such a way that the fine particles surround each cement grain, thus densifying the matrix, improving the bond with aggregate and reinforcing materials such as glass fibers *(Isaia et al 2003).* The chemical phase consists of the pozzolanic reaction that transforms the weak calcium hydroxide crystals into the strong C-S-H gel. It affects the concrete properties by the following mechanisms:

- It eliminates the growth of calcium hydroxide at the cement – aggregate interface, or transforms calcium hydroxide into calcium silicate hydrate by the pozzolanic reaction between silica and lime.
- It eliminates large pores at the cement – aggregate interface, making it denser
- It is able to pack between the cement grains due to its extremely fine particle size, thus lowering the capillary pores, and increasing the density of the material.

As a result of these actions of silica fume, it provides significant improvement in mechanical properties and drastic improvement in durability and impermeability. While imparting significant contribution to concrete strength and durability, silica fume can create an increase in water demand to attain specific workability levels due to the increase in specific area. It has very low bulk density, which may cause difficulty in transporting and handling. If silica fume is densified and compacted in order to improve transporting and handling properties, high degree of agglomeration of silica fume takes place, which considerably decreases its chemical reactivity with calcium hydroxide *(Yajun and Cahyadi 2003).* Along with this, it can cause plastic shrinkage problems in concrete if not properly used. These factors, coupled with the higher cost of silica fume as compared to Portland cement and other pozzolans, has been barrier to its wider use in routine 'day to day' concreting jobs.

1.3. ROLE OF FLY ASH IN CONCRETE

Fly ash is a combustion residue (coal mineral impurities) in coal burning electric power plants, which flies out with the flue gas stream and is collected by mechanical separators, electrostatic precipitators or big filters. Fly ash has been widely utilized in concrete since it reduces cost of concrete materials, conserves energy resources and reduces environmental problems. It has become an essential ingredient in concrete mixtures.

It mainly consists of SiO_2, Al_2O_3, Fe_2O_3, and CaO and some impurities. According to ASTM C 618, fly ash belongs to Class F if the sum of (SiO_2+ Al_2O_3+ Fe_2O_3) content is greater than 70 % and belongs to Class C if the sum of (SiO_2+ Al_2O_3+ Fe_2O_3) content varies from 50% to 70%. Usually, Class F fly ashes have a low content of CaO (<8%) and exhibit cementing properties, but Class C fly ash contain up to 20% CaO and exhibit no cementation properties. Class C fly ash is further divided into two types by Canadian Standard Association (CSA) specifications for fly ash i.e. Type C I called intermediate calcium with 8% to 20% CaO and Type C II, i.e., high calcium if CaO is greater than 20%. Low calcium fly ash is produced by burning of anthracite or bituminous coal and high calcium fly ash is produced by burning of lignite or sub-bituminous coal.

Most fly ashes, regardless of composition, improves the workability, tends to reduce the water demand of concrete and hence reduces the water reducing admixtures demand. It reduces cracking due to autogenous and plastic shrinkage. It increases the packing densities of cementitious system, thus creating a less permeable structure. It significantly reduces the permeability of resultant concrete to chloride, water and oxygen and increases concrete's resistance to alkali silica reaction, sulfate attack and other chemical attacks. In addition, it consumes calcium hydroxide and creates calcium-silicate-hydrate, thus making the concrete stronger *(Malik et al 2005).*

However, problems are also associated with using this material. Unlike silica fume, fly ash has relatively low surface area and accompanying pozzolanic activity. At normal temperatures, the pozzolanic reaction is slow to start and it does not progress to any significant degree until several weeks after the start of hydration. This results in slow strength development and inadequate strength at the normal age of loading, even though the concrete may have higher strength and durability in the longer term. It has been reported that at 28 days, the degree of fly ash reaction is just 10% *(Poon et al 2000; Lam et al 2000; Chen et al 2000; Fu et al 2000).* Although, at 91 days the strength of mixes incorporating fly ash was shown to outperform specimens without additives *(Langley et al 1989)*. One explanation for the low activity of fly ash at room temperatures is that the pH of the solution is normally 13, which does not meet the pH requirements of activation of fly ash reaction that is found to be nearly 13.3 *(Gopalan 1993).* Due to its low strength development rate, fly ash concretes are more sensitive to poor curing than that of ordinary Portland cement concrete and thus requires more number of curing days *(Ozer and Ozkul 2004).* Along with this, the performance of fly ash depends on its fineness too. It is reported that fly ash exhibited low pozzolanic activity since it contained a high proportion of crystalline phases and thus cannot be used *(Jaturapitakkul et al 2004).* Compared to silica fume, fly ash mixes using excessive amounts of high range water reducing agents may cause segregation of different materials, resulting in lower strengths *(Toutanji et al 2004).*

1.4. SYNERGIC EFFECTS OF SILICA FUME AND FLY ASH

From the above discussion, it can be said that there are definite benefits of using silica fume or fly ash in concrete as partial replacement of cement. However, both materials have certain shortfalls and neither could be described as a panacea for all concrete problems. However, using a combination of silica fume and fly ash along with cement as a ternary system should results in a number of synergistic effects. Some of the possibilities can be the following:

- Silica fume compensates for low early strength of concrete with Class F fly ash.

- Fly ash increases long term strength development of silica fume concrete
- Fly ash offsets increased water demand of silica fume
- Fly ash compensate for higher heat release of silica fume
- The relatively low cost of fly ash offsets the increased cost of silica fume, thereby leading to overall economy of the project.

1.5. OBJECTIVES OF RESEARCH WORK

Silica fume has widely been used to produce high strength concrete. However, in India, silica fume is imported and is expensive. Its cost is about ten times higher than Portland cement. On the other hand, fly ash is abundantly available in India and its amount is increasing every year. Thus, use of small proportion of silica fume along with large proportion of Indian fly ash can make the overall system economical without compensating the desirable properties of concrete.

The synergic effect of silica fume and fly ash in the ternary cement system is established in Europe and these systems are widely used in Europe and America .The purpose of this investigation is to establish whether there is synergistic action when the system of Indian materials are used in concrete. In other words, the answer is sought for the question of whether a suitable combination of Indian fly ash and silica fume would improve the properties of fresh and hardened concrete more than these materials when used separately. The properties are studied not only to estimate strength characteristics of ternary concrete, but due emphasis is laid on the durability aspect of concrete as well. Keeping this basic aim in mind, the emphasis of the present study is on following objectives:

1. To study the effect of silica fume and fly ash on the concrete system in terms of fresh properties of concrete at variable water-to-binder ratios and mineral admixture content.
2. To study the effect of silica fume and fly ash, when used in binary or ternary combinations, on strength development characteristics and permeability of

concrete at variable water-to-binder ratios and mineral admixture content and to find the best ternary combination for all water-to-binder ratios.

3. To study the effect of curing regimes on strength development and impermeability properties of concrete and to establish the minimum number of curing days required for each mix.

4. To establish the mathematical relationships between various strengths that are applicable to a wide strength range and to the variable curing practices adopted.

5. To subject some selected mixes to chemical attack by acids, sulfates and chlorides in order to judge the durability of these mixes in specific environments.

1.6. ORGANIZATION OF THESIS

Thesis presentation has been organized in six chapters as detailed below:

Chapter – 1 introduces the thrust area and need for research on synergistic action of silica fume and Indian fly ash and objectives of the study have been briefly discussed.

Chapter – 2 presents the comprehensive review of relevant literature based on the research work carried out by various investigators.

Chapter – 3 details the scheme of experimentation, materials used, variables involved, concrete mixes cast using different combinations of silica fume and fly ash and techniques adopted for casting and testing of specimens. The test results and a brief discussion on fresh properties of concrete have also been presented in the chapter.

Chapter – 4 deals with results and discussions on strength development characteristics of various mixes and the effect of curing practices on the properties of the resultant system. The mathematical models developed from analysis of compressive strength and tensile strength data generated have also been presented in the chapter.

Chapter – 5 presents the durability aspects of the concrete systems developed by using variable combinations of mineral admixtures on the basis of the data generated after subjecting them to aggressive chemicals for fixed time durations.

Chapter – 6 enlists the relevant conclusions drawn from the present study and gives suggestion for further work.

The relevant Tables, Figures and Plates are placed at the end of each chapter.

Table 1.1: Brief comparison of cementitious materials *(Lewis et al 2003)*

S. No.	Property	Portland Cement	Fly ash	GGBS	Silica fume
1.	Surface area (m^2/kg)	350-500	300-600	300-500	15000-20000
2.	Bulk density (kg/m^3)	1300-1400	1000	1000-1200	200-300
3.	Specific gravity	3.12	2.30	2.90	2.20
4.	Chemical composition				
	SiO_2	20	50	38	92
	Fe_2O_3	3.5	10.4	0.3	1.2
	Al_2O_3	5	28	11	0.7
	CaO	65	3	40	0.2
	MgO	0.1	2	7.5	0.2
	$Na_2O + K_2O$	0.8	3.2	1.2	2.0

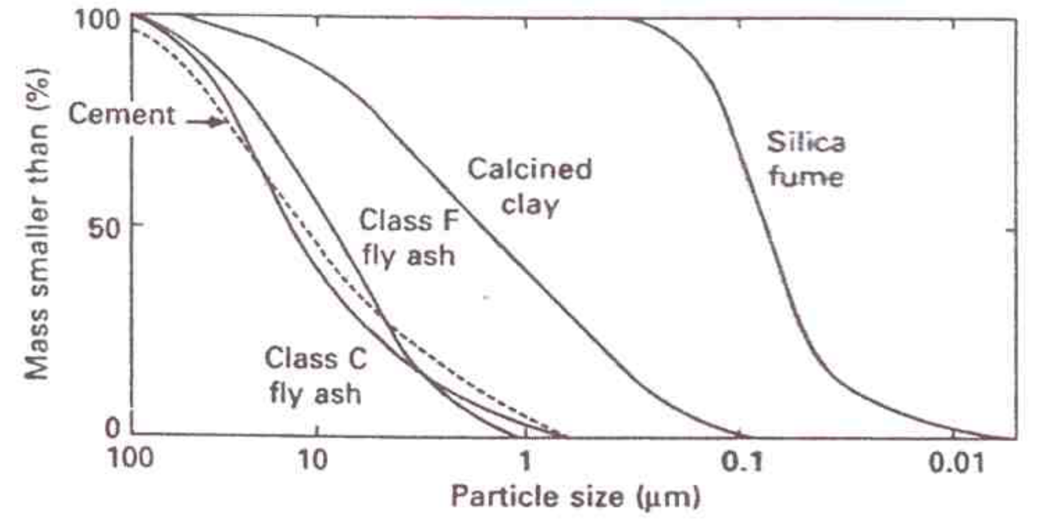


Fig. 1.1. Particle size distribution of some supplementary cementing materials *(Mindess 2006)*

CHAPTER 2

LITERATURE REVIEW

2.1. GENERAL

Concrete is the most commonly used construction material and its use in structures is more than three quarter of a century old. Last two decades of 20th century saw a major boom in the development in technology of concrete as a material. The compressive strength of ordinary concrete has increased from 15 MPa in 1910 to 60 MPa in 2001. In addition, this development led to introduction of a number of new materials into cement. The beneficial effects of incorporating these materials in concrete are widely discussed in literature *(Guneyisi et al 2005; Hussain and Rasheeduzzafar 1994).* The addition of a wide range of building materials of different chemical composition has also introduced significant diversity into the cement system. The wide variation in the performance of building materials may be illustrated to the variation in their physical, chemical and mineralogical composition resulting from the industrial processes that are further related to the raw materials used in the making of these materials. Furthermore, due to the pozzolanic reaction of these materials, which is often slow, blended cement concrete is reported to have longer curing period as compared to plain concrete *(Manmohan and Mehta 1981).*

In this chapter, a thorough review is presented of the effect of two major blending materials, silica fume and fly ash, on various properties of resultant concrete. Firstly, the mode of action of silica fume and fly ash, when used in concrete, is presented. Along with this, the action of super-plasticizers is also discussed briefly. This is followed by the brief overview of the modification in fresh properties of concrete that are brought about by the use of these mineral admixtures and the role of super-plasticizers in altering the fresh properties of concrete. Further, a discussion on the strength development characteristics of mineral admixture concrete is presented. Along with this, the importance of minimum number of curing days required for concrete in terms of strength and impermeability aspects of concrete are presented. Lastly, a review is made of the effect of various aggressive chemicals on the properties of concrete made with blended materials. The aggressive chemicals include different types of acids and various salts of sulfates and chlorides, which may attack concrete from outside.

2.2. SILICA FUME

2.2.1. General

Silica fume is a by-product resulting from the reduction of high purity quartz with coal and wood chips in an electric arc furnace during the production of silica metal or ferrosilicon alloys. The silica fume, which condenses from the gases escaping from the furnaces, has a very high content of non-crystalline silicon oxide and consists of extremely fine particles. The SiO_2 content of silica fume is roughly related to the manufacturing process of silicon alloys. Ferrosilicon alloys have nominal silicon content of 61% to 91%. When the silicon content is greater than 91%, the product is called silicon metal rather than ferrosilicon. The majority of published data and field use of silica fume has been from its alloys having silicon content of 75% and higher. A unique feature of silica fume procured from a single source is little or no variation in chemical composition from one day to another.

2.2.2. Mode of Action of Silica Fume

The strength improvement due to incorporation of silica fume in concrete occurs due to chemical and physical processes; the physical effect is primarily due to the micro-filler action and the chemical affect is largely due to the pozzolanic activity.

On the physical level, silica fume consists of very fine vitreous particles with a surface area of 20,000 m^2/kg and the particle size of 0.1 μm, which is approximately 100 times smaller than the average cement particle. Due to this, silica fume grains fill the voids between cement thus making a dense structure. On the chemical level, due to high silica content, silica fume reacts pozzolanically with lime to form the stable cementitious compound called calcium-silicate-hydrates (C-S-H). This reaction improves the microstructure of concrete. *De Larrad and Aitcin (1993)* compare the effectiveness of different fillers in the production of high strength concrete and found that silica fume is the most effective filler because of its physical and chemical actions. According to

Bhanja and Sengupta (2003 a), both pozzolonic and filler effects of silica fume are highly significant in improving the strength of concrete.

2.3. FLY ASH

2.3.1. General

Fly ash is the ash precipitated electro-statically or mechanically from the exhaust gasses of coal fired power stations. It is the most common artificial pozzolana. The American classification of fly ash, given in ASTM C 618, is based on the type of coal from which the ash originates. Class F fly ash is normally produced from burning anthracite or bituminous coal and has pozzolanic properties, but little or no cementing properties. Class C fly ash is normally produced from burning lignite or sub-bituminous coal, and in addition to having pozzolanic properties, it has some autogenously cementation properties. In general, Class F fly ash is available in Eastern US and Canada; while Class C fly ash is available in Western US and Canada.

In India, most of the available fly ash is of Class F type. One major problem in the use of fly ash is that fly ash is not a single material of nearly same composition. Even the same power station can produce fly ash with varying properties if the coal used is non-uniform. Therefore, the user of fly ash has to be aware of the properties of actual material used in concrete and one cannot rely on standardized assumptions about the properties of fly ash. Because of the variability of fly ash produced even from a single plant, quality control is particularly important in the case fly ash. This involves determination of the Blaine specific surface area, as well as the chemical composition like content of SiO_2, Al_2O_3, Fe_2O_3, CaO, alkali, carbon and sulfates.

2.3.2. Mode of Action of Fly Ash

Like silica fume, fly ash has both physical and chemical effects on concrete. The fly ash particle has a very high fineness with the vast majority of particles having the diameter between 1μm to 100 μm; due to which it fill the voids in between the cement particles, thus acting as a filler material. Also, fly ash particles are generally spherical, that confers significant benefits to the fluidity of concrete in plastic state by optimizing the packing of particles. The fly ash spheres tend to act as ‘ball bearings’ within the concrete, thus reducing the amount of water required for a given workability. Secondly, the fly ash particles chemically react with lime to produce secondary C-S-H gel.

However, the pozzolanic reaction of fly ash does not start until sometime after mixing and take as long as one weak or even more to start. Further progress of the pozzolanic reaction is slow. *Fraay et al (1989)* has quoted that at the end of one year, as much as 50% of class F fly ash remained unreacted.

2.4. SUPER-PLASTICIZERS

2.4.1. General

The use of super-plasticizer in concrete began in 1960s and was a milestone in concrete technology and the field of construction. They have the ability of increasing the workability of concrete considerably. Super-plasticizers are water-soluble organic polymers, which have to be synthesized, using a complex polymerization process, to produce molecules of high molecular mass.

Super-plasticizers are divided into four groups according to their chemical contents as: sulfonated melamine formaldehyde condensate (called melamine based super-plasticizers), sulfonated naphthalene-formaldehyde condensates (called naphthalene based super-plasicizers), modified lignosulfates and copolymers containing sulfonic and carboxylic group. The family of super-plasticizers which are based in poly-carboxylic products are more recent (1980s). These materials are of higher reactivity, they do not contain the sulfonic group and they are totally ionized in alkaline environment *(Papayianni et al 2005).*

2.4.2. Formation of Cement Flocs

Portland cement particles have a strong tendency to flocculate when mixed with water *(Rixom and Mailavaganam 1986).* This is due to several types of interactions, like

Vander walls interactions between particles, electrostatic interaction between sites bearing opposite charges and strong interactions between water molecules or hydrates. The flocculation process leads to the formation of an open network of particles. The network of voids can trap part of the water, which is then unavailable for surface hydration of the cement particles and for fluidification of the mix. These effects result in stiffening or increase in apparent viscosity of the cementitious system. To achieve a homogeneous distribution of the water and optimal water-cement contact, the cement particles must be properly deflocculated and kept in the state of high dispersion.

2.4.3. Mode of Action of Super-Plasticizers

The main action of the long molecules of super-plasticizers is to wrap themselves around the cement particles and give them a highly negative charge so that they repel each other. This creates particle-to-particle repulsive force that overcomes the attractive forces. It results in deflocculation and dispersion of cement particles homogenously in fresh concrete. Internal friction existing between cement particles is decreased due to stearic effect and the resulting workability is increased considerably. This action will last as long as sufficient super-plasticizer molecules are available at the particle solution interface, i.e, the quantity of available super-plasticizer will progressively decrease as the polymers become entrapped in hydration products *(Aitcin et al 1994).*

2.4.4. Dosage of Super-Plasticizers

There is no ‘a priori’ way of determining the required super-plasticizer dosage, it must be determined by some trial and error procedure. These admixtures do not entrain a significant amount of air as they do not markedly lower the surface tension of the pore water of concrete with respect to conventional plasticizers and they can, therefore, be used rather in higher proportions *(Erdogdu 2000).* Before using any super-plasticizer, it is however important to establish a compatible super-plasticizer cement combination *(Agarwal et al 2000).*

2.4.5. Effect of Super-Plasticizers on Concrete

Super-plasticizer improve concrete properties in early age and they do not have adverse effect later *(Erdogdu 2000).* Super-plasticizers increase the workability of the mix. Although the super-plasticizers do not react by a chemical action on hydrated products, they affect the microstructure of cement gel and concrete. The porosity and bleeding decrease significantly and on a second level, the drying shrinkage and creep deformation reduces. Thus, beyond the increase of strength, there is also an increase of the durability of concrete with the use of super-plasticizers *(Mehta, 1992).*

2.5. CHARACTERISTICS OF FRESH CONCRETE

2.5.1. Effect of Silica Fume and Fly Ash

Durekovic and Popovics (1990) in their study on demand for super plasticizer and air entraining agent in the case of blends of ordinary Portland cement with different replacement of silica fume used in mortar found that replacement of ordinary Portland cement by condensed silica fume cause the change in particle size distribution of anhydrous blends increasing the smaller particles, that result in higher demand for super plasticizer and air entraining agent. *Khatri et al (1995)* also observed that the addition of silica fume decreases the setting time but increase the super plasticizer demand for similar workability. They attributed the higher demand of super plasticizer in silica fume concrete to the fine particle size of silica fume. The decrease in setting time by the addition of silica fume was explained by taking into account the effect of fine particle size on the hydration process. The small silica fume particles fill the interface of the cement particles and acts as nucleation sites for the hydration and thus accelerate the rate of cement hydration. Similar observations was made by *Mazloom et al (2004)* while conducting the tests on concrete specimen at water-to-binder ratio of 0.35 and varying percentage of silica fume from 0% to 15%. They further observed that mixes incorporating silica fume were more cohesive then the corresponding mixes without silica fume.

Nehdi et al (1998) studied the effect of ultrafine particles like limestone fillers, finely ground silica and silica fume when used individually as partial replacement of cement on rheology of high strength concrete. In addition, triple blended composite cements containing different proportions of limestone filler and silica fume were also studied. A rheometer and the slump cone were used to measure the rheological properties. It was found that in the presence of super plasticizer, the finer the micro filler, the lower was the flow resistance of the mix. Among the various fillers, up to 20% ground silica or limestone did not increase the super plasticizer requirement to achieve a constant workability. Silica fume, however, increased the super plasticizer demand at a constant workability. They suggested that high surface area is not the sole parameter influencing the super plasticizer demand of silica fume mixtures and inferred that silica fume may have a strong affinity for multi-layer adsorption of super plasticizer molecules. It was further concluded that it is possible to design triple blended composite cements including different fillers to achieve improved rheological characteristics.

Langan et al (1987) studied various properties of high strength concrete incorporating silica fume as replacement of cement. They observed that up to 5% replacement level, there is no increase in water demand to maintain constant slump of 50 mm. The water requirement however increases linearly as the percentage of silica fume replacement increases from 10% to 30%. Similarly, the dosage of super plasticizer required to maintain constant slump increases linearly with the percentage of silica fume replacement level.

Duval and Kadri (1998) studied the workability of silica fume concrete at low water- cementitious materials ratio with napthelene sulfonate super plasticizer. They observed that 10% silica fume by mass of cement does not reduce concrete workability. Thus, 10% of cement may be replaced by silica fume without harming the concrete workability. The super plasticizer dosage depends upon the cement characteristics, i. e. C_3A content and alkali sulfate content of cement. It was observed that the super plasticizer dosage doubles when the percentage of C_3A increase from 2% to 10%.

Ferraris et al (2001) studied the influence of six mineral admixtures on the rheology of cement paste and found that mixtures with ultra fine fly ash represented the best rheological improvement while silica fume represented the worst. It was observed that the replacement of cement by silica fume result in increase in water demand and increase in high range water reducer dosage to maintain the rheological properties of the control. In contrast, the replacement of cement by ultra fine fly ash results in reduction of the water demand and in high range water reducer dosage to maintain the same rheological properties of the control. They concluded that if the goal is to reduce high range water reducer dosage and water-cement ratio in a mixture containing mineral admixture, the best selection would be to use ultra fine fly ash and not silica fume. The other mineral admixtures like metakaolin, coarse fly ash, fly ash and fine fly ash gave results in between silica fume and ultra fine fly ash. They further observed that the mini slump and the marsh cone test results could not be relied upon in order to predict concrete rheological parameters from cement paste rheological parameters. It was found that mini slump test results correlate in certain cases with the yield stress, but there is a wide scatter of data. However, no correlation was observed between the time of flow in marsh cone and plastic viscosity results.

Park et al (2005) carried out work to study the rheological properties of cementitious materials containing blast furnace slag, fly ash and silica fume. They observed that the yield stress and plastic viscosity increases steeply with increase in silica fume content. They found that silica fume has very high specific surface area and very fine particles which are chemically highly reactive and easily adsorb super-plasticizer molecules with multilayers. As a result, as the replacement of ordinary Portland cement with silica fume increases, the quantity of super plasticizer needed to maintain required workability in the system decreases and the yield stress and plastic viscosity increases. On the other hand, addition of fly ash improves the flowability of the system because of the spherical shape of fly ash particles that reduces the frictional forces among the angular particle of ordinary Portland cement. They also observed that unburnt carbon in the fly ash absorbs super-plasticizer, thus resulting in reducing the effect of super-plasticizer on better flowability of cementitious materials. *Hassan et al (1997)* reported that for each 10% replacement of ordinary Portland cement by fly ash in a concrete mix, the water requirement reduces by 3% to 4%.

Popovics (1993) conducted studies on mortar specimens made with ordinary Portland cement and various combinations of fly ash and silica fume. It was observed that the substitution of 30% by weight of Portland cement by fly ash increases the flow of the fresh mortar by approximately 10%, i.e., a significant plasticizing occurs with fly ash. On the other hand, silica fume addition makes the consistency stiffer. Different reasons were given for the plasticizing effect of fly ash. The general assumption that fly ash particles act in the fresh mortar as ball bearings because of their spherical shape and smooth, glassy surface was overruled as even ground fly ash, with sharp angular particles increased the mortar flow under certain circumstances. He proposed the idea that there is an optimum grading for cementitious materials similar to concrete aggregates. This optimum is defined as the one that provides the best consistency with a given water content. Grading, significantly coarser or finer than the optimum, provide stiffer consistency of cement paste or mortar.

Roncero et al (2002) conducted marsh cone test and normal consistency test on paste to study the effect of silica fume on fluidity, loss of fluidity, saturation dosage of super plasticizer and water demand at a temperature of 5ºC to 45ºC. They observed that the fluidity of cement-silica fume paste decreases and saturation dosage of super-plasticizer increases. Addition of 5% silica fume (by weight of cement) leads to significant increase in super-plasticizer demand due to higher specific surface area of silica fume. Increase in temperature over the range leads to decrease in fluidity of cement-silica fume paste but this is contrary to cement paste alone. In either case, the saturation dosage remains unaffected by the change in temperature. *Gallias et al (2002)* carried out standard consistency test to study the effect of fine mineral admixture on water requirement of cement pastes for constant workability without water reducing admixtures. They observed that water requirement increase with specific surface area. They also found higher water requirement for blended mixtures containing mineral admixtures like silica fume.

2.5.2. Research Significance

It can be seen from the literature that the studies on concrete workability and selection of chemical admixtures is based mostly on testing the cement pastes or mortars *(Gallias et al 2002; Chandra and Bjornstrom 2002; Park et al 2005)*. The results are then correlated to concrete workability. Unfortunately, the relation between the cement paste workability and concrete workability has never been completely established *(Ferraris et al 2001).* The main reason behind it is that cement rheology is typically measured under conditions that are never experienced by the cement paste in concrete. The values that are reported in literature for cement paste do not take into account the contribution of the aggregates. The aggregates act as heat sink and shear the cement paste during mixing process. Therefore, in order to predict the concrete workability accurately, the studies must be carried out on concrete directly. Out of the various tests available for measuring the concrete workability, slump cone test is typically quantified field test and in Vee-Bee time test, concrete experience same vibrations as experienced in the field. Therefore, in the present study, slump test and Vee-Bee time tests are conducted in order to know the amount of super plasticizer required to ensure that the concrete is workable, before proceeding to study other aspects such as strength and durability.

2.6. COMPRESSIVE STRENGTH OF CONCRETE

2.6.1. General

Strength is an important indication of quality because it is directly related to the structure of hardened cement paste. Although strength is not a direct measure of concrete durability, it has a strong relationship to the water-cement ratio of concrete, which in turn influences durability and other properties of concrete by controlling porosity. Compressive strength of cement-based materials is one of the most important properties and is normally used as a qualitative measure for other properties of hardened concrete.

2.6.2. Effect of Mineral Admixtures on Compressive Strength

Strength development of mineral admixture concrete is generally influenced by various parameters such as water-binder ratio, properties of constituent materials, curing regime adopted etc. The effect of these parameters on strength of mineral admixture concrete is presented schematically in the following sections. The special emphasis is on two admixtures, silica fume and fly ash, either used as binary or ternary combinations.

2.6.2.1. Mode of Action of Silica Fume

The use of silica fume, as partial replacement of cement in combination with super plasticizer results in significant improvement in the strength of concrete. The strength improvement occurs due to chemical (pozzolanic reaction) and physical processes (filler effect). The quantification of these two effects and their relative contribution on the improvement of concrete strength is still a subject of controversy.

Chatterjee et al (1982) concluded that the reasons for the improvement of properties of the concrete samples due to addition of silica fume are of physical nature and not due to the pozzolanic activity. *Cohen et al (1994)* investigated different properties of mortar mixtures made with either Portland cement alone or with Portland cement and silica fume with varying aggregate size. They reported that the pozzolanic action of silica fume mortars was not as significant as the microfiller effect. *Detwiler and Mehta (1989)* inferred that although the physical filling of voids with fine silica fume particles may lead to initial pore refinement, the subsequent chemical reaction is also significant. According to *Cohen (1990),* it is not certain as to whether pozzolanic or filler action contributes more to the improvement in strength and durability of concrete.

Cong et al (1992) reported that replacement by silica fume and addition of super plasticizer increases the strength of concrete. The higher strength of silica fume concrete was ascribed to be mainly because of improved strength of its cement paste constituent and that the changes in paste-aggregate interface have little effects on the compressive strength of concrete.

Goldman and Bentur (1993) studied the effect of addition of inert carbon black as microfiller and compared it to the effect of addition of silica fume on the performance of high strength concrete in pastes at water-to-binder ratio of 0.46. The authors concluded that silica fume concrete has largest increase in strength. They inferred that silica fume modifies the microstructure of the transition zone, making it denser and stronger, resulting in a true composites material where the aggregate strength also contributes to the concrete strength. It was also inferred that silica fume modifies the ordinary concrete behavior by improving the aggregate paste bond rather than increasing the paste strength and the microfiller effect is as important (perhaps more significant than) as the pozzolanic influence.

Bhanja and Sengupta (2003 a) concluded that both the pozzolanic and filler effects of silica fume are highly significant in improving the strength of concrete. They observed that out of a total silica fume content of 33.33% by weight of cement responsible for increasing the strength of concrete, 14.53% contributed to the pozzolanic effect and 18.80% contributed to the physical effect.

Isaia et al (2003) compared the contribution of pozzolanic effect and filler effect at different strength level and concluded that on an average, the pozzolanic effect is more significant in lower strength concrete mixtures (35MPa), while the filler effect is more significant in higher strength concrete mixtures (65MPa).

2.6.2.2. Optimum Silica Fume Dosage

There is a disagreement among researchers regarding the optimum silica fume content required to achieve the maximum strength improvement. *Toutanji (1995)* studied the influence of silica fume on the compressive strength of cement paste and mortars. Five water-binder ratios and two contents of silica fume (16% and 25%) by mass of cement were selected for experimental investigations. It was reported that regardless of water-to-binder ratio, strength increases with increase in silica fume content in the mix. The increase in strength due to silica fume addition was associated with the formation of less porous interfacial zone and better interlock between the paste and the aggregate.

Yogendran et al (1987) investigated the strength of silica fume concrete at constant water-to-binder ratios of 0.345 and 0.28 and replacement percentage of silica fume ranging from 0% to 25%, with varying dosage of super plasticizers and reported that the maximum 28 days strength can be achieved by 15% of replacement level for water-to-binder ratio of 0.345. However, at water-binder ratio of 0.28, the replacement of 5%, 10% and 15% of silica fume obtain equal or marginally lower compressive strengths, compared to the control mix at 28 and 56 days.

Hooton (1993) also concluded that 15% is the optimum silica fume level for maximizing strength. *Khedr and Abou-Zeid (1994)* investigated the effect of silica fume on concrete at water-to-binder ratio of 0.35 and 0.57. The optimum silica fume replacement level for 28 days strength was obtained as 15% at water-binder ratio of 0.35, while the same was found to be 20% at water-to-binder ratio of 0.57.

Duval and Kadri (1998) reported that the optimum silica fume replacement level for 28-days strength is 10% for water-binder ratio ranging from 0.25 to 0.45 and with varying dosage of super plasticizer. *Bhanja and Sengupta (2003 a)* carried out a comprehensive study to determine the optimum constitution of silica fume in concrete over a wide range of water-to-binder ratios ranging from 0.26 to 0.42 and cement replacement percentage of 0% to 30%. The results indicated that other mixture proportioning parameters remaining constant; the optimum silica fume replacement percentage is not constant but a function of water-to-binder ratio of the mixture. The optimum silica fume content was found to range from 15% to 25%. *Toutanji et al (2004)* studied the effect of different supplementary cementitious materials on strength and durability of concrete and concluded that the optimum replacement percentage of silica fume for maximum strength is 8%.

Kovler et al (2000) developed a standard relationship between the compressive strength of high performance concrete, water-binder ratio, silica fume concentration and the concrete age. It was observed that out of all the parameters, compressive strength showed the maximum dependence on an optimum percentage of silica fume. This optimum percentage slowly shifts with concrete age to higher contents of silica fume. The optimum silica fume replacement from the point of view of maximum compressive strength was found to be approximately 5% to 10% for very young high performance concrete (1day age) and the same was 15% to 20% for ordinary concrete (28 days age).

Papadakis (1999) described the pozzolanic activity of silica fume in concrete in terms of simplified chemical reactions. For material used and the mix proportions adopted, it was inferred that the optimum amount of silica fume required for consuming all the calcium hydroxide produced as a result of cement hydration was 18.9% by weight of cement.

2.6.2.3. Strength Development of OPC – Silica Fume System

The presence of silica fume particles in concrete leads to early strength development of concrete. The major reason for increase in early strength is the pozzolanic reaction between amorphous silica in silica fume and calcium hydroxide (produced by hydration of Portland cement). The reaction proceeds at very high rate initially. Out of the total 10% silica fume present, one half of silica fume was observed to react in one day; and two-third during the first three days. However, subsequent reaction was observed to be very slow, with only three-forth of silica hydrated at 90 days *(Neville 2004 a).* Along with early age strength development, the strength development ceases much early in silica fume concrete. *Hooton (1993)* investigated the performance of silica fume concrete with silica fume content ranging from 10% to 20% at water-to-binder ratio of 0.36 and the specimens were maintained under moist conditions. The test duration was ranged from 1 day to 5 years. It was found that there is no increase in compressive strength for silica fume concrete beyond 56 days. They concluded that due to high reactivity of silica fume, the mix water is rapidly used up, i.e. self-desiccation takes place. At the same time, the dense microstructure of the hydrated cement paste makes it difficult for water to penetrate from outside towards the unhydrated remnants of Portland cement or silica fume particles.

Another problem with silica fume is that it is light and has low bulk density. That is why; it is densified to reduce transporting and handling problems. Due to densification, high degree of agglomeration of silica fume in cement paste or mortars can take place. The agglomerate of silica fume particles can not be easily broken up due to high inter particle forces, for example, forces due to electrostatic charging, Vander wall forces and forces due to moisture. *Yajun and Cahyadi (2003)* investigated the effect of densified silica fume on microstructure and compressive strength of hardened cement pastes and found that the agglomerates of silica fume cannot be broken down by normal mixing. Due to agglomeration, compressive strength of blended cement paste was not significantly increased up to 28 days and the pore structure was not sufficient refined. They concluded that a total dispersion of densified silica fume in pastes must be carried out in order to get the maximum performance of blended matrixes. Similar observation was made by other researchers also *(Mitchell et al 1998; Boddy et al 2000; Bonen and Diamond 1992; Sanchez et al 1999).*

2.6.2.4. Strength Development of OPC – Fly Ash System

Mehta and Aitcin (1990) showed that the addition of fly ash, whose particles are smaller than those of Portland cement, cause segmentation of larger pores and increases the number of nucleation sites for the precipitation of hydration products of the cementitious paste. This process accelerates the hydration reaction and leads to formation of smaller calcium hydroxide crystals. The chemical action of the pozzolanic reactions enhances the physical effect further because of the higher segmentation of pores and the refinement of calcium hydroxide grains as curing time progresses. *Lane and Best (1982)* investigated the strength development of OPC concrete and fly ash concrete up to one year and reported that in fly ash concrete, the strength at the end of one year was 20% more than ordinary Portland cement concrete.

Like silica fume, the strength of concrete increases with increase in amount of fly ash up to an optimum value, beyond which strength starts to decrease with further addition of fly ash. *Oner et al (2005)* carried out an experimental study on strength development of concrete containing different percentages of fly ash varying from 15% to 58%. They observed that optimum value of fly ash is about 40% of cement. Along with this, they observed that fly ash to cement ratio is an important factor determining the efficiency of fly ash. *Pandey et al (2003)* studied the effect of fly ash (5% to 35% weight replacement of cement) on compressive strength of the blends. At 25% to 35% fly ash level, a decreasing effect in strength was observed due to corresponding decrease in primary cementitious material, which cannot be compensated by the pozzolanic activity of fly ash.

There is one major drawback in using fly ash; it results in slow strength development. *Hassan et al (2000)* carried out a laboratory study on the influence of silica fume and fly ash on short-term and long-term properties of high performance concrete. They concluded that while silica fume contributed to both short and long-term properties of concrete, fly ash required a relatively longer time to get its beneficial effects. They further observed that fly ash concrete has relatively porous characteristics at early ages, but achieves similar strength and transport characteristics to silica fume concrete in long term. In case of fly ash, the pozzolanic reaction does not start until sometime after mixing. *Fraay et al (1989)* observed that in the case of class F fly ash, the pozzolanic reaction starts after about one week of mixing. They explained the delay is due to the fact that the glass material in fly ash is broken down only when pH of pore water is at least about 13.2, which mean a certain amount of hydration of the Portland cement has taken place in the mix. Also, the further progress of the pozzolanic reaction is slow. They observed the presence of as much as 50% unreacted fly ash even after one year. *Barry (1994)* also detected that fly ash particles that are not completely reacted may fill the void and increase paste density.

Many researchers further concluded that the fineness of fly ash is an important factor in the improvement in properties of fly ash. *Jaterrapitakkul et al (2004)* carried out a study on ground coarse fly ash as replacement of cement for 15% to 50%. The coarse fly ash was ground until the average particle size was reduced to 3.8µm. It is found that the addition of ground fly ash can produce high strength concrete and 25% cement replacement gave the highest compressive strength. They further observed that performance of ground coarse fly ash concrete is similar to the concrete with condensed silica fume.

2.6.2.5. Ternary System

Thomas et al (1999) carried out a study on various properties of concrete containing ternary blends of Portland cement, silica fume and fly ash. They observed that the combination of silica fume and low calcium fly ash is complementary: the silica fume improves the early age performance of concrete and fly ash continuously refines the properties of the hardened concrete as it matures.

Isaia et al (2003) studied the properties of ternary mixtures containing a combination of fly ash and rice husk ash. They observed that the strength values of the ternary mixtures are higher than the binary mixtures. They informed that in ternary mixture, the combination of less active pozzolona (such as fly ash) with a more reactive one (such as rice husk ash) produces a synergistic effect, in relation to respective binary mixtures. The similar effect was observed by *Shehata and Thomas (2002)* while studying the use of silica fume and fly ash together in suppressing expansion due to alkali-silica reaction in concrete.

Nassif et al (2005) studied the effect of various combinations of silica fume and fly ash on strength and elastic modulus, when the specimens were moist cured. Among various fly ash and silica fume combinations, it was observed that the best combination for improving compressive strength and modulus of elasticity is the mix with 5% silica fume and 10 % fly ash. It was also noticed that adding more than 10% fly ash decreased both strength and modulus in comparison with control specimens**.** *Popovics (1993)* studied the synergistic action of a ternary system of Portland cement – fly ash – silica fume used in mortar. Standard flow tests, compressive strength as well as ultrasonic pulse velocity tests were performed on hardened mortar at various ages up to 28 days. It was found that certain fly ash – silica fume combinations can improve the strength of mortar more than fly ash or silica fume, when used alone. The use of super plasticizers also appears to be more effective in mortars containing fly ash and silica fume.

2.6.3. Effect of Water-to-Binder Ratio on Compressive Strength

Sarkar (1990) observed the strength development of cement-silica fume paste using shrinkage compensating (Type K) cement at water-binder ratio of 0.5 and 0.4 for silica fume replacement of 5% and 10%. Results indicated increase in strength with decrease in water-to-binder ratio. Highest strength was observed with water-binder ratio of 0.4 and 10% silica fume replacement. *Feldman and Cheng-Ji (1985)* studied the compressive strength of Portland cement-silica fume pastes at water-binder ratio of 0.25 and 0.45; and silica fume replacement level of 10% and 30%. At water-binder ratio of 0.25, the pastes with 10% silica fume exhibited highest strength between 28 and 90 days of curing. At water-to-binder ratio of 0.45, 30% silica fume exhibited highest strength between 1 day and 180 days. *Yogendran et al (1987)* investigated the efficiency of silica fume at a wide range of water-binder ratios. Their results indicated that the efficiency of silica fume is much lower at water-to-binder ratio of 0.28 as compared to the efficiency at water-binder ratio of 0.48.

Bhanja and Sengupta (2003 b) examined the applications of Abram's water-cement ratio law, which was originally formulated for conventional concrete containing cement as the only cemet-iatious material, to the concrete containing cement plus silica fume as a supplementary material. They observed that Abrams law is not directly applicable to silica fume concrete and the modified expression was developed based on water-binder ratio and the mineral admixture content. *Rao (2001)* investigated the validity of Abrams water-cement ratio law for mortar with silica fume at all ages. The water-to-binder ratios were varied between 0.35 to 0.5 at a constant increment of 0.05 and the silica fume content was varied from 0% to 30%. The strength development was studied at the ages of 3, 7, 28 and 90 days. From the test results, it was observed that in plain cement mortars, the strength of mortar decreased as the water-binder ratio increases at any age of mortar. However, the mortar mixes containing silica fume did not follow the same variation as was observed in plain cement mortar. At early ages of 3 to 7 days, the strength of mortar with silica fume was found to decrease with water-binder ratio up to 0.45 and between water-binder ratio 0.45 and 0.5, the strength was observed to increase with water-binder ratio. However, at the age of 28 days and 90 days, the strength of mortars at water-binder ratios of 0.35, 0.4 and 0.5 were observed to the more or less the same. But at water-to-binder ratio of 0.45, the strength was observed to be lowest at any silica fume concentration. In general, it was observed that the variation in strength with water-binder ratio could not comply with Abram's generalized water-cement ratio law in mortars containing silica fume.

2.6.4. Effect of Curing Regime and Curing Age on Compressive Strength

Curing of concrete is important with respect to both strength and durability properties. The necessity for curing arises for the fact that hydration of cement can take place only in water filled capillaries. Therefore, in order to obtain good concrete, the placing of an appropriate mix must be followed by curing in a suitable environment during the early stages of hardening and a loss of water by evaporation from capillaries must be prevented. The temperature of curing and the duration of moist curing are the key factors for proper curing. It is because the rate of hydration is controlled by quality and quantities of the cementitious materials present in the mix as well as the ambient temperature and availability of moisture in the mix. Not only is it recognized as important to minimize the evaporation of mix water, but also it is equally emphasized to provide a source of curing water to replace that consumed by chemical reaction during the hydration of cement. A cement paste, mortar or concrete cured under sealed condition will desiccate, resulting in the creation of coarse capillary pores within the microstructure. For water-cement ratio greater than approximately 0.42, there is sufficient water in the mix such that complete hydration of the cement can be achieved theoretically without supply of additional water to the cement paste. Even if complete hydration is possible in this case, the lack of additional curing water may still result in the creation of relatively large pores within the final microstructure. In this case, the addition of curing water would assure that all pores remain water filled and eligible as locations for the precipitation and growth of hydration products during curing *(Bentz and Slutzman 2006).* Water curing for high strength concrete is highly recommended due to its low water-cement ratio. At water-cement ratio below 0.4, the ultimate degree of hydration is significantly reduced if free water is not provided. *Carrasquillo et al (1981)* investigated the effect of two different curing conditions on concrete strength. The two conditions were moist curing for seven days followed by drying at 50% relative humidity until testing at 28 days; and moist curing for 28 days followed by drying at 50% relative humidity until testing at 95 days. Higher strength concrete demonstrated a large reduction in compressive strength when allowed to dry before completion of curing.

The curing becomes even more important if the concrete contains supplementary cementitious materials such as fly ash, granulated blast furnace slag, silica fume etc. *(Tasdemir 2003; Ramezanianpour and Malhotra 1995).* Since the pozzolonic reaction is highly dependent on good curing practice, there is often a concern as to the effect of curing on the permeability of pozzolonic cement concrete. *Manmohan and Mehta (1981) and Marsh et al (1985)* reported that a curing period about 28 to 90 days might be required for concrete with mineral admixtures to attain properties similar to that of ordinary Portland cement concrete. This is attributed to pozzolonic reaction of these materials, which is often quite slow. *Khan and Michael (1995)* in an experimental investigation, determined the minimum length of curing of silica fume concrete and compared it further with plain Portland cement concrete and fly ash concrete. Four silica fume replacements (5%, 10%, 15% and 20%) and six curing ages (0, 1, 2, 7, 14 and 28 days) were adopted in the investigation and from the regression equation relating strength and curing time, minimum length of curing for silica fume concrete mixes was proposed to be 3 days; whereas for plain concrete and fly ash concrete mix, the same minimum lengths were 3.75 days and 6.5 days respectively. *Khatri et al (1997)* investigated the effect of curing on the water permeability of slag and Portland cement concrete. They found that the coefficient of water permeability of slag concrete was less than that of Portland cement concrete even after seven days of curing.

Ozer and Ozkul (2004) investigated the effect of initial water curing period on the strength properties of ordinary Portland cement concrete and natural pozzolanic cement concrete. The concrete specimens were subjected to six different curing regimes ranging from continuous water curing to continuous air curing. In the remaining four regimes, the specimens were stored under varying water-curing periods of 3, 7, 14 and 28 days respectively. The evaluation of curing practice was carried out in terms of compressive strength tests on the cubic specimens at the ages of 7, 14, 28, 90 and 180 days. It was found that curing conditions affect the strengths of both ordinary Portland cement concrete and pozzolanic cement concrete. However, poor curing affects the strength properties of pozzolanic cement concrete more adversely than ordinary Portland cement concrete. Among all the curing conditions, air curing condition was found to be worst curing practice. For pozzolanic cement concretes, at least 7 days of initial water curing was found to be necessary to initiate the pozzolanic activity. It was further observed that pozzolanic cement concretes, water cured for at least 14 days, can reach the strength level of the ordinary Portland cement concrete cured continuously in water in periods shorter than 2 months. However, when the pozzolanic concrete is initially moist cured for 3 days, it can never reach the strength of ordinary Portland cement concrete continuously cured in water.

Toutanji and Bayasi (1999) studied the effect of curing procedure on hardened silica fume concrete. The silica fume contents were varied from 10% to 30% by weight of cement. Three different curing methods were adopted: steam curing, moist curing and air curing and their effect on concrete in terms of various mechanical properties were studied. It was observed that the specimens under steam curing experienced the highest compressive strength as compared to both moist curing and air curing for all mixtures. Air curing was found to have the maximum detrimental effect on the strength, particularly on specimen with silica fume content of 10% to 30%. *Ramjanianpour and Malhotra (1995)* investigated the performance of fly ash, silica fume and slag concretes under four different curing regimes. These included moist curing; curing at room temperature immediately after demoulding; room curing after 2 days of moist curing; and curing at 38°C and 65% relative humidity. They reported that the continuous moist curing of concrete is essential to achieve the highest strength and lowest porosity. The concrete that received no curing after demoulding showed the poorest performance in terms of strength, durability, porosity and resistance to the chloride ion penetration. However, the concrete mixes moist cured for only 2 days demonstrated significant improvement in strength and other characteristics as compared with the concrete without any curing. They further observed that in case of curing at 38°C and 65% relative humidity, the early strength gains of the specimens were even higher than moist cured concretes, however, the later age compressive strength at 180 days was significantly lower than the strength of corresponding moist cured concrete. It was reported that the strength of the concrete containing fly ash or slag is more sensitive to poor curing, than that of control concrete, with the sensitivity increasing with the increase in amount of fly ash or slag in the mixtures. Compressive strength loss was 38% for 25% slag and about 50% for 25% fly ash or high volume fly ash while it was only 28% for control concrete and silica fume concrete measured between moist curing and room curing condition.

Guneyisi et al (2005) carried out an experimental investigation to find the effect of different curing procedures on plain and blended cement concrete. The compressive strength, steel reinforcement corrosion and electrical resistivity were measured after subjecting the specimens to three different curing procedures: uncontrolled curing in which the specimens were air cured at uncontrolled temperature and relative humidity until the test age; control curing in which the specimen were immersed in water at 20 ± 2°C for 7 days and then air cured in a room at 20 ± 1°C and 50 ± 5% relative humidity until the test age; and wet curing in which the specimens were immersed in water at 20 ± 2°C until the test age. It was observed that the quality of curing affects the compressive strength of concrete. Improving the quality of curing was observed to be more effective on the later age compressive strength development of the plain cement concrete with higher water-cement ratio than the concrete with lower water-cement ratio. Out of all the three curing conditions, uncontrolled curing was found to be the worst curing regime. For both plain and blended cement concretes, uncontrolled curing resulted in lower 28 days and 180 days strength as compared to the other curing conditions. The application of controlled curing gave average compressive strength within 5% of that obtained at wet curing for both concrete types. However, strength of the plain and blended cement concrete specimens under uncontrolled curing conditions deviated within the range of -10% and -20% from those cured under wet curing respectively. In uncontrolled curing condition, blended cement concrete was found to suffer more than plain cement concrete due to adverse curing practice. This was attributed to the lack of development of hydration and pozzolanic reactions to produce a dense microstructure as well as the extensive shrinkage cracking developed due to continuous air curing.

Bentz and Stutzman (2006) studied the effect of curing on hydration characteristics and microstructure of cement pastes with water-to-binder ratio of 0.35 and 0.435. Degree of hydration was quantified by loss of ignition measurements and the microstructure of hydrated pastes was evaluated by using scanning electron microscopy and low temperature calorimetry. Cement pastes were prepared at water-binder ratios of 0.35 and 0.435. Three curing conditions were then employed to the specimens. In saturated curing, a small amount of distilled water was placed on the top of paste wafers after removing the bleed water. In sealed curing, the wafers were simply sealed in their plastic vials after removal of bleed water. In sealed / saturated curing, the wafers were cured under sealed conditions for seven days, then the plastic vials were opened and a small amount of distilled water was added on top of the wafers. It was observed that the connectivity of pores is strongly influenced by the water-cement ratio, curing condition and alkali content of the cement. Optimum curing was found to be a function of water-cement ratio, as well as whether curing is to optimize strength or permeability or durability. It was observed that at water-cement ratio of 0.35, under sealed curing, the specimens form a disconnected capillary pore system initially that later reconnects due to self-desiccation and autogenous shrinkage. Conversely, at water-cement ratio of 0.435, sealed curing actually leads to an earlier disconnectivity of capillary pores than saturated curing, but without a subsequent connectivity. The authors suggested different curing practices to produce concrete with optimum properties. For example, for very low water-cement ratios (≤0.35), internal curing was suggested to avoid self-desiccation of specimens, internal or external curing was found to be a viable option at low water-cement ratio of 0.35 to 0.4 and sealed/saturated curing was recommended for intermediate water-cement ratios (0.4 to 0.45) etc.

Aldea et al (2000) studied the effect of curing conditions on properties of slag cement concrete. The curing practices adopted were autoclaving (at temperature of 175°C and pressure of 0.5 MPa), steam curing (at 80°C) and normal curing (at 20°C and 100% relative humidity until 28 days). Comparing the compressive strength results, it was concluded that normal curing is the best curing practice. Normal curing was observed to provide higher compressive strength as compared to fast curing. On the other hand, steam curing induced the greatest decrease in compressive strength for most of the mixes. This is due to a less uniform distribution of the hydration products in the paste because of rapid initial hydration. It was further suggested that steam curing could be preferred to autoclave curing, if the rapid strength development is required.

Nassif et al (2005) studied the effect of curing methods on the properties of high performance concrete made with various percentages of silica fume, fly ash and granulated blast furnace slag. Several series of concrete mixes were made with varying proportions of fly ash, silica fume and slag and the specimens were cured under three different curing practices: (i) air-drying, (ii) curing by using curing compound and (iii) wet curing with burlaps. The evaluation of modulus of elasticity was made and was compared with the strength results. The strength results showed that wet curing with burlaps result in higher strength than air-dry curing and using curing compound. Similar to strength results, burlap curing resulted in higher elastic modulus of concrete compared to air-dry curing or curing by using a curing compound. Further, with burlap curing, the modulus of elasticity value, was found to increase with age; while with air-dry curing and compound curing, there was no increase with age. Rather, the value decreased in some cases.

It is noted that fly ash concrete is more sensitive to curing condition and requires longer curing time because its hydration rate is slower than that of the plain concretes *(Bijen 1996).* The benefit of using fly ash in concrete is even reported to be diminished due to inadequate curing. *Poon et al (1997)* studied the influence of two different curing conditions (in water at 27°C; and in air at 15°C and 60% relative humidity) on mechanical and durability properties of fly ash cement pastes and mortars prepared at two water-binder ratios. They found that air curing at 15°C and 60% relative humidity has the negative effect on fly ash paste and mortar. It was also observed that fly ash has significantly different influence on the strength, porosity and durability parameters of cement pastes and mortars when cementitious materials are subjected to two different curing conditions.

Tan and Gjorv (1996) investigated the effect of curing conditions on the strength and permeability of concrete. Test results showed that after 3 days and 7 days moist curing regime, only the concretes with water-cement ratio equal to or less than 0.45 were accepted, while after 28 days of moist curing, even the concretes with water-cement ratio of 0.6 were acceptable based on water-penetration results. They further observed that silica fume concrete is less sensitive to early drying.

Cakir and Akoz (2008) studied the effect of curing conditions on the properties of mortars with and without granulated blast furnace slag. In order to study effect of curing temperature, the specimens were subjected to two different curing conditions: (i) lime saturated water at 20°C standard curing and (ii) temperature and humidity control curing at 40°C and 100% relative humidity. It was observed that the flexural strength and compressive strength of specimens exposed to elevated temperature and relative humidity leads to higher early age strength but eventually lower later age strength compared to specimens cured in water. The result obtained indicated that elevated temperature increases performance of mortar at early ages but decreases at later age and their effect was found to be more significant at slag replaced mortars.

2.6.5. Research Significance

It is established that the proper proportioning of OPC- silica fume-fly ash may lead to strength improvement and overall economy in the cementing system. Along with this, it is important to study the effect of various curing regimes in strength development pattern of mineral admixture concrete. Most of the standards recommend increase in initial curing days for the blended cements (IS 456: 2000, BS 8110-Part 1: 1985, ACI 308-81). Many investigators *(Manmohan and Mehta 1981; Marsh et al 1985)* believe that a curing period of about 28 to 90 days is required for pozzolanic cement concrete specimens to attain properties superior to that of plain cement concrete. It is due to the fact that the pozzolanic reaction is highly dependent on good curing practice. Therefore, it is intended to investigate upon the effect of curing regimes on relative performance of a range of mixes made with OPC, silica fume and fly ash, used either as binary or ternary combinations.

2.7. TENSILE STRENGTH OF CONCRETE

2.7.1. General

Although, it is generally assumed that concrete performance is governed mostly by its compressive strength and the tensile strength of concrete is not normally relied upon to carry loading, tensile strength is of substantial importance in the theory and design of many reinforced concrete structures. Tensile strength governs the cracking and post cracking behavior of concrete, the knowledge of which is important for any accurate finite element analysis of structural members *(Marzouk and Chen 1995).* Tensile strength affects stiffness, damping action, bond to embedded steel and durability of concrete. It is also of importance with regard to the behaviour of concrete under shear loads. Tensile strength is even important for non-reinforced concrete structures such as dam under earthquake excitations *(Zain et al 2002).* Other structures such as pavement slabs and airfield runway, which are designed based on bending strength, are subjected to tensile forces. Therefore, in the design of these structures, tensile strength value is more important than the compressive strength. The tensile strength becomes even more important as the compressive strength of concrete increases. According to *Marjouk and Chen (1995)* concrete can be considered a brittle material and the tensile strength of a brittle material is due to the rapid propagation of a single flaw or microcrack. High strength concrete is more brittle and stiffer than normal strength concrete and their tensile strength is important.

2.7.2. Tests Available for Measuring Tensile Strength

Tensile Strength of concrete is a physical property that has no absolute meaning; it is always expressed in terms of a specific test procedure. It is determined either by direct tensile test or by indirect tensile tests on the specimens. The direct tension test, the beam flexure test and the split cylinder test are the three kinds of tests that are commonly used to measure tensile strength of concrete. The last two tests are indirect in the sense that the tensile stresses are applied indirectly to the specimens. In the split cylinder test, a concrete cylinder is laid horizontally between the plates of a compression machine and compressive loads are applied to two diametrically opposite edges of the cylinder. According to the theory of elasticity, this loading generates almost uniform tensile stress along the diameter, which causes the specimen to fail by splitting along two vertical planes. In the beam flexure test, a concrete beam is subjected to bending by applying center point or third point loading until the beam fails by flexure.

2.7.2.1. Utility of Various Tests

In brittle materials like concrete, where there is little redistribution of stresses, the directly tensile strength is difficult to obtain and the direct tensile test usually results in underestimation of tensile strength. The under estimation arises from the difficulty in insuring that the applied load is truly axial *(Oluokun 1991).*

Between the two indirect tests, neither of them is believed to yield the true tensile strength. This is because, in both methods, the tensile strengths are evaluated on the assumption that the concrete is linearly elastic until failure, while in reality, the stress-strain curve becomes non-linear when the concrete is close to failure *(Zheng et al 2001).*

In the case of beam flexure test, because of the development of minute and invisible micro cracks, the load at first crack is difficult to establish. The ultimate load used in estimating the modulus of rupture is therefore not the same as the load at which cracking first occurred. Because of this fact and the non-linearity of the stress-strain curve for concrete in tension, the modulus of rupture is found to overestimate the tensile strength of concrete.

It is established that out of the three available tests, the splite tensile strength test on the cylindrical specimens gives more reasonable tensile strength estimation than the direct tensile test or modulus of rupture test. It is because, in this test, the stress distribution is reasonably uniform along the vertical diameter of the cylinder, which is the plane of principal tensile stress for about 80% of its length. It is also called the Brazilian test, after being first proposed by Lobo Carniero and Barcellous during the fifth conference of the Brazilian Association for Standardization in 1943 *(Rocco et al 2001).* However, *Conroy-Jones and Barr (2004)* suggested that when the influence of curing is to be studied, which effects the hydration, permeability and residual moisture gradient at the time of testing, the surface failure tests like flexure tests may give better indication than the spilt cylinder tests. It is because inadequate curing affects the surface failure tests more than spilt cylinder tests.

2.7.3. Effect of Mineral Admixtures on Tensile Strength

Although the literature is rich in reporting the contribution of mineral admixtures in improving properties of concrete, most of the research works are centered on the compressive strength and technical data on tensile strength is quite limited. A brief review of some the existing works is presented hereunder.

Lam et al (1998) studied the effect of replacing cement by fly ash and silica fume on various properties of concrete prepared at different water-to-binder ratios. For determining tensile strength, split tensile test was conducted. It was observed that with the addition of 5% silica fume, the split tensile strength increases. Also, the enhancement effect of silica fume was found to be more on tensile strength and cylindrical compressive strength than on cube compressive strength. The addition of silica fume led to about 17% increase in cylindrical compressive strength and 13% increase in split tensile strength, but only 7% increase in cube compressive strength. The higher tensile strength of silica fume concrete was attributed to the improved interfacial bond between the paste and the aggregates. Similar to silica fume, proper amount of fly ash was found to improve interfacial bond and thus split tensile strength of concrete. Among the fly ash mixes, low volume fly ash improved the tensile strength of concrete while high volume fly ash showed slightly lower tensile strength as compared to the corresponding control mixes. At compressive strength level of 80 MPa, the split tensile strength of mixes with 15% to 25% fly ash was about 7% higher than the corresponding plain cement mixes. The mixes containing 45% to 55% fly ash showed lower tensile strength, probably due to the lower concentration of cement hydration products. It was further said that the interfacial bond development in high volume fly ash concrete requires a longer period of curing.

Bhanja and Sengupta (2005) carried out extensive experiments in order to study the isolated contribution of silica fume on the tensile strength of high performance concrete. The experiments were carried out over water-binder ratios ranging from 0.26 to 0.42 and silica fume-binder ratios of 0 to 0.3. The specimens were moist cured and the strength was determined at the end of 28 days. The tensile strength was measured by split tensile test and flexure test. It was observed that incorporation of silica fume increases the split tensile strength of concrete. However, very high percentage of silica fume did not significantly increase the split tensile strength, the increase being almost insignificant beyond 15%. For all water-to-binder ratios, 5% to 10% replacement considerably improved the split tensile strength with respect to control. The initial filling of the voids by silica fume was believed to be the reason behind the improvement of tensile strength of concrete. It was further observed that between the flexure test and split tensile test, silica fume has more pronounced effect on the flexure strength than on the split tensile strength. For flexural strengths, even very high percentages of silica fume significantly improved the strength. The gain in splitting tensile strength was found to be higher than the flexural strength at lower silica fume replacement levels, but the trend was reversed at higher replacement levels. It was observed that the optimum silica fume replacement percentage for tensile strength is not constant but a function of water-to-binder ratio of the mix. The optimum replacement level of silica fume was found to be in the range of 5% to 10% for 28 days split tensile strength, whereas the corresponding value for flexural strength ranged from 15% to 25%.

Khatri et al (1995) compared the mechanical properties of concrete containing silica fume, granulated blast furnace slag, fly ash and general purpose Portland cement. Flexural strength of concrete was investigated at 28 days and at one year. It was observed that the addition of silica fume significantly increased the flexural strength of general-purpose concrete, while the increase of flexural strength of slag concrete by the addition of silica fume was marginal. The effect of silica fume on flexural strength of concrete was found to be similar to its effect on compressive strength. *Khatib and Hibbert (2005)* found an increase in flexure strength of concrete containing metakaolin and granulated blast furnace slag with respect to control concrete. *Carette and Malhotra (1983)* also observed that strength development pattern of flexural strength and split tensile strength of concrete incorporating silica fume is similar to that for compressive strength.

On the other hand, *Jianyong and Pei (1997),* while studying the effect of slag and silica fume on various mechanical properties of high strength concrete, observed that the development of compressive strength and split tensile strength of concrete did not synchronize; the compressive strength developed faster than spilt tensile strength. They further observed that the addition of mineral admixtures accelerate the growth of split tensile strength as compared to the growth of compressive strength.

2.7.4. Effect of Curing Conditions on Tensile Strength

The effect of curing on tensile strength is relatively an under studied research area, rarely still with the mineral admixture. *Iravani (1996)* while presenting the results on various properties of high performance concrete, reported the findings of *Burk et al* that the moist cured specimens have higher split tensile strength and flexure strength than the corresponding air-cured specimens. *Aldea et al (2000)* compared the effect of normal curing, steam curing and autoclaving on split tensile strength of concrete made with different replacement levels of slag. It was found that the trend of split tensile strength was comparable to that of compressive strength, i.e., room temperature curing was found to be the best among all the curing regimes. However, *Toutanji and Bayasi (1999)* studied the effect of steam curing, moist curing and air curing on mechanical properties of silica fume concrete. They observed that the effect of curing on flexure strength is not the same as that on compressive strength in silica fume concrete. They attributed this to the fact that flexure strength is more sensitive to micro cracks as compared to compressive strength. The addition of silica fume to the cement matrix result in micro-shrinkage cracking, which could have a more prominent effect on the flexure strength as compared to compressive strength.

Cakir and Akoz (2008) studied the effect of curing on the properties of mortars with or without granulated blast furnace slag. The curing conditions adopted were water curing at 20°C and moisture cabinet curing at 40°C temperature and 100% relative humidity. The flexural strength was investigated at 7, 28, 56, 90 and 180 days. It was found that similar to compressive strength, the flexural strength of slag-replaced mortar is lower than that of control mortar for both curing condition. Also, the elevated temperature and lower relative humidity leads to higher early age strength but eventually lower later age strength compared to specimens cured in water. The effect of elevated temperature and lower relative humidity condition is found to be more significant in slag-replaced mortar.

Conroy-Jones and Barr (2004) measured the relative effect of curing practices on the tensile strength of medium and high strength concrete. Five concrete grades with 28 days compressive strength ranging from 40 MPa to 110 MPa were cured in two environments: air curing and water curing. Tensile strength was measured by surface failure tests (i.e. flexural strength test and torsional strength test) and spilt cylinder tests. It was found that in split cylinder test, the tensile strength of air cured specimens was lower than the corresponding water cured results, indicating that the negative effects of reduced hydration and differential shrinkage dominate over any pre-stressing effect. However, the surface failure tests exhibit long term air cured strengths that approach, and in some cases surpass, their water-cured counterparts. This unexpected large strength of air-cured specimens cannot be attributed to increased hydration. It was thought that in surface failure tests, the positive pre-stressing effects caused by differential shrinkage, overweight any strength loses from shrinkage cracks in the case of air curing.

2.7.5. Relationship between Compressive Strength and Tensile Strength

Generally concrete is specified through its compressive strength and it is customary to relate tensile strength of concrete to the compressive strength *(Oluokun et al 1991; Choi and Yuan 2005).* According to Neville, the two strengths are closely related but there is no direct proportionality *(Neville 2004 a).* When the compressive strength of concrete gets higher, some of its characteristics and engineering properties become different from normal strength concrete. The available relations in the major building codes are based on the tests conducted on normal strength concrete. Linear extrapolation of the available design equations to cover the higher range of concrete strengths may lead either to unsafe and therefore potentially dangerous results, or too over conservative and hence unduly restricted design *(Rashid et al 2002).* Therefore the relationship between compressive strength and tensile strength must be critically analyzed for wide range of compressive strengths. Along with this, the relation between tensile strength and compressive strength depends on many parameters which include age and strength of concrete, type of curing, aggregate type, amount of air entrainment, degree of compaction, specimen size etc. *(Zain et al 2002).*

Many researchers have suggested tensile strength relationship that involved the square root function, similar to that proposed by ACI. *Iravani (1996)* carried out a test program to develop information about mechanical properties of high performance concrete. High performance concretes with 56 days compressive strength of 65 MPa to 120 MPa, made with or without silica fume were studied. Among other properties, compressive strength, split tensile strength and flexure strength were measured at the end of 56 days, after subjecting the specimens to two different curing regimes: (i) moist curing regime at 100% relative humidity and 23 ± 2°C temperature and (ii) air dried curing regime in a controlled environment room at 50 ± 3% relative humidity and 23 ± 2°C temperature. After obtaining the data, a possible relationship was developed between compressive strength and tensile strength. The equation of the fit line for the results in this study were:

$$f_{st} = 0.57\sqrt{f_c^{'}} \qquad 50MPa < f_c^{'} < 100\,MPa \qquad \ldots(2.1)$$

$$f_r = 0.97\sqrt{f_c^{'}} \qquad 50MPa < f_c^{'} < 100\,MPa \qquad \ldots(2.2)$$

Based on these results, it was concluded that the square root law of ACI for the tensile strength of normal strength concrete that is moist cured can be extended to apply to high performance concrete with or without supplementary cementitious materials with compressive strength up to 120 MPa.

Zheng et al (2001) analyzed the relationship between compressive strength and split tensile strength for compressive strength ranging from 10MPa to 70 MPa. Correlation of split tensile strength to the corresponding cube compressive strength indicated that split tensile strength increased more or less as a square root function of compressive strength. The actual best fit obtained for their test data was

$$f_{sp} = 0.32(f_{cu})^{0.56} \qquad \ldots(2.3)$$

They observed that the power value for their data was close to half, so the best fit that was got for the square root function was

$$f_{sp} = 0.41(f_{cu})^{0.5} \qquad \ldots(2.4)$$

The correlation coefficient for equation 2.4 was 0.878 while for equation 2.3 was 0.883, which are close to each other, indicating that that the square function can be taken as possible relation between compressive strength and split tensile strength. This 0.5 power law model was even used to determine the relationship between split tensile strength and compressive strength of fiber reinforced concrete *(Choi and Yuan 2005).* The similar relationship was observed by *Khatri et al (1995).*

However some researchers carry different view regarding the relationship between tensile strength and compressive strength. *Oluokun et al (1991)* concluded that the split tensile strength of concrete is not proportional to the 0.5 power of the compressive strength. They were investigating the relationship between the concrete compressive strength and its split tensile strength especially at early ages. Instead of 0.5 power relationship, 0.79 power was found to be a much more realistic representation. They further proposed that 0.79 power equation is applicable to concrete at early ages, as well as to high strength concrete.

Bhanja and Sengupta (2005) developed the relationship between 28 days flexural strength and split tensile strength with the compressive strength of silica fume concrete. The following equations were developed for split tensile strength and flexure strength respectively.

$$f_{st} = 0.248 f_c^{\,0.717} \qquad \ldots(2.5)$$

$$f_{fl} = 0.275 f_c^{0.81} \qquad \ldots(2.6)$$

The value of correlation coefficients was 0.94 and 0.93 respectively indicating a good accuracy of the equation for the data obtained.

Gardner (1990) carried out large-scale experimental investigations to determine the relationships between mechanical properties for concretes when cured in water at different temperatures. Regarding the relationship between split tensile strength and compressive strength, it was concluded that the ACI relationship should be reviewed to cover a wide range of compressive strength levels. The relationship proposed was:

$$f_{st} = 0.33 f_c^{2/3} \qquad \ldots(2.7)$$

This relationship was found to be valid over the whole range of temperatures considered. *Oluokun (1991)* investigated the validity and accuracy of various available relations by taking several sets of data from the literature. It was found that the split tensile strength is not proportional to the 0.5 power of compressive strength. Out of all the available relations, 0.69 power relation was found to be most accurate power relation.

Arioglu et al (2006) carried a regression analysis by using experimental data generated by various sources with compressive strength ranging 4 MPa to 120 MPa. It was concluded that the 0.5 power relationship between split tensile strength and cylinder compressive strength is not realistic for high strength concrete. Further a simple power function is proposed to evaluate the ratio of the split tensile strength to compressive strength as a function of the cylinder compressive strength. This relation was found to be applicable to concrete with compressive strength ranging from 4 MPa to 120 MPa regardless of mixture proportions, the nature of cementitious materials, curing time and curing temperature.

Not only the relationship between compressive strength and tensile strength varies with the compressive strength level, it also depends on many parameters which include age and strength of concrete, type of curing, aggregate type, amount of air entrainment, degree of compaction, specimen size etc. *(Gardner 1990; Zain et al 2002).* Among the various factors, water-binder ratio is considered to be the most important factor because it affects both the compressive strength and tensile strength of concrete and hence can affect the relationship between the two. Concrete age also plays a significant role in concrete strength development. Beyond about one month, the tensile strength is found to increase less rapidly than compressive strength *(Neville 2004 a).* According to *Komlos (1970),* the ratio of split tensile strength and compressive strength depends on age of concrete: the ratio being 0.092, 0.067 and 0.06 for the specimen tested at 7, 180 and 360 days respectively. The tensile strength is also reported to be more sensitive to inadequate curing than compressive strength. *Zain et al (2002)* tried to correlate split tensile strength as a function of water-to-binder ratio and concrete age along with compressive strength. The following relations were developed.

$$f_{st} = 0.54\sqrt{f_c}\,(W/B)^{-0.07} \qquad \ldots(2.8)$$

$$f_{st} = 0.59\sqrt{f_c}\left(\frac{t}{t_{28}}\right)^{0.04} \qquad \ldots(2.9)$$

The average value of the experimental / predicted ratio for these equations was found to be close to unity, indicating good accuracy of the equations. On comparing the equations among each other, the Equation 2.9, containing age of concrete as a variable was considered to be more advantageous as it can be used for concrete of every age.

Dinakar et al (2007) studied the effect of the type of cement on the relationship between split tensile strength and compressive strength and found that the relationship does not change irrespective of the type of cement. *Rashid et al (2002)* collected a large volume of experimental data from the literature and then analyzed the adequacy of the existing relationships for predicting the tensile strength of concrete for a wide range of compressive strengths (20 MPa to 120 MPa). They found that the size of cylinder for split tensile strength or those of prisms for flexural strength have no recognizable effect on the respective tensile strengths. It was observed that the ACI 318 specified relation highly under estimates the flexural strength and this under estimation was found to be higher for higher strength concrete. However, the ACI 318 specified relation for split tensile strength was found to give a reasonable prediction for normal strength concrete as well as high strength concrete. They suggested inverse S curve relationship for both flexural strength and split tensile strength that gave a good correlation coefficient for the whole strength range.

2.7.6. Relationships Between Various Tensile Strengths

As per ACI, the ratio of flexural strength and split tensile strength should range between 1.4 to 1.6. *Zhou et al (1995)* carried out the studies on high strength concrete with compressive strength ranging from 80 MPa to 115 MPa. Silica fume content was varying from 10% to 15% as cement replacement. The ratio between flexural strength and split tensile strength was found to be approximately 1.5 for high strength concrete. Theoretical relationship was also established between flexural strength and split tensile strength based on fictitious crack model, which was in good agreement with the experimental data.

Zheng et al (2001), while referring works of previous researchers, have reported that flexure tensile strength is generally 35% higher than split tensile strength. *Bhanja and Sengupta (2005)* found that the average ratio between the flexural strength and split tensile strength of silica fume concrete is 1.65.

2.7.7. Research Significance

The validity of the existing relationships between compressive strength and tensile strength must be checked for mineral admixture concrete and for a wide range of compressive strengths. The present investigation has been aimed to develop a mathematical model for the combined relation between tensile strength, compressive strength, water-to-binder ratio, concrete age and the initial water curing conditions for concrete containing mineral admixtures. Tensile strength is measured by split tensile strength test and flexure strength test in order to look at the applicability of the model to the testing procedure adopted for measuring tensile strength.

2.8 PERMEABILITY OF CONCRETE

2.8.1. General

The primary requirements of durability of concrete are strength, workability and permeability. Apart from the mechanical damage to concrete, the adverse influence on concrete involves the transportation of fluids through the concrete. The ease with which the fluids can enter into, and move through the concrete is commonly referred to as permeability of concrete. Attempts to correlate permeability with strength for different concrete types have indicated the difficulty of obtaining a unique relationship *(Abbas et al 2000).* Consequently it has been suggested that to ensure long-term durability performance of concrete structures, transport properties of concrete must be considered in addition to compressive strength. Like compressive strength, permeability is also influenced by various parameters which include presence of mineral admixtures, water-to-binder ratio of the mix, curing conditions etc. All these parameters are discussed schematically in the following sections.

2.8.2. Effect of Mineral Admixtures on Permeability

Pozzolanic materials such as silica fume, fly ash, granulated blast furnace slag etc. are increasingly being used to produce dense and impermeable cement concrete. It was reported that the addition of silica fume may have substantial effect on the permeability of concrete. By adding 20% of silica fume to 100kg/m^3 of cement, the same permeability as that of 250kg/m^3 cement can be obtained *(Shah and Ahmed 1994).*

Kim et al (2007) conducted rapid chloride permeability test for mixes containing silica fume and metakaolin as replacement of cement. Concrete mixes containing 0% to 20% of either silica fume or metakaolin as cement replacement, were cast. It was observed that all the mixes with metakaolin and silica fume has very low level of permeability. The increase in resistance to chloride permeability was attributed to the continued hydration and pozzolanic reaction, accompanied by a decrease in porosity and pore sizes. *Mehta and Gjorve (1982)* have shown that mortar and concrete incorporating silica fume are less permeable. It was attributed to a decrease in the numbers of coarse pores of the cement-silica fume paste system, although the total porosity remains nearly same as that of paste with ordinary Portland cement. Improvement in other mechanical properties of silica fume concrete has also been attributed to this change in the nature of porosity and microstructure of the hardened paste.

Memon et al (2002) investigated the effect of mineral admixtures and chemical admixture namely fly ash, granulated blast furnace slag, silica fume and super plasticizers on the porosity, pore size distribution and compressive strength development of high strength concrete in sea water curing condition exposed to tidal zone. A water-to-binder ratio of 0.4 was used to produce a concrete having compressive strength between 54 MPa and 63 MPa at the age of 28 days. The pore size distribution of mineral admixture concrete was found to be significantly finer and mean volume pore radii at the age of 6 months were reduced to three times as compared to the control concrete without mineral admixtures. Results indicated that the mineral admixture mixes exhibit better performance than the control concrete in sea water exposed to tidal-zone**.**

Hassan et al (2000) conducted a laboratory study on the influence of silica fume and fly ash on the long term and short-term properties of high performance concrete. The mixes were air cured at 20°C and 65% relative humidity. The permeability of the concrete was assessed by porosity and oxygen permeability. It was found that silica fume concrete has lower porosity (as low as 25%) as compared to ordinary Portland cement concrete. It was attributed to the combined effect of extremely fine silica fume particles that improve the packing of the mortar matrix and early pozzolanic reaction. Silica fume was found to contribute more to the improvement of porosity that compressive strength. On the other hand, fly ash concrete gave the highest porosity value at early ages. However, the porosity decreased with age and ultimately the porosity became lower than ordinary Portland cement concrete. In terms of oxygen permeability, ordinary Portland cement concrete exhibited the highest permeability value with only a slight reduction with age. Both silica fume and fly ash concrete mixes showed lower permeability at early ages. After 28 days, the fly ash concrete was the only mix to show a considerable reduction of permeability with time to reach a permeability value almost similar to that of the silica fume concrete at 365 days. The ultimate reduction in permeability was 87% and 84% respectively for silica fume and fly ash concrete as compared to OPC concrete.

Baronio et al (1990) conducted impermeability test as per DIN 1048 to find the depth of water penetration for checking permeability of silica fume mortar and found that with the increase in silica fume content, impermeability of the mortar increases due to physical and chemical effect of silica fume.

Huseyin et al (1995) conducted experiments to determine water permeability of concrete made by replacing 20% of cement by Class F fly ash. They found that the volume of permeable voids in plain concrete was 1.4 to 1.22 times higher than the voids in fly ash concrete. The reason for lower permeability of fly ash concrete was attributed to its increased denseness due to addition of fly ash. This resulted in the transformation of larger pores into smaller pores, thus causing pore-refinement. Further fly ash decreased the thickness of transition zone between the aggregate and cement paste that has micro cracks.

Vaish and Nautiyal (1995) carried out tests on plain concrete and concrete containing various proportions of silica fume and fly ash. Replacement of cement by 5% to 15% of silica fume was observed to show a significant reduction in permeability. They found that replacing 5% cement by silica fume reduces the permeability of concrete by 20% to that of plain cement concrete at the same curing age condition. However, addition of 30% to 50% fly ash to concrete made the concrete more permeable than the corresponding plain concrete at 28 days curing. They attributed this effect to the little pozzolanic action that would have occurred till 28 days in the case of fly ash concrete. However after 6 months, considerable water tightness was observed even in fly ash concrete. *Bamfort (1987)* also reported similar findings that the use of fly ash and slag has no significant effect on permeability at 28 days when compared to ordinary Portland cement concrete of equal strength.

2.8.3. Effect of Water-to-Binder Ratio on Permeability

Watson and Oyeka (1981) studied the permeability of both cement paste and concrete using oil as the medium. The size of the specimens was 150 mm diameter and 50 mm thickness with water-cement ratio varying from 0.4 to 0.8. The oil pressure was maintained at 10 kg/cm^2. It was found that the coefficient of permeability decreased with an increase in cement content. But permeability increased linearly with increase in applied pressure and increase in water-cement ratio. According to *Mehta (1985 a),* water-cement ratio determines the size, volume and continuity of capillary voids, which ultimately influences the permeability of concrete. The permeability of concrete was found to be more than the cement paste because the transition zone between the aggregates and the cement paste in concrete contains micro-cracks which are wider than capillary cavities present in cement mortar paste. These cracks allow inter-connectivity of pores, which increases the permeability of cement concrete as compared to cement mortar paste.

Guneyisi et al (2005) conducted experiments on plain and blended concrete at water-binder ratios of 0.65 and 0.45 after subjecting them to wet curing, air curing, and controlled curing regimes. It was found that for a given curing conditions, lowering water-to-binder ratio of the mixes increases the concrete resistivity and for a given water-cement ratio, better curing procedure yields higher electrical resistivity for all concretes. Further, blended cement concrete was found to have greater resistivity than the plain Portland cement concrete for all water-cement ratios and at all ages.

2.8.4. Effect of Curing on Permeability

Poon et al (1997) studied that the influence of water curing at 27°C and air curing at 15°C and 60% relative humidity on the properties of fly ash concrete. It was found that the addition of fly ash substantially reduces the water permeability of water cured concrete specimen. It was also noticed that the effect of fly ash is more when there is extra addition of fly ash, rather than only direct replacement of cement. Subjecting the fly ash concrete to inadequate curing, the water permeability of concrete specimens was found to be two orders of magnitude higher than that of concrete with water curing.

Aldea et al (2000) studied the effect of curing conditions of properties of concrete containing slag as admixture. It was found that the addition of slag as replacement of cement has beneficial effect, as it reduces the chloride penetrability drastically for all curing regimes. Out of three adopted curing regimes; viz. autoclaving, steam curing and normal curing; autoclaved concrete was found to have higher chloride penetrability values regardless of the level of slag replacement. This behavior was attributed to the increased micro-porosity of the material due to autoclaving.

Toutanji and Bayasi (1999) studied the effect of curing procedure for silica fume concrete. Three different curing methods were employed: steam curing, moist curing and air curing. As compared to moist curing, steam curing decreased permeability of silica fume concrete, whereas air curing increased the permeability. The effect of steam curing became even more significant as silica fume content increases. However, concrete with

30% silica fume content exposed to air curing experienced a significant increase in permeability. This is attributed to the extensive shrinkage cracking which develops due to air curing.

Cakir and Akoz (2008) studied the effect of curing at elevated temperature (40°C) on the permeability of mortars with or without slag. It was found that in general, the porosity of slag-replaced mortar is lower than control mortar. However, the decrease in porosity of slag replaced mortars cured in water is higher than slag replaced mortars cured in humidity chamber at 40°C and 100% relative humidity. They reported that higher degree of hydration due to increased temperature is not continual and the hydration products that are formed at elevated temperature are more porous than the products formed in moist curing, that lead to higher porosity of mortars cured at elevated temperatures.

2.8.5. Effect of Other Factors on Permeability

Chan and Wu (2000) conducted durability studies of concrete made from non-reactive waste materials. Water permeability and sorptivity were studied to access durability of concrete. It was found that sorptivity of a given concrete mix is independent of the cement content to provide nearly the same compressive strength. However, the values decreased with increase in compressive strength. They concluded that water content and densification of the mix proportions are the governing factors that control permeability.

Soong-swang et al (1991) carried out experiments to check the effect of aggregate size and type on the permeability of concrete. Cylinders of 100mm diameter and 50mm thickness were used to check water permeability of concrete under a pressure of 7kg/cm^2. It was concluded that maximum size of aggregates has no significant effect on the permeability. However, the porosity of aggregate significantly increases the permeability of concrete.

2.9. NON-DESTRUCTIVE TESTS

2.9.1. General

To keep a high level of structural safety, durability and performance of the infrastructure, the quality assurance during and after the construction of structure is becoming a serious concern. Non-destructive testing methods have a large potential to be a part of such a system *(Maierhofer 2006).* The term non-destructive is given to any test that does not damage or affect the structural behaviors of the elements and also leaves the structure in an acceptable condition for the client *(Qasrawi 2000). Malhotra (1976)* presented a comprehensive literature survey for the non-destructive methods normally used for concrete testing and evaluation. The available non-destructive testing methods for concrete structures are rebound number, pulse velocity, pull out, probe penetration, small diameter cores and combined methods. Out of these tests, core test and pull out tests are partially destructive in nature. *Leshchinsky (1991)* summarized the following advantages of non-destructive tests, as compared to core testing.

(i) A reduction in the labour consumption for testing.

(ii) A smaller amount of structure damage in testing.

(iii) A lower probability of such structural damage which may cause the need for reinforcement.

(iv) A possibility of testing concrete strength in structures where cores cannot be drilled.

(v) An application of less expensive testing equipment.

These advantages are however of no value if the results are not reliable, representative and as close as possible to the actual strength of the tested part of the structure. Among the available non-destructive methods, rebound hammer and ultrasonic pulse velocity tests are the most commonly used ones in practice. The available literature discussions on these two tests are presented here under**.**

2.9.2. Ultrasonic Pulse Velocity Test

This test is described in ASTM C597, BS-1881: Part 203 and IS 13311 (Part 1):1992. The principle of the test is that the velocity of sound in a solid material ‘V’ is the function of the square root of the ratio of its modulus of elasticity, E to its density d, i.e.

$$V = f\left(\frac{gE}{d}\right)^{1/2} \qquad \ldots(2.10)$$

where g is the gravity acceleration *(Qasrawi 2000).*

This method start with the determination of the time required for a pulse vibrating at an ultrasonic frequency to travel through concrete. Once the time is recorded, the velocity is calculated as

$$V = \frac{L}{T} \qquad \ldots\ (2.11)$$

where V = pulse velocity (m/s), L= length (m) and T = effective time (s), which is the measured time minus the zero time correction. Ultra sonic pulse velocity measurements are typically performed using a pair of transducers in contact with the specimen through a coupling medium. Piezoelectric transducers are the most common type used for generating the ultrasonic pulse waves *(Yaman et al 2001).* Ultrasonic waves are generated by exciting the piezoelectric element in one transducer by an electric voltage signal in the shape of a spike, which causes it to vibrate at its resonant frequency. These vibrations excite the material with a wide range of ultrasonic frequency through contact and generate stress waves that are transmitted through the material to the receiving transducers. The time it takes for the ultrasonic wave to propagate to the receiving transducer is measured and defined as the time of flight. This time of flight is further used in expression given in Equation 2.11 to obtain velocity of the ultrasonic wave.

The velocity of the wave gives an idea about quality, uniformity, condition and strength of the tested concrete. This test is fast and easy to perform, thus, it is considered as a successful site test for quick comparative study.

The ultrasonic wave is conducted by various ways of transmission: direct transmission, indirect transmission and semi-direct transmission. Direct transmission is defined as the propagation of ultrasonic stress waves along the straight-line path between the opposite surfaces of a specimen. Indirect or surface transmission is defined as the propagation of ultrasonic stress waves between points that are located on the same surface of the material. The indirect transmission is carried out when, in the field, access to opposite surfaces of the component is not available, for example, concrete pavement and bridge decks. Semi-direct transmission is the one where propagation of ultrasonic stress waves is carried out through adjacent faces of the material. It is not generally recommended.

It is often stated that indirect measurement is not reliable. It is also described as less sensitive testing arrangement. British standards (BS1881) state that the indirect velocity is 5% to 20% lower than direct velocity, depending mostly on the concrete quality. ASTM C 597 does not recommend indirect transmission except when only one surface of the material is accessible. Furthermore, it is stated that measurements on the surface are indicative of properties only of the layers that are close to the surface. However, *Sansolone et al (1997)* presented an application of indirect transmission of concrete. A P-wave velocity measurements technique was developed for impact echo testing. The technique was proposed for detecting the thickness of concrete element and to locate defects in concrete. *Popovics et al (1998)* compared the indirect ultrasonic pulse velocity measurements with direct measurements by using the technique developed by the *Sansolone et al (1997).* In addition, *Benedetti (1998)* made recommendation for optimum transmitting and receiving transducer spacing for achieving measurement resolution. *Yaman et al (2001)* investigated the relationship between velocity of ultrasonic stress waves transmitted along direct and indirect paths. It was concluded that the indirect ultrasonic pulse velocity is statistically similar to direct ultrasonic pulse velocity provided that there are uniform properties, including moisture gradient along the surface and along the depth.

In the nutshell, it can be said that although several studies are available in literature on indirect ultrasonic pulse velocity measurement on concrete, no agreement has been reached on the relation between direct and indirect ultrasonic pulse velocity and on the methods of indirect ultrasonic pulse velocity measurements.

2.9.3. Relationship between Compressive Strength and Ultrasonic Pulse Velocity Test

The possibility of correlating the pulse velocity to the compressive strength is a consequence of the physical relation between velocity and modulus of elasticity, in conjunction with the empirical relation between the modulus of elasticity and compressive strength of concrete *(Sharma and Gupta 1996; Pascale and Leo 1984).* However, the relationship between the compressive strength of concrete and the ultrasonic pulse velocity is not simple. Over the years, considerable research has been undertaken to study this relationship. *Sturrup et al (1984)* proposed a relationship between ultrasonic pulse velocity and the logarithm of the compressive strength. *Ben-Zatun (1986) and Price and Hynes (1996),* on the other hand, proposed a linear relationship between ultrasonic pulse velocity and compressive strength. *Tharmaratnam and Tan (1990)* gave the exponential relationship between ultrasonic pulse velocity and compressive strength of the form $f_c^{'} = ae^{bV_c}$, where V_c is the ultrasonic pulse velocity in concrete and a and b are constants. *Liang and Wu (2002)* have further presented theoretical justification for the exponential dependence of strength on velocity. *Phoon et al (1999)* developed a probabilistic framework to incorporate some of the fluid uncertainties while calculating compressive strength from ultrasonic pulse velocity measurements.

Regardless of the functional form, it is widely recognized that the relationship is not unique. According to *Sturrup et al (1984),* factors other than concrete strength can affect pulse velocity and changes in pulse velocity may overshadow changes due to strength. *Yun et al (1988)* showed that the pulse velocity test results have little degree of correlation with five different tests used to estimate strength of concrete. *Kheder (1998) and El-Shikh (1998)* found little correlation between ultrasonic pulse velocity and strength under general conditions. Infact, the relationship was observed to be affected by numerous factors such as the properties and proportions of the constituent materials, age of concrete, presence of micro-cracks, moisture content and stresses in the concrete specimens. Apart from this, the validity of the existing relations is directed to normal strength concrete, up to 50 MPa due to the absence of tests on high strength concrete. The relationship currently used to evaluate compressive strength of normal strength concrete by non-destructive tests may not be valid for high strength concrete. The bond at the matrix-aggregate interface is very important in high strength concrete and this could modify the response of non-destructive parameters to strength variations *(Pascale et al 2000). Pascale et al (2003)* carried out the study on non-destructive assessment of actual compressive strength of high strength concrete with strength ranging from 30 MPa to 150 MPa. The concrete mixes were prepared with 5 different water-to-binder ratios and subjected to the curing regime of 21 ± 2°C and 72 ± 5% relative humidity. The non-destructive tests and compressive strength studies were conducted at the end of 28 days. It was found that the relationship of the form C.S = α (Non-destructive parameter)$^{\beta}$ (which is similar to the one employed for normal strength concrete also) is applicable to high strength concrete also for some non-destructive tests like pulse velocity, rebound hammer and combined SonReb method.

Demirboga et al (2004) used ultrasonic pulse velocity to evaluate compressive strength of concrete with mineral admixtures. The mineral admixtures used were fly ash and granulated blast furnace slag, either alone or in combination. The compressive strength and the corresponding ultrasonic pulse velocities were determined at the end of 3, 7, 28 and 120 days. It was found that the relationship between ultrasonic pulse velocity and compressive strength is exponential for mineral admixture concrete; however, the constants were different for each mineral admixture and at each replacement level.

Popovics et al (1990) concluded that the composition, especially the aggregate content of the tested specimen has a major influence on the strength verses pulse velocity relationship. It was stated that the bottom portion of the concrete element usually contains more coarse aggregate that its top and this has a major effect on pulse velocity, although not necessarily on concrete strength.

On the other hand, *Yaman et al (2001)* while carrying out the literature review stated that Udegbunan et al (1999) measured ultrasonic pulse velocity of concrete at water-to-binder ratio between 0.35 and 0.55 and established that ultrasonic pulse velocity measurements are better correlated to rapid chloride permeability test data. The correlation showed that an increase of 1000 coulombs measured by rapid chloride permeability test correspond to a decrease of ultrasonic pulse velocity of 65m/sec.

2.9.4. Rebound Hammer Test

The rebound hammer test is described in ASTM C 805, BS 1881-Part 202 and IS 13311 (Part 2): 1992. The test is classified as a hardness test and is based on the principle that the rebound of an elastic mass depends on the hardness of the surface against which the mass impinges. The energy absorbed by the concrete is related to its strength. The test method starts by the careful selection and preparation of the concrete surface to be tested. Once the surface is chosen it should be prepared by an abrasive stone so that the test surface is ground smooth. Then a fixed amount of energy is applied by pushing the hammer against the test surface. The plunger must be allowed to strike perpendicular to the surface. The angle of inclination affects the results. After impact the rebound number is recorded. At least ten readings must be taken from each tested area. Rebound number reflects only the surface of concrete. BS 1881-Part 202 suggests that the measured number is an indication of about first 30 mm depth of concrete. According to *Teodoru (1988)* the results obtained are only representative of the outer concrete layer with a thickness of 30mm to 50mm.

The use of rebound hammer is not suitable to estimate and predict concrete strength. *Neville (2004 a)* presented that this test all alone is not a strength test. He stated that the changes affecting only the surface of concrete such as degree of hydration at the surface, carbonation, temperature, surface preparation, location and type of surface finish have little influence on the properties of the concrete at depth and hence compressive strength of resultant concrete, although, these variations affect rebound number significantly. The result is also affected by the type of aggregate, mix proportion, hammer type and hammer inclination. However, *Kheder (1998)* compared both rebound hammer test and ultrasonic pulse velocity test to predict compressive strength of concrete under general conditions and showed that ultrasonic pulse velocity test was less reliable in predicting concrete strength if the concrete constituents are not known .

2.9.5 Combined Methods

When variation in properties of concrete affect the test results; especially in opposite directions, the use of one method alone would not be sufficient to study and to evaluate the required property. Therefore, use of more than one method yields more reliable results. For example, the increase in moisture content of concrete increases the ultrasonic pulse velocity but decreases the rebound number *(Neville 2004 a).* Hence using both methods together will reduce the error produced by using one method alone to evaluate concrete strength. *Qasrawi (2000)* combined rebound hammer and ultrasonic pulse velocity test to estimate the concrete strength. The use of combined method was found to yield more reliable and closer results to the actual strength. *Liang and Wu (2002)* developed the combined method that includes both measured ultrasonic pulse velocity and amplitude in predicting the compressive strength of concrete. *Matusinovic et al (2004)* established a linear relationship between compressive strength and the product of the amplitude and angular frequency of the signal.

2.9.6. Research Significance

Non-destructive methods of investigation such as ultrasonic measurements are often proposed for evaluating the state of concrete structures already in use. However, the conclusions that evolved over years about correlation between velocity of ultrasonic waves and compressive strength of cement materials is that some additional properties have to be measured, for example, hammer rebound index, hardness etc. *(Neville 2004 a)*. Most of the studies on the use of combined methods to predict compressive strength of concrete are conducted mainly for normal strength concrete and the applicability of the combined methods is required to be checked for high strength concrete also.

2.10. CHEMICAL RESISTANCE OF CONCRETE

A significant engineering property of cement-based materials is their chemical resistance. The study of chemical resistance of concrete is not only an interesting and useful scientific property but also an economical one due to possible enormous damages it confers on concrete structures. It determines the service life of concrete structures very significantly. Due to interaction of concrete with external influences, the durability of concrete may be threatened and lost. Some of the threatening factors that may deteriorate the concrete structures are freezing and thawing, abrasion, corrosion of steel, chemical attack etc.

ACI committee 201 (1982) classified chemical attacks into six categories, which include (1) acidic attack, (2) alkali attack, (3) carbonation, (4) chloride attack, (5) leaching and (6) sulfate attack.

Biczok (1972) classified the chemical attack into three types depending upon the predominant chemical reaction-taking place. Leaching corrosion of concrete is the process where part or all of the hardened cement paste is removed from the concrete. This is caused by the action of water of low carbonate hardness or carbonic acid content. The next process is corrosion by exchange reactions and by removal of readily soluble compounds of hardened cement paste. This process occurs as a result of a Base Exchange reaction between the readily soluble compounds of hardened cement paste and aggressive solution. The third process is the swelling corrosion, largely due to formation of new and stable compounds in hardened cement paste. This process is primarily the result of attack by certain salts.

Chemical attack on concrete occurs due to its exposure to harmful chemicals that may be found in nature, such as in some ground water, industrial effluents, acid rain, acid mist and seawater *(Shannang and Shaia, 2003).* The chlorides, sulfates and acids belong to the aggressive chemicals that affect the long-term durability of concrete structures.

Mineral Acids such as hydrochloric acid, nitric acid and sulfuric acid are highly corrosive to concrete because they form soluble calcium salts that are easily leached away. This increases the porosity and lowers the strength of material. High molecular weight organic acids are not as corrosive as mineral acids but acetic and lactic acids, which are found in many food products, are very corrosive to concrete *(Mehta 1985 b).*

Concentrated solutions of sodium, potassium or magnesium sulfates, when comes in contact with permeable concretes made with cement having high C_3A content (>5%), cause expansion and cracking of the concrete. Among the sulfates, ammonium sulfate solution is believed to be most aggressive because it not only reacts with Portland cement hydration products to form gypsum but also can dissolve the gypsum coating.

Chlorides and deicer chemicals are usually not harmful to plain concrete but can be instrumental in expansion and cracking of concrete containing embedded steel because of the reaction between chlorides and the steel reinforcement. Some of the aggressive chloride salts are calcium chloride and sodium chloride.

The degradation rate of the concrete exposed to harmful chemicals depends mainly on the fraction of the chemicals in water, the exposure time and the chemical resistance of concrete *(Huang et al 2005).* The resistance of concrete to chemical attack further depends on the pore structure characteristics of concrete, the ability to neutralize the chemical solution and the passivation caused by the deposition of the reacted products *(Shi and Stegemann 2000).*

2.11. ACIDIC ATTACK ON CONCRETE

2.11.1. General

Acidic attack represents a worrying topic of increasing significance, owing to the spread of damage of concrete structures all over the world due to acids. This unfavorable situation is a consequence of two factors:

(i) The spreading of sources of acidic media coming into contact with concrete structures due to growing activities in both urban and industrial areas over the past 20-30 years.

(ii) The universal alkalinity of cement based materials (mortars, concretes etc.), making them highly sensitive and vulnerable in acidic environment.

The acidic corrosion of hardened cementing materials has drawn more and more attention recently due to the corrosion of concrete sewer pipes and concrete structures at municipal wastewater treatment plants, the impact of aggressive substances from animal feed, manure and concerns regarding the acid corrosion resistance of cement solidified wastes *(Shi and Stegemann, 2000).* Resistance of cement matrix to acid corrosion depends on (1) Pore structure characteristics, (2) the ability of the matrix components to neutralize acid and (3) the products of acid corrosion *(Shi and Stegemann, 2000).*

2.11.2. Sources of Acidic Environment

The sources of acidic attack represent natural acidic waters, acidic wastewaters, acidic rains and silage effluent *(Di Belie et al 1997).* Among the highly aggressive media are the solutions of various mineral acids like sulfuric acid, hydrochloric acid, nitric acid etc. In natural groundwater, only sulfuric acid is likely to be found as a result of the oxidation of sulfide mineral such as pyrites and marcasite, a process that is catalyzed by the presence of the aerobic bacterium, thiobacillus ferrooxidante *(Fattuhi and Hughes 1988 a).* Sulfuric acid is also one of the main acidifying agents of acid environment. Leakage and random spillage of sulfuric acid can also occur in industrial environment resulting in localized deterioration of concrete. Another form of sulfuric acid attack on concrete, which is especially severe in hot climates, occurs in sewage systems. The domestic sewage is alkaline in nature. However when the anaerobic bacteria attack sulfur compounds, hydrogen sulfide gas (H_2S) is generated, which can dissolve in water condensed on the walls of the concrete sewer pipes and undergoes oxidation by aerobic bacteria, finally producing sulfuric acid. Along with sulfuric acid, nitric acid is the second main agent of acid precipitation, both being occurring in the molar ratio of 2:1 in acid rain. Similarly, hydrochloric acid is one of the major constituents of industrial effluent.

Most acids attack concrete by a process of dissolution and leaching. During acid attack, the hydrogen ions in acid molecules are predominantly transported by diffusion across a porous barrier to a relatively thin reaction zone inside the specimen. Here, the chemical reaction takes place between the constituents of the cement matrix and the acid which results in the formation of calcium salts, which, when are soluble, may be leached away by the aqueous solution. Due to the action of acidic solutions, pH of the pore solution in concrete is decreased contributing to instability of the hydration products in the cement matrix. The principal chemical factors that determine the rate of corrosive attack are the properties of the aggressive medium and the chemical composition of the cementitious binder. Both these factors are discussed in the following sections.

2.11.3. Aggressivity of the Acidic Medium

The degree of aggressivity of an acid depends on the kind of acid and its concentration.

2.11.3.1. Kind of Acid

The ionic strength and the solubility of calcium salt formed in the process of acid attack depends on the kind of acid causing the attack. In the case of formation of highly soluble salts, the severity of the attack is higher. This is caused by dissolving and leaching of the formed salt from the material. On the other hand, if the calcium salt formed is insoluble, it forms a protective layer thus decreasing the extent of attack. For example, solutions of hydrochloric acid and nitric acid are highly aggressive because their calcium salts are highly soluble *(Zivica and Bajza 2002; Zivica and Bajza 2001).* However, calcium oxalate and calcium fluoride are insoluble calcium salts and are used in practice for protective purposes *(Zivica and Bajza 2001).*

Sulfuric acid is very corrosive due to the fact that the sulfate ions tend to initiate the sulfate attack in addition to the dissolution process caused by the hydrogen ions. The corrosion of concrete by sulfuric acid consists of two stages. In the first stage, sulfuric acid chemically reacts with hydration products such as calcium hydroxide (CH) and calcium silicate hydrate (C-S-H) to form gypsum. In the second stage, gypsum reacts with hydrated tri-calcium aluminates (C_3A) to form ettringite *(Monteny et al 2000).* Both Gypsum and ettringite are believed to cause expansion, which initiates cracks in the concrete.

2.11.3.2. Concentration of Acid

The aggressivity of acid solutions is judged either by the concentration of acid or by the pH value of the solution. *Revertag et al (1992)* suggested that the concentration of the aggressive species in the acting solution is a more reliable parameter than the pH value because the pH value is dependent on the dissolution degree of the acid. Therefore, a strong acid having a high dissolution degree (example HCl, HNO_3) may cause, in the small quantities in solution, significantly decreased pH values than a weak acid in multiple quantities in the solution, owing to its low dissociation degree.

Fattuhi and Hughes (1987) conducted experiments on specimens of cement pastes, mortar and concrete mixes when suspended in a channel containing 1% and 3% nominal solution of sulfuric acid. The loss of weight was monitored for 93 days. It was observed that the loss of weight increases with an increase in acid concentration. *Kong and Orbison (1986)* evaluated the response of Portland cement concrete cylinders to simulated acid precipitation solutions of varying pH levels and concluded that the loss of specimen surface material increased with increasing acidity of the simulated acid precipitation solution. *Hewayde et al (2007)* reported that the concentration of sulfuric acid play the most important role in defining the amount and rate of concrete degradation under sulfuric acid exposure. The mass loss of the specimens increased as the pH of the solution containing sulfuric acid decreased. The pH levels less than 1.5 were found to be extremely aggressive.

Huang et al (2005) studied the degradation of concrete in HCl solution of concentration ranging from 5% to 20% for 24 hours. It was noticed that the law of strength degradation depends on both the strength grades of the concrete and the HCl content of solution. The strength degradation was approximately described as an exponential function of HCl content. *Pavlik (1994)* described the depth of corrosion of cement paste in acetic acid and nitric acid solutions as a power function of the concentration of acid.

2.11.4 Effect of Chemical Composition of Cementitious Binders

The chemical composition of the binders is decided by a number of factors like cement content, water-to-binder ratio, cement type, presence of mineral admixtures, curing conditions etc. Some of the important factors are discussed here under.

2.11.4.1. Effect of Water-to-Binder Ratio

The mechanism of the entire deterioration phenomenon is permeability oriented and permeability of concrete is a direct function of water-binder ratio *(Zivica and Bajza 2002).* It is reported that the permeability is significantly reduced if the water-to-binder ratio is below 0.45. Keeping this in mind, the authors suggested that in order to ensure an acid resistance concrete, it is necessary to keep water-to-binder ratio less than 0.45. *Sersale et al (1998)* carried out an experimental research to study the influence of major factors on the deterioration of concrete under the action of acid precipitation. The cement content was kept at 300 kg/m^3 and the water-to-binder ratio was varied from 0.55 to 0.71 and 0.77. The cylindrical specimens were cast and moist cured for 14 days and then exposed to acid rain consisting of sulfuric acid and nitric acid in molar ratio of 2:1. It was observed that the weight loss and hence the attack increases with the increase in water-to-binder ratio, probably owing to its influence on porosity of concrete.

Other researchers have different views about the effect of water-to-binder ratio on the acid attack. *Fattuhi and Hughes (1988 b)* conducted experiments on cement pastes and concrete mixes prepared with ordinary Portland cement and subjected to sulfuric acid attack. For cement paste mixes, water-binder ratio ranged between 0.260 and 0.417 and for concrete mixes, the ratio ranged between 0.4 and 0.7. The change in weight with time was monitored for the period of 50 days. The results indicated that the weight loss was high for low water-to-binder ratio mixes. The main reason for this is considered to be the higher cement content of the mixes prepared at lower water-to-binder ratios, and hence higher CH content, which is readily attacked by the acid. The similar observations were made by them while studying the effect of various admixtures in concrete to sulfuric acid attack *(Fittuhi and Hughes 1987).*

Hewayde et al (2007) studied the effect of concrete mix design parameters including water-binder ratio on the resistance of concrete to sulfuric acid attack. The water-to-binder ratio of the mixes was varied from 0.25 to 0.5. They made the similar observation as made by earlier research regarding the mass loss of concrete specimens. They proposed that the mechanism of degradation under sulfuric acid exposure for concrete with higher water-to-binder ratio is different from that for concrete at low water-to-binder ratio. When a sulfuric acid solution attacks the concrete with low water-binder ratio, the dense structure prevents the absorption of acid by the concrete. Therefore the acid reacts with the cement paste at the concrete surface causing significant surface degradation. In the case of concrete with high water-binder ratio, due to its porous structure, the concrete absorbs the acid, which reacts with hydration products of the concrete to form a layer of gypsum that envelops the exposed surface of concrete and acts as a protective shell and decreases further chemical reaction between the acid and the unaffected hydration products.

Kong and Orbison (1986) also evaluated the response of concrete having design strength ranging from 20 MPa to 60 MPa when exposed to acid precipitation solution for three months. The response was evaluated through visual examination, weight change and compressive strength change. The results indicated that specimen deterioration, as evidenced by material loss and discoloration, increases with increase in design compressive strength. However, compressive strength tests conducted before and after the test period showed no significant strength increase or decrease during the three months. Longer test duration was recommended to have reliable compressive strength loss results.

Huang et al (2005) studied the influence of HCl corrosion on mass loss, dynamic modulus of elasticity, flexural strength and compressive strength loss for concretes with strength ranging from 25 MPa to 55 MPa. After HCl corrosion, the flexural strength loss of high strength concrete was found to be larger than that of normal strength concrete which indicates that the sensitivity to HCl corrosion increases with increasing strength grade of concrete.

2.11.4.2. Effect of Type of Cementitious Material

It is well known that no type of cement has a satisfactory and long-term acidic resistance. This unfavorable situation arises from the fact that cement based materials are of alkaline nature. Therefore, they are willing partner in the reaction with acidic species. The type of cement used still has an important bearing on the performance of concrete in an aggressive environment.

Kim et al (2007) carried out an experiment investigation in order to measure resistance of concrete made with silica fume and metakaolin to acid attack. Seven mix proportions of mortar were manufactured with metakaolin or silica fume mixed at 0%, 5% and 15% of the binder weight and with 0.5 water-to-binder ratio. The specimens were immersed in 2% sulfuric acid solution until 8 weeks after 28 days of water curing and the reduction in compressive strength was evaluated. Significant strength reduction was observed in all the specimens, with or without mineral admixtures. However, the specimens without silica fume or metakaolin showed the maximum strength reduction (about 70%), indicating the positive effect of silica fume and metakaolin on the resistance to sulfuric acid attack. *De Ceukelaire (1992)* studied the effect of hydrochloric acid attack on mortar prisms made from three different kinds of cements: Portland cement, Portland cement without C_3A and blast furnace cement. The specimens were initially moist cured for 28 days followed by total immersion in a solution of 1% hydrochloric acid during a period of two years. Blast furnace cement was found to be more resistant to acid attack.

Torii and Kawamura (1994) carried out a long-term study on resistance of mortar prepared with and without fly ash and silica fume, to sulfuric acid attack. Changes in physical and chemical properties in the mortar mixes prepared with different replacement levels of fly ash and silica fume, when immersed in 2% H_2SO_4 for three years, were investigated. The physical change was monitored by changes in length and weight of the specimens, while chemical changes were monitored by DSC-TG analysis, XRD analysis and measurements of pore size distribution by mercury intrusion porosimetry. It was observed that under a very low pH of 2% H_2SO_4 solution, the replacements of cement by fly ash and silica fume could not effectively prevent acid type deterioration involving scaling and softening of the mortar. Plain mixes showed the influence of the attack within one month of exposure, leading to complete decomposition at seven months. On the other hand, mixes with fly ash and silica fume maintained reasonably good external shape within one year of exposure, but it was impossible to effectively prevent the sulfuric acid attack during the long-term exposure.

Zivica (1999) established that chemically modified silica fume is a highly effective material in enhancing the engineering properties of concrete. Based on the observations of chemical composition, pore structure and mechanical properties of the test specimens, a high acidic resistance to 1% hydrochloric acid solution was found of the cement based materials when modified silica fume was used.

Sobolev and Yeginobali (2005) oriented their research to improve acid resistance of granulated blast furnace slag - Portland cement binder by using any other mineral admixture along with GGBS. For that, mortar specimens were prepared, cured in water for 28 days and then placed in 30% hydrochloric acid solution. Weight, length and shape investigations were performed till five weeks on till complete deterioration of the specimens occurred. It was found the silica fume-slag-cement mortars, modified with super-plasticizer, showed excellent resistance to acid attack. While the reference mortars (i.e. Portland cement-slag cement mortar) lost more than 5% weight after four weeks of exposure, Portland cement-slag-silica fume mortar lost only 0.6% of their weight. This fact led to the conclusion that the enhancement in the acid resistance property of slag-Portland cement binder can be achieved with the help of proper use of silica fume and super-plasticizer.

Chindaprasirt et al (2004) studied the influence of fly ash fineness on acid resistance of cement mortars. The fly ash replacement level of 40% by weight of the cementitious material was used for all the mortars mixes. The specimens were cured until the age of 28 days and then immersed in the 5% sulfuric acid solution. The weight loss of the specimens was monitored at 1, 3, 7, 28, 56 and 84 days after immersion. The results showed that the incorporation of fly ash significantly reduced the rate of early weight loss of the samples. Also, resistance to the acid attack increased with the use of coarser fly ash. It is thought that the coarser fly ash particles with rougher surface would have a better bond with the cement matrix as well as occupying a larger volume and hence reduced the volume of OPC and therefore resulted in a higher resistance of the mix to the sulfuric acid attack. *Roy et al (2001)* also found that the ordinary Portland cement mortar showed poor resistance to 5% sulfuric acid solution and the use of fly ash increased the resistance.

Pavlik and Uncik (1997) reported that silica fume or fly ash have little or no effect on the durability performance of concrete and cement mortars when they are under the attack of acid solution. *Pavlik (2000)* further monitored the rate of corrosion of cement pastes and mortars containing additional finely ground limestone, silica fume, travertine sand, quartz or glass balls in a solution of nitric acid. The corrosion process was monitored by visual inspection and by measuring the depth of corrosion, mass loss and shrinkage of the layers of corrosion products. It was found that adding finely ground limestone to cement pastes increased the rate of corrosion, while travertine sand decreased the corrosion rate. The addition of silica fume did not seem to have a significant effect on corrosion rate.

Kilinckale (1997) investigated the effect of adding pozzolans such as silica fume, rice husk ash, blast furnace slag, fly ash, trans, in 20% replacement for Portland cement, on strength and durability of mortars. The durability to hydrochloric acid solution (pH = 2) was checked by measuring strength and weight loss after immersion in the solution for 56 days. It was observed that silica fume mortars have highest loss of strength, followed by fly ash mortars and other pozzolanic mortar. *Sersale et al (1998)* studied the influence of cement type on the resistance to attack by simulated acid precipitation. Three types of cements were studied: Portland cement, Slag cement and Pozzolanic cement. It was observed that pozzolanic cement show a high degree of weight loss, followed by slag cement. The Portland cement was found to undergo the least amount of weight loss. They attributed the poor performance of Pozzolanic cement to the fact that calcium hydroxide is the compound that is readily attacked, and therefore, represents a bulwark against assault of the silicate framework. In the case of Portland cement concrete, lot of calcium hydroxide is present and therefore, the attacks start on calcium hydroxide, leaving the C-S-H gel safe. On the contrary, in the case of pozzolanic cement concrete, whole of calcium hydroxide gets converted into C-S-H gel due to secondary pozzolanic reaction, making the C-S-H gel vulnerable to acid attack.

Fattuhi and Hughes (1983) studied the use of different admixtures and coatings in order to improve the chemical resistance of concrete mixes. Cubes containing different admixtures or coatings were immersed in 1% solution of sulfuric acid and change in weight with time was monitored up to 172 days of exposure. It was observed that the cubes with admixtures started to lose weight almost immediately after immersion and severity of attack became more pronounced after 2-3 weeks. They concluded that, in general, coatings provide better protection to concrete than admixtures.

Chang et al (2005) investigated the effect of use of limestone aggregates and various mineral admixtures like granulated blast furnace slag in binary combinations with cement, ternary combinations of slag and silica fume or fly ash and silica fume. All the concretes were made at water-to-binder ratio of 0.4 and were water cured for 7 days and then immersed in 1% sulfuric acid solution. The specimens were periodically examined for appearance, mass change and tested in compression up to 168 days. The test results indicated that concretes made with both binary slag cement, ternary cement with slag and silica fume are less durable than Portland cement concrete in the acid environment. The concrete made with limestone aggregates and ternary cement containing 7% silica fume and 33% fly ash was found to have excellent acid resistance in 1% sulfuric acid solution. They further concluded that the crushing load method is a more reliable performance test method than the mass change measurements for assessment of concrete deterioration in acid environments.

Shi and Stegemann (2000) investigated the corrosion of four hardened cement pastes, which include conventional Portland cement, alkali activated blast furnace slag, a lime-fly ash blend and high alumina cement with gypsum and lime; in pH 3 nitric acid, pH 3 acetic acid and pH 5 acetic acid solutions. The corroded depth of specimens was measured till 580 days of immersion in the acid. It was concluded that the resistance of cement pastes to acidic corrosion depends on the protective layer or the nature of hydration products rather than on the porosity of hardened cement paste. For example, pastes with Portland cement, blast furnace slag or fly ash formed a protective layer consisting of $SiO_2.nH_2O$ gel, which provided a barrier for the further corrosion of uncorroded pastes. In high alumina cement paste, ettringite is formed which decomposes completely in acid solution leading to higher degree of attack on this cement.

Similar conclusion was drawn by *Rendell and Jauberthie (1999).* According to them, the skin of concrete plays an important role in the durability of cementitious materials. In the sulfate environment, this surface reaction can cause deterioration, or in some cases protection. They subjected the mortar specimens to sulfuric acid and ammonium sulfate solution for a period of 6 months. It was observed that when the cement mortar is exposed to sulfuric acid, a dense layer of gypsum is formed that is capable of retarding the deterioration process by acting as a surface sealing layer. On the other hand, in ammonium sulfate, the surface deposit of gypsum is sparse and the damage to the concrete occurs to a greater depth.

2.11.5. Research Significance

The use of supplementary cementitious materials (SCM) like fly ash, silica fume is believed to increase durability of concrete through pore refinement and the reduction of calcium hydroxide content of the cement paste matrix. However, as can be seen from the literature, the beneficial effects of these materials on acidic attack are still questionable, especially when they are used in certain combination. While some research works point towards the improvement brought about with the use of silica fume or fly ash, *(Kim et al 2007; Sobolev and Yeginobali 2005; Roy et al 2001),* some others report that silica fume or fly ash has only a little or no effect on durability of concrete under acid attack *(Pavlik and Uncek 1997; Torii and Kawamura 1994; Pavlik 2000).* Some others even pointed towards the negative effects of mineral admixtures on acid resistance of concrete *(Kilinckale 1997; Sersale et al 1998).* In this study, the effect of water-to-binder ratio and the presence of silica fume and fly ash on the resistance of concrete to acidic attack have been investigated by taking three different acids.

2.12. SULFATE ATTACK ON CONCRETE

2.12.1 General

Sulfate attack represents very dangerous kind of deterioration of concrete structures. It has been reported to be a cause of damage to concrete for over a century. If fact, concrete deterioration due to sulfate attack received much more attention compared to all other concrete distresses *(Al-Amoudi 1995).* Vicat, as early as 1818, reported a chemical attack on concrete due to the presence of sulfate ions in seawater, while Candlot established the formation of an expansive hydration product by the interaction of calcium aluminates and calcium sulfate in 1890. Michaelis, in 1892, attributed the disruption of concrete to the reaction between C_3A in the Portland cement and sulfate ions to form ettringite *(Al-Amoudi 2002).* The research on sulfate attack is continuing even today, which is motivated by several factors:

(1) Modification of physical and chemical characteristics of Portland cement with the passage of time.

(2) The use of blended materials with Portland cement. The resultant blend is reported to improve durability of concrete due to pore refinement occurring by the pozzolanic reaction. However, these materials have introduced complexity into the system, thus making the study of sulfate attack even more complex.

Sulfates are found in the ground water, soil or sea water in the form of sodium sulfate, potassium sulfate, magnesium sulfate and calcium sulfate. When the sulfate salts are present above a certain threshold level (>1000 ppm), they are known to be detrimental to concrete *(Mehta, 1983).* Previous studies on sulfate attack are conducted by using solutions of sodium sulfate, magnesium sulfate and calcium sulfate. However, due to limited solubility of calcium sulfate at normal temperatures (approximately 1400 mg/l sulfate ions), sulfate attack is normally ascribable to the presence of magnesium sulfate and sodium sulfate *(Hossain and Lachemi, 2006)*

2.12.2. Chemical Reactions Involved

Sulfate attack is a complex process that involves a series of chemical reactions between the hydration products and sulfate ions. At least six kinds of reactions could be described by sulfate attack.

1. **Gypsum Formation:** The sulfate ions that are introduced into concrete have greater affinity to react with porlandite (calcium hydroxide), one of the principal phases during cement hydration and convert it into calcium silicate dihydrate, i.e., gypsum. It is about 2.2 times more voluminous as compared to the corresponding reactants *(Zivica 2000)*.

2. **Ettringite formation:** The reaction of calcium aluminate hydrate present in the cement matrix with sulfate ions leads to the formation of voluminous calcium aluminate sulfate hydrate, i.e., ettringite. The increase in the original solid volume is approximately 2.8 times the volume of the reactants *(Zivica, 2000).* The accumulation of gypsum and ettringite can result in the development of initial expensive stresses, thus causing expansion, cracking and eventually the loss of cohesion among the solid components of concrete.

3. **Degradation of C-S-H gel:** In the case of magnesium sulfate, degradation and disintegration to calcium-silicate-hydrate (C-S-H) to magnesium-silicate-hydrate (M-S-H) may take place, which is a non-cementitious product and leads to softening of the cement matrix *(Gallop and Taylor 1992; Bonen 1993; Cohen and Mather 1991).*

4. **Brucite formation:** In the case of magnesium sulfate attack, calcium hydroxide reacts with magnesium ions and forms magnesium hydroxide, i.e., brucite. Brucite has low solubility and is assumed to envelop the remainder of the cement gel and protect it against further deterioration *(Cohen and Bentur 1988; Al-Amoudi et al 1995; Gallop and Taylor 1992).* However, *Turker et al (1997)* reported that this process is effective at early stages only. At later stages, deterioration processes due to brucite formation was found to be more dominate that any other form of deterioration.

5. **Thaumasite formation:** It involves C-S-H gel, along with a sulfate source and a carbonate source. It is believed to form during sulfate attack at low temperatures. Thaumasite is able to transform hardened concrete or mortar into a soft pulpy mass due to the direct attack on C-S-H gel *(Santhanam et al 2003 a).*

6. **Salt crystallization:** In addition to chemical deterioration, repeated dissolution of solid parts and recrstalization can occur in concrete pores due to variation in temperature and relative humidity. This process can cause tensile stresses and leads to rupture of cementitious matrix *(Him and Mather, 1999).*

2.12.3. Factors Affecting Sulfate Attack

Sulfate attack on concrete is a complex process and depends on many factors related to concrete properties and aggressive medium *(Hekal et al 2002).* Water-to-binder ratio and the proportions of supplementary cementing materials are, in particular, two key factors affecting the sulfate resistance of concrete mixtures *(Naik et al 2006; Kurtis et al 2000; Monteiro and Kurtis 2003). Naik et al (2006)* also emphasized on the influence of presence of aggregates in understanding the progress of sulfate attack. Among the parameters related to aggressive medium, the cations associated with sulfate ions is believed to be the most important factor that affects the sulfate resistance of concrete. All these factors are discussed in the following sections.

2.12.3.1. Effect of Water-to-Binder Ratio

It is well known that low water-to-binder ratio concrete is recommended for any construction from durability perspective. This is because the entire deterioration phenomenon is inversely proportional to water-to-binder ratio *(Al-Amoudi 2002; Neville 2004 b; Marchanda et al 2002). Marchanda et al (2002)* carried out a theoretical analysis of the detrimental influence of weak sodium sulfate solution on the durability of concrete. Among the various parameters, the influence of water-to-binder ratio was also studied. It was concluded that water-to-binder ratio remains the key parameter that controls the durability of concrete to sulfate attack.

Boyd and Mindess (2004) investigated the influence of cement type and water-to-binder ratio on sulfate resistance of concrete. The concrete specimens were subjected to 5% sodium sulfate solution for a period of one year. The results indicated that the use of low water-to-binder ratio is far more effective than cement type, viz. sulfate resisting cement, in offsetting the detrimental effects of sulfate attack on concrete. Similar observation was made by *Lee et al (2005)* while subjecting the mortar specimens to 5% sodium sulfate solution and 5% magnesium sulfate solution for 510 days. *Maltais et al (2004)* also observed the positive effect of using low water-binder ratio to increase the durability of cement pastes in sodium sulfate solutions. *Corr et al (2001)* used the expansion equations to conduct a reliability analysis of concrete exposed to sulfate attack. They observed that the effect of water-to-binder ratio on the expansion of concrete was even higher than the effect of C_3A content.

Monteiro and Kurtis (2003) reported a long tem, non-accelerated test program to study the influence of water-binder ratio, cement composition and fly ash addition on resistance of concrete mixes to severe sodium sulfate exposure. It was found that the samples with higher water-binder ratio tend to fail at early ages. For water-to-binder ratio below 0.45, the concrete samples did not fail during the test period of 40 years, independent of C_3A content of cement.

Some researchers, however, have different opinion on the role of water-binder ratio on sulfate attack. *Al-Amoudi et al (1995)* exposed the mortar specimens to sodium sulfate and magnesium sulfate solutions. It was observed that lowering of water-to-binder ratio tends to improve the performance of mixes in sodium sulfate exposure. On the other hand, reducing the water-to-binder ratio tends to aggravate the sulfate attack in magnesium sulfate solution. The strength loss was reduced from 39% to 26% when the water-binder ratio was reduced from 0.5 to 0.35 in sodium sulfate attack, while it increased from 62% to 82% with the same decrease in water-to-binder ratio. The inferior performance of mixes in MS solutions at low water-to-binder ratio was attributed to the dense microstructure that did not allow the expansive reaction products (primarily gypsum and M-S-H) to accumulate. Similar behaviour was noted in the concrete specimens exposed to mixed magnesium-sodium sulfate environment *(Al-Amoudi 1995)*. The results indicated that the reduction in water-to-binder ratio enhanced the loss of concrete materials. It was further observed that despite the higher degree of sulfate deterioration in low water-binder ratio concrete mixtures, the low negative corrosion potentials revealed that the embedded reinforcing steel was still in the passive state.

Similar observation was made by *Hossain and Lachemi (2006)* while studying the effect of volcanic pumice on sulfate resistance of concrete. The concrete mixtures were made at two water-binder ratios (0.35 and 0.45) and were subjected to mixed magnesium-sodium sulfate solution for 48 months. *Naik et al (2006)* observed that under sodium sulfate attack, the onset and propagation of physical deterioration (i.e. cracking, spalling and disintegration) in cement paste specimens, as detected by micro CT occurred more rapidly at the lower water-to-binder ratios.

2.12.3.2 Effect of Mineral Admixtures

Pozzolanic concrete is now being increasingly used to improve the concrete durability. The pozzolanic reaction is believed to have the following beneficial impacts on the sulfate attack:

1. The consumption of portlandite, which reduces the formation of gypsum.
2. Replacement of part of cement by a pozzolanic material entails a reduction in C_3A content, thus reducing the formation of ettringite.
3. Even if the ettringite is formed, it is not expansive at pH lower than 12 and the introduction of pozzolana reduces calcium hydroxide content and thus pH of concrete and, therefore, the ettringite becomes less expansive.
4. The formation of secondary C-S-H results in the densification of hardened cement paste, therefore, sulfate ions cannot easily penetrate the concrete mix *(Al-Amoudi 2002; Santhanam et al 2003 b).*

Different researchers however have different views about the effect of various mineral admixtures on sulfate resistance of concrete. *Monteiro and Kurtis (2003)* examined the total expansion of concrete specimens after 40^+ years of sulfate exposure. It was seen that the samples containing no fly ash expanded about 0.4%, while those prepared with 25% fly ash expanded only about 0.15%. They concluded that the partial replacement of cement with fly ash in the range of 25% to 45% result in considerable improvement in sulfate resistance. *Wee et al (2000)* also reported greater resistance of concrete containing granulated blast furnace slag and silica fume to 5% sodium sulfate solution irrespective of the water-to-binder ratio and the moist curing period. The concrete prisms were immersed in 5% sodium sulfate solution for 32 weeks and periodically monitored in flexural strength and linear expansion. The superior resistance of concrete mixtures containing silica fume was attributed to the pore refinement process occurring due to the conversion of portlandite into secondary C-S-H gel by strong pozzolanic reaction and to the filler action by the finer particle size of silica fume particles.

Santhanam et al (2002) also observed that in sodium sulfate exposure, the expansion of pozzolana substituted mortars is drastically reduced. In magnesium sulfate exposure also, the overall expansion was lesser than the corresponding plain cement mortars, although the deterioration was more than that observed in sodium sulfate solution. Similar observation was made by *Binici and Aksogan (2006)* while studying the sulfate resistance of blended cements made with high volume granulated blast furnace slag and natural pozzolana. It was observed that the sulfate resistance of blended cement mortars was significantly higher than reference cement mortars, both against sodium sulfate and magnesium sulfate attacks.

Torii and Kawamure (1994) studied the resistance of mortars containing silica fume or fly ash in 2% sulfuric acid, 10% sodium sulfate and 10% magnesium sulfate solutions. Fly ash and silica fume appeared to significantly increase the resistance of mortars, but only above certain content, which depended on the type of sulfate solution.

Turker et al (1997) carried out an investigation on the resistance of mortars to magnesium sulfate attack. Silica fume was used as the mineral admixture and the mortar specimens were immersed in variable concentration of magnesium sulfate solutions for a period of 300 days after 28 days of lime saturated water curing. The deterioration process of mortars was observed to be retarded by the presence of silica fume.

Al-Dulaijan et al (2003) conducted a study to evaluate the performance of plain and blended cements when exposed to varying concentrations of sodium sulfate solutions for up to 24 months. The sulfate resistance was evaluated by visual examination and measuring the reduction in compressive strength. It was observed that the performance of ASTM Type V cement, ASTM Type I cement + SF and ASTM Type I cement + FA was not significantly different from each other and was better that ASTM Type I cement. *Brown et al (2004)* also found that slag was effective in reducing the sulfate attack, regardless of whether the attack is by sodium sulfate or magnesium sulfate.

Khatib and Wild (1998) found that mortars containing higher replacement levels of metakaolin exhibit superior resistance against sodium sulfate attack during test period of 520 days. *Shannag and Shaia (2003)* carried out an investigation on high performance concrete mixes containing various proportions of natural pozzolana and silica fume to the attack by sodium sulfate and magnesium sulfate solutions, Dead Sea and Red sea water. The deterioration was evaluated through visual observations, ultrasonic pulse velocity measurements and relative strength determinations. The investigations indicated that the concrete mix containing a combination of silica fume and natural pozzolan exhibit the best protection against sulfate attack.

Hekal et al (2002) reported that the partial replacement of Portland cement by silica fume (10% to 20%) did not show a significant improvement in sulfate resistance of hardened cement pastes. The samples were immersed in 10% magnesium sulfate solution. They attributed the poor performance of silica fume blended pastes to the depletion of calcium hydroxide content due to the pozzolanic reaction. Therefore, the decalcification of C-S-H gel to form non-cohesive M-S-H was accelerated.

Lee et al (2005) studied the effectiveness of silica fume in sodium sulfate and magnesium sulfate attack. It was observed that in sodium sulfate environments, the use of silica fume has a beneficial effect in terms of controlling the strength loss of OPC mortar specimens, due to its strong pozzolanic reaction and subsequent reduction in calcium hydroxide. On the other hand, the presence of silica fume showed a negative effect under magnesium sulfate attack. This phenomenon was largely attributed to the possible conversion of C-S-H into M-S-H, which is non-cementitious. Similar observation was made by *Al-Amoudi et al (1995).*

Lawrence (1992) also concluded that in magnesium sulfate attack, the use of sulfate resisting cement is significantly better than using any mineral admixture like fly ash, silica fume, GGBFS etc.

Rasheeduzzafar et al (1994) investigated the sulfate resistance of plain and blended cements when exposed to combined magnesium sulfate and sodium sulfate environments. After 2 years of exposure, the deterioration was noted to be more pronounced in blast furnace slag cements and silica fume cements. They attributed the aggravated deterioration of silica fume and GGBFS cements to the depletion of C-S-H gel and to the absence of protective brucite layer.

Moon et al (2003) also investigated performance of silica fume blended mortars in various sulfate bearing exposure conditions. Mortars were exposed to 5% sodium sulfate, 5% magnesium sulfate and mixed 5% sodium sulfate-5% magnesium sulfate solutions for 270 days. Silica fume demonstrated a beneficial effect in mitigating compressive strength loss of mortars in sodium sulfate solutions. However, the strength reduction factor of silica fume mortars was found to be greater than the mortar specimens without silica fume under Mg^{2+} ion oriented attack. It was also observed that if both sulfates coexist, the MS attack is more pronounced than NS attack. Similar observation was made by *Hossain and Lachemi (2006)* while studying the performance of volcanic ash and pumice based blended cements in the mixed MS-NS attack

Al-Amoudi (1995) assessed the performance of 15 reinforced cement concrete mixtures in a mixed magnesium-sodium sulfate environment. Blended cement concretes, particularly those made with fly ash and GGBFS, exhibited an advanced degree of deterioration due to both sulfate attack and reinforcement corrosion. Silica fume concrete also had an inferior performance in terms of sulfate resistance, but displayed the best performance in terms of electrical resistivity. The better electrical resistivity of concrete was attributed to the dense microstructure of silica fume concrete.

Ganjian and Pouya (2005) studied the effect of silica fume on deterioration resistance to sulfate attack in sea water. Changes in the compressive strength and capillary water absorption of specimens were investigated as a function of silica fume content. The performance of paste and concrete specimens containing silica fume was found to be inferior to those without silica fume replacement. The strength reduction further increased with the increase in silica fume replacement level. They suggested that to enhance the deterioration resistance of concrete against sulfate, use of water resistant epoxy coating etc. may be considered instead of using mineral admixtures.

On the other hand, *Shannag and Shaia (2003)* found that the concrete mix containing a combination of 15% silica fume and 15% natural pozzolan show maximum protection against sulfate attack after one year of immersion in sulfate solution.

2.12.3.3. Effect of Presence of Aggregates

Although most of the studies on sulfate attack are conducted either on cement pastes or mortar specimens, it is well emphasized on the importance of presence of aggregates by many researchers. *Cohen and Mather (1991)* established five major criteria for systematic research on sulfate attack. Out of the five criteria, one criterion is to establish a relationship between paste and concrete durability. The authors said that the neat cement paste and concrete are two different things that cannot be compared due to the transition zone effect which is present in concrete but is absent in paste. They further stated the finding of Winslow and Cohen that the microstructure of pure paste and the paste within the concrete are two different things because the effect of transition zones extends far beyond the aggregate surface and individual effects of surfaces overlap; and there is little or no paste in concrete that is not affected.

Yang et al (1996) concluded that the resistance to sulfate attack is influenced by the content of the interfacial zone. It is said that the structure of the interfacial zone is characterized by high porosity and richness of the hydrated crystals. The resistance to sulfate attack was found to reduce with the increase in content of interfacial zone and found to enhance by the improvement of structure of interfacial zone.

Naik et al (2006) studied the influence of aggregates on the sulfate attack by monitoring strength change, expansion, micro CT and ED XRD. It was found that in the presence of aggregates, the physical distress was rapid and the propagation was also fast. Samples containing aggregates failed by 35 weeks of exposure, while the corresponding cement paste samples did not disintegrate completely after 78 weeks exposure.

Khatri et al (1997) stated that sulfate resistance in concrete depends on physical and chemical aspects of concrete mix. The sulfate ions must first diffuse into concrete and subsequently react with the cement portion of concrete, leading to disintegration. The physical resistance of concrete can be correlated to its permeability and the chemical resistance of concrete depends on the type of binder. They compared the expansion of concrete samples with permeability in order to establish the role of permeability in controlling the expansion due to sulfate attack. It was concluded that both permeability and type of binder play an important role in governing the sulfate resistance of concrete. The relative expansion of concrete can be better explained by combining the information of permeability and chemical resistance of binder.

2.12.3.4. Effect of Cation Type

The cation type (sodium ions or magnesium ions) associated with sulfate ions significantly influence concrete deterioration due to sulfate attack. *Al-Amoudi et al (1995)* studied the durability performance of plain and blended cements in magnesium sulfate (MS) and sodium sulfate (NS) solutions. The performance of cements was evaluated by measuring expansion and determining reduction in compressive strength of mortar specimens when exposed to test solution for 360 days. The data indicated that while the performance of all blended cements was generally excellent in the NS environments, their performance was not satisfactory in MS environments. They attributed the inferior performance of blended cements in MS solution to the reduced calcium hydroxide in the hardened cement matrix which provides an opportunity to MS to react more directly with the primary and secondary C-S-H due to the destabilization of these phases by magnesium hydroxide. *Al-Amoudi (2002)* further studied the mechanism of NS and MS attack and concluded that NS attack is manifested by expansion and strength reduction. Low water-to-binder ratio decreases the extent of NS attack by mitigating the diffusion of sulfate ions into the matrix of specimens. The MS attack is manifested by weight loss of the material and strength reduction. The expansion is lesser in MS attack due to the formation of non-expansive M-S-H. It was further stated that the low water-binder ratio concretes display inferior performance as compared to normal water-to-binder ratio in MS attack, due to finer pore structure of former mixes.

Cohen and Bentur (1988) studied the durability of pastes in MS and NS solutions. Pastes were made with ASTM Type I and ASTM Type V cements with partial replacement of cement by 15% silica fume. It was observed that in NS solution, the attack was mainly exhibited by increase in length, with only smaller effects on strength change and particularly, no effect on mass change. The use of ASTM Type V cement largely eliminated the NS attack and the addition of silica fume had an advantageous effect in improving resistance to NS solutions, bringing the performance of ASTM Type I Portland cement to level with ASTM Type V Portland cement. On the other hand, in MS solution, the attack was exhibited by the softening of C-S-H gel, accompanied by strength and mass loss. Further, no difference was observed between the extents of damage of Type I and Type V cements. The use of silica fume was found to be extremely deleterious in both these cements. Similar observation was made by *Dehwah (2007)* while studying the combined effect of chloride and sulfate ions.

Lee et al (2005) studied the effectiveness of silica fume in controlling the damage arising from NS and MS attack. The major variables in the study were the water-to-binder ratio and the level of cement replacement. It was found that the mortar specimens stored in NS solution behave very differently from those exposed to MS solution with respect to the form and degree of damage. In NS solution, there was considerable mass loss in OPC mortars due to significant expansion and consequent disintegration. On the other hand, the mass loss of silica fume mortar specimens was negligible even after 510 days. Unlike the role of silica fume in NS solution, the mortar specimens with silica fume displayed more severe deterioration compared with OPC mortar specimens in MS solution. They explained that the better performance of OPC mortar specimens in MS solution was due to presence of abundant calcium hydroxide at the surface that reacted with MS to form brucite and gypsum. The partial replacement of OPC with silica fume reduced calcium hydroxide availability and allowed MS to directly attack C-S-H, leading to decalcification, M-S-H formation and destruction of cement bond. Similar observation was made by *Moon et al (2003) and Shannag and Shaia (2003).*

Brown et al (2004) studied the micro structural changes in concrete when exposed to NS and MS solutions for four years. It was observed that the depth of attack reduced when the specimens were immersed in MS solutions as compared to NS solution. The reduced depth of attack in MS was attributed to the deposition of magnesium-containing compounds near the surface of concrete.

Santhanam et al (2002) monitored the length change of cementitious mortars when subjected to NS and MS solutions, along with the micro structural observations using SEM. It was suggested that the expansion of mortars in NS solutions follow a two-stage process. In the initial stage, there is little expansion which is followed by a sudden and rapid increase in expansion in the later stage. Micro structural studies concluded that the second stage corresponds to the appearance of cracks in the chemically unaltered interior of the mortar. Beyond this stage, the expansion proceeds at an almost constant rate until the complete deterioration of the specimen takes place. In the case of MS attack, the expansion occurs at a continuously increasing rate. Micro-structural studies suggest that a layer of brucite (magnesium hydroxide) forms on the surface almost immediately after the introduction of specimen into the solution. After the formation of brucite layer, the diffusion of sulfate ions takes place leading to decalcification of C-S-H and its conversion into M-S-H.

2.12.4. Research Significance

Although significant progress has been made on understanding the mechanism of sulfate attack, it is still not completely understood and knowledge still remains inadequate. It is because most of the research has been carried on mortar or cement paste specimens and the results are then extrapolated to concrete. According to researchers, cement paste and concrete cannot be compared just like that due to the presence of aggregates and the appearance of transition zone between coarse aggregate and the paste *(Cohen and Mather 1991)*. Also mortar or paste samples are of significantly smaller cross section than the concrete samples and hence the influence of permeability is expected to be significantly less for mortar samples than for concrete samples. The sulfate resistance in mortar is expected to be dependent on the binder type, whereas in concrete, both permeability and binder type control the sulfate resistance *(Khatri et al 1997)*. The objective of this study is to give a comparative evaluation of sulfate resistance of concrete specimens made by using different binders and at different water-to-binder ratios when subjected to sulfate solution having magnesium and sodium ions associated with it.

2.13. CHLORIDE INGRESS IN CONCRETE

2.13.1. General

Under most circumstances, reinforced concrete is an extremely durable material and can provide a long service life to structures. However, like any other material, it has weakness and deteriorates with time. Corrosion of steel reinforcement is identified as the most common and serious form of deterioration *(Mcpolin et al 2005; Shroff 1988)*.

Corrosion of reinforcing steel can damage the serviceability of concrete structures in several different ways. First, corrosion produces expansive products that generate tensile stresses in the concrete surrounding the reinforcing steel, which may cause the concrete to crack. Cracks reduce the overall strength and stiffness of concrete structures and accelerate the ingress of aggressive ions, thus results in further cracking *(Mehta and Gerwick 1982).* Second, corrosion products are highly porous and weak. It decreases the bond between the reinforcing steel and concrete *(Wang and Monteiro, 1996).*

Protection of steel reinforcement from corrosion is usually provided by the highly alkaline environment of concrete due to formation of calcium hydroxide. It is called as passivation film. For corrosion to occur, passivating film needs to be destroyed that allow oxygen and water to come in contact with steel. Chloride ingress is one of the primary reasons for the destruction of film. When chloride ions come into contact with the protective passive layer surrounding the reinforcing steel, they will destroy it by activating the surface of steel to form an anode, while the passive surface forms the cathode *(Nevillie 2004 a).*

Chlorides can be introduced into concrete via internal and external sources. The internal sources include aggregate or water contamination with chloride and the use of admixtures containing chlorides, while the external sources include use of chloride salt as a deicer or exposure to seawater etc. In the case of internal contamination, if the chloride content in the pore solution around the reinforcing steel reaches a threshold value, the presence of chloride will immediately initiate depassivation of reinforcing steel in concrete. In the case of chloride penetration from external sources, the chloride content in concrete will build up with time leading to a condition under which the concrete is no longer able to protect the reinforcing steel from depassivation *(Ismail and Soleymani 2002).* In most of the modern concretes, the sources of chlorides are external and therefore, for corrosion of reinforcement, there must be movement of chlorides into concrete.

Ismale and Soleymani (2002) discussed that the service life of a concrete structure, when controlled by the corrosion of steel reinforcement, can be divided into two periods (according to model developed by Tuutti) (i) initiation period and (ii) propagation period. The initiation period lasts from the beginning of service life of concrete structure to the point at which the concentration of chloride ions around the reinforcing steel in the concrete has reached the critical value for initiating corrosion. The propagation period extends from the onset of corrosion to the limiting state of the concrete structure, beyond which the structure cannot be safely used. When the chloride source is external, chloride penetration from the external source into concrete is a far slower process in comparison with the corrosion propagation. Thus, the initiation period could be used to conservatively estimate the service life of a concrete structure. The factors that affect the penetration of chlorides, and therefore, initiation period are discussed in the following sections.

2.13.2. Effect of Water-to-Binder Ratio

Dehghanian and Arjemandi (1997) conducted experiments to investigate the influence of water-to-binder ratio ranging from 0.45 to 0.75 on chloride diffusion rate in ordinary Portland cement concrete and slag concrete. The slag content was varied from 0% to 30%. It was observed that with the increase in water-to-binder ratio, the chloride diffusivity of concrete increases. The effect of water-to-binder ratio was more pronounced for higher slag contents. *Castro et al (2000)* studied the effect of microclimates and water-to-binder ratio for the concrete exposed to tropical marine environments. For this, concrete cylinders were made with water-binder ratios varying from 0.76 to 0.46. The cylinders were initially water cured for 1, 3 and 7 days and then exposed to the tropical marine climate of Yucantan at distances of 50m, 100m and 780m from the seaside. It was observed that the chloride concentration in the concrete nucleus decreases with the decrease in water-binder ratio. *Dhir et al (1997)* studied the effect of water-to-binder ratio on chloride binding capacity of plain and fly ash cement pastes and observed that the chloride binding capacity increases with the increase in water-to-binder ratio.

Jaegermann (1990) developed a linear relationship between threshold chloride depth and water-binder ratio. It was recommended that at the water-to-binder ratio of 0.4, the required concrete cover to provide protection to reinforcing steel is 30 mm, if the threshold chloride value is 0.4%. However for the same threshold value, the concrete prepared at water-to-binder ratio of 0.5 requires minimum cover of 40mm for providing protection to steel.

Gjorv and Vennesland (1979) studied the rate of chloride diffusion from seawater into concrete made with different water-to-binder ratios (0.4, 0.5 and 0.6) and different types of cements (ordinary Portland cement, trass cement, slag cement and sulfate resisting cement). The specimens were subjected to seawater for two years. The investigation indicated that for longer duration of exposure, the cement type has a great influence on the depth of chloride penetration than the water-to-binder ratio.

2.13.3. Effect of Mineral Admixtures

Bouzoubaa et al (2000) studied the performance of concrete made with high volume fly ash blended cements using fly ashes from Canada and USA. It was observed that the use of high volume fly ash blended cements improved the resistance of concrete to chloride ion penetration and the improvement in resistance increases with an increase in the inter-grinding time of fly ash and cement. *Thomas and Bamforth (1999)* analyzed the data from long term field and laboratory studies of concrete incorporating fly ash and slag, exposed to chloride environments by using a chloride transport model. Three concrete mixes were prepared: control mix, the mix with 30% fly ash and the mix with 70% slag as partial replacement of cement. The specimens were subjected to three curing conditions for 28 days: air curing, membrane curing and wet curing for 3 days followed by air curing. After 28 days, the cores were placed at the marine exposure site for a maximum period of 8 years. The results show that the incorporation of fly ash and slag can lead to significant improvement in transport properties in long term. It was seen that the rate of chloride penetration during the first six months or so of exposure was similar for concretes with or without mineral admixtures. However, after a few years of exposure, chloride ingress slows to a much-decreased rate in fly ash and slag concrete leading to dramatic increase in the predicted service life.

Haque et al (1992) also observed that the presence of fly ash significantly reduce the concentration of free chloride ions in concrete when the chloride ingress is from the surrounding sodium chloride solution. They suggested that a judicious use of fly ash in concrete making could decrease the incidence of chloride-induced corrosion of the reinforcement in concrete structures. *Dhir and Jones (1999)* also noted from the laboratory tests that the use of fly ash, at 30% replacement level, can result in up to two to four times better performance then that of corresponding Portland cement concrete. The improved performance of fly ash mixes was attributed to the role of fly ash in improving the pore structure through its physical, chemical and pozzolanic effects and the role of fly ash in improving chloride binding due to the presence of active alumina. It was stated that further improvement is possible by processing fly ash or by using fly ash along with silica fume or metakaolin as ternary blends.

Oh and Jang (2007) studied the effect of material and environmental parameters on chloride penetration profiles of concrete structures and found that among material parameters, the addition of fly ash into concrete reduces the diffusion coefficients by about 15% to 50%, which leads to lesser penetration of chloride ions into concrete structures. *Chindaprasirt et al (2007)* concluded that the resistance to chloride penetration of concrete is significantly increased with the incorporation of fly ash and the increase is further enhanced with an increase in fly ash fineness.

Leng et al (2000) concluded that the chloride ion diffusion coefficient of concrete (determined by using Nernst-Einstein equations) decreases with increasing replacement of Portland cement with PFA. The decrease was attributed to changes in pore size distribution, increased C-S-H gel formation and increased alumina levels enabling more chlorides to be fixed as Friedel's salt. *Papadakis (2000)* demonstrated that the concrete specimens incorporating mineral admixtures, whether as substitutes for aggregates or cement, exhibit significantly lower total chloride content for all depths from the surface. Of all the supplementary cementitious materials tested, silica fume exhibited the lowest degree of chloride penetration, then low calcium fly ash and high calcium fly ash the highest. It was concluded that the use of supplementary cementitious materials significantly lengthens the initiation stage of chloride induced corrosion.

Hisada et al (1999) investigated the effect of mineral admixtures on ion migration through mortar specimens. It was found that the mobility of chloride ions through mortar changes remarkably by using mineral admixtures, especially when silica fume or granulated blast furnace slag were used. *Memon et al (2002)* tried to identify the composition of cement matrix that would produce not only high strength but also durable concrete. It was observed that by addition of pozzolanic and cementitious materials namely fly ash, silica fume and granulated blast furnace slag, pore refinement or transformation of larger pores into finer pore occur that leads to production of durable concrete.

Asrar et al (1999) studied the corrosion protection behavior of micro silica in ordinary Portland cement and sulfate resistant cement. For this, carbon steel reinforced specimens of both the cements containing 10% each of densified and undensified micro silica were exposed to 5% sodium chloride solution and sea water and the corrosion of bars was monitored by using open circuit potential measurements. It was observed that micro silica causes drastic decrease in the permeability of chloride ion in ordinary Portland cement concrete as well as sulfate resisting cement concretes. Blending of ordinary Portland cement with micro silica decreases the corrosion of rebar when the concrete is exposed to a chloride environment due to presence of sulfate and magnesium ions. Blending of sulfate resisting cement with micro silica suppress the corrosion of rebars when concrete is exposed to marine environment.

Yeau and Kim (2005) carried out an experimental study on the corrosion resistance of concrete made with granulated blast furnace slag as mineral admixture. It was found that the corrosion rate is highly dependent on the depth of concrete cover, cement type and slag content. The diffusion coefficient was observed to decrease as the amount of slag is increased. Chloride diffusion measurements have also been carried out on concrete made with ternary binders involving pulverized fly ash and silica fume. The concrete employed were Portland cement concrete, Portland cement-8% silica fume concrete, Portland cement-25% fly ash concrete, Portland cement-8% silica fume- 25% fly ash concrete and were cured for up to two years. Chloride diffusion coefficients were determined for concrete of various ages placed in a chloride diffusion cell. Observing the effect of age of concrete on diffusion coefficient, it was found that the silica fume concrete produced a sharp fall in diffusion coefficient followed by a gradual decline, where as the fly ash concrete showed continuous and progressive reduction. In the ternary blends, the reduction in chlorides diffusion coefficient was even greater in the early age concrete and continued to decline with concrete age more steeply than the silica fume concrete, suggesting that the ternary blends should provide very high resistance to chloride penetration. Similar observation was made by *Bai et al (2003)* while studying ternary systems made with Portland cement – pulverized fly ash – metakaolin and subjected to seawater.

2.13.4. Chloride Binding Capacity of Concrete

Chlorides in concrete can be either dissolved in the pore solution (free chlorides) or are bound to the cement hydrates (bound chlorides). The chloride binding capacity of concrete may influence the durability of concrete in chloride containing environment. The effect of chloride binding in concrete on the initiation of corrosion is two fold: (i) the rate of chloride ion transport in concrete is reduced, since the amount of available mobile ions (free chlorides) is also reduced by the binding mechanism, and (ii) the reduction of free chlorides in concrete results in lower amount of chlorides being accumulated at the reinforcing steel layer *(Martin-Perez et al 2000).* Several mechanisms are developed to explain the phenomenon of chloride binding in concrete. Chlorides can react with the unhydrated aluminate phases to form calcium monochloroaluminate called friedel's salt, or chlorides can be physically adsorbed to the amorphous calcium hydrates (C-S-H gel) *(Delegrave et al 1997; Pruckner and Gjorve 2004; Thangavel and Rangaswamy 1998).* A wide range of parameters, some of which are discussed here under, influences the chloride binding capacity of concrete.

Oh and Jang (2006) developed a prediction model of chloride penetration into concrete structures. It was found from the study that among other parameters, chloride-binding affect greatly the chloride penetration profiles in concrete. It was observed that the apparent diffusion coefficients of ASTM Type I cement mix were smaller than that of ASTM Type V cement mix. They attributed this difference to the difference in C_3A contents in the cement that usually affects the binding capacity. *Hussain et al (1995)* reported that the chloride binding capacity and reinforcement corrosion initiation time could be increased by 2.43 and 2.45 folds respectively, in accordance with increase of C_3A content from 2% to 14%. *Arya et al (1990)* reported that mixes containing pulverized fly ash have a greater chloride binding capacity, which further increases with the increase in pulverized fly ash content. The increase in binding capacity of fly ash was attributed to the substantial increase in the amount of adsorbed chloride, the formation of compounds with aluminate phases were considered to play only a minor role.

Dhir et al (1997) also observed that pulverized fly ash content increases the chloride binding capacity of cement paste upto a level of 50% replacement. Beyond this level, binding capacity begins to decline with increasing pulverized fly ash replacement. This decline in binding capacity was attributed to the instability of Friedel's salt at low pore solution pH. This leads to decomposition of these compounds that would release chloride ions into the pore solution thus raising their concentration level.

Crizmadia et al (2000) investigated the chloride binding capacity of alumino-ferrites (C_4AF, C_6AF_2 and C_6A_2F) after immersing them in 10% NaCl solution. It was found that the chloride binding of aluminoferrites is similar to C_3A. Like C_3A, C_4AF binds chlorides by the formation of Friedel's salt or its iron analogue.

Delagrave et al (1997) studied the interaction mechanism of the cement paste hydration products with chlorides for various types of cements and different types of chloride solutions. Test results show that the total amount of bound chloride increases with the chloride concentration in the solution. The total amount of bound chlorides was found to be more related to the total aluminate content ($C_3A + C_4AF$) than to the C_3A content. The chemical composition of the chloride solution also has a significant influence on the binding capacity. For example, the use of $CaCl_2$ increases the amount of bound chlorides as compared to NaCl. Similar observations were made by *Tritthart (1989), Al Hussain et al (1990) and Arya et al (1990).*

2.13.5. Relationship between Total Chlorides and Free Chlorides

As has already been said, free chlorides are believed to be responsible for the initiation of corrosion. However, the chloride threshold value necessary to initiate corrosion of steel bars in concrete is mostly provided in terms of total chlorides *(Alonso et al 2000).* Therefore there is a necessity of a reasonably accurate relationship between free chlorides and total chlorides. This matter is pointed out in the literature and several authors have tried to develop the desired relationship.

Mohammed and Hamada (2003) proposed a linear relationship between free chloride and total chloride contents in concrete based on the results of several long term exposure tests under marine environments for various cements like ordinary Portland cement, high early strength Portland cement, slag cement, fly ash cement etc. Similar observation was made by *Sandherg (1999).*

Siegwart et al (2003) analyzed the relationship between free chlorides and bound chlorides based on already published data. They choose an empirical method (least square analysis) for finding the correlation between the two. It was further assumed that total chloride content and C_3A content are main factors influencing the equilibrium between free chlorides and bound chlorides. The biquadratic fitting equation was found to be best for describing the phenomenon of chloride binding in concrete. *Lu et al (2002)* developed the relationship between free chloride and total chloride diffusivity in concrete by using electrochemical method. A rough linear relationship was obtained between the free chloride and total chloride diffusivities in concrete. It was found that the total chloride diffusivity is 2.2 to 3.4 times that of free chloride diffusivity. However, *Martin-Perez et al (2000)* pointed out in their study that the linear relationship between bound chlorides and free chlorides underestimates the amount of bound chlorides at low free chloride concentration, whereas it overestimates the amount of bound chlorides at high free chloride concentrations.

Sergi et al (1992) recognized non-linear nature of the relationship between free chlorides and total chlorides. Some of the earlier developed non-linear relationships are Langmuir isotherm and Frendlich isotherm *(Martin-Perez et al 2000). Luping and Nilsson (1993)* concluded that the relationship between bound chloride and free chloride can be described by Freundlich isotherm at high free chloride concentrations and Langmuir Isotherm at low chloride concentration.

2.13.6. Effect of Curing Conditions

Initial curing to which concrete is subjected, prior to exposure to chloride environment, plays an important role in determining the chloride penetration rate in concrete. Drying of concrete particularly at concrete surface, caused by a poor curing regime, leads to restricted hydration in the surface layers, thus, higher permeability, leading to greater ingress of the aggressive materials to the concrete system.

A considerable volume of research has been conducted on chloride penetration of concrete. Some researchers have adopted curing regimes that allow maximum hydration of concrete to take place, that is, specimens were immersed in water or sealed before the exposure to chloride environment *(Page et al 1981). Detwiler et al (1994)* investigated the effectiveness of using supplementary cementing materials to increase the chloride resistance of accelerated cured concrete. They found that concretes containing cementing materials performed better than the Portland cement concrete. *Khatib and Mangat (2002)* studied the influence of high temperature and low humidity curing on chloride penetration in concrete containing supplementary cementitious materials. Three different mixes were studied: a control mix in which no cement replacement materials were added and two mixes where cement was partially replaced by 20% fly ash and 9% silica fume respectively. It was observed that at early periods of exposure, initial curing has a substantial influence on chloride penetration of concrete. The effect of initial high temperature curing is much reduced after a long period of exposure. Use of fly ash or silica fume was found to further increase the chloride penetration resistance.

2.13.7. Research Significance

In the previous studies on the ternary systems, curing regime adopted was the one that allowed maximum hydration to take place before exposure to chloride environment. However, it is an established fact that fly ash is highly sensitive to the initial curing regimes applied. In the present work, curing that simulates more realistic curing condition has been adopted to check the durability aspects of both binary and ternary systems. Along with this, the objective is to develop a relationship between free chlorides and total chlorides for mineral admixture concrete when the additional ions associated with chloride is sodium and calcium.

CHAPTER 3

EXPERIMENTAL PROGRAMME

3.1. GENERAL

Recent developments in concrete technology have made it possible to produce concrete mixtures of strength greater than the values specified in the codes of practice. However, very often it is not the improved strength which is the primary objective. Rather the improved durability – the ability of concrete to perform satisfactorily with minimal maintenance over the anticipated service life of the structure – and overall performance is the major goal of any development. This revolution in concrete technology has occurred with the use of supplementary cementitious materials like fly ash, silica fume, blast furnace slag etc. These property-enhancing admixtures are believed to improve both strength and durability of the resulting concrete. With the advent of high range water reducers, the possibility for the use of mineral admixtures has further increased.

Broadly speaking, mineral admixtures not only fill the large voids of the concrete granular structure, thereby improving the packing density of the matrix, but they also contribute towards the binding of matrix by its pozzolanic reaction.

Keeping in view the increasing use of these admixtures in concrete industry, the major objectives of the study is to experimentally investigate the effect of silica fume and fly ash, as a partial replacement of cement, on the resultant matrix in terms of strength and durability of resulting concrete. The investigation is carried out for wide range of water-to-binder ratios and under variable curing conditions.

In this chapter, first the basis for choice of experimental parameters and their levels are discussed, followed by the properties of materials used, specimen preparation, casting and test description that is carried out in the investigation. Along with this, the procedure adopted for finding out optimum super-plasticizer dosage is discussed followed by the results and discussions on the fresh properties of concrete.

3.2. EXPERIMENTAL PARAMETERS AND THEIR LEVELS

The various parameters that are taken as variables for investigating the strength and durability aspects of concrete include water-to-binder ratio, presence of mineral admixtures, concrete age and curing conditions adopted and aggressive environments. The basis of choice of these parameters is discussed here under.

3.2.1. Water-to-Binder Ratio

It was in 1918 that a turning point happened in the history of concrete technology with the 'Abrams water – cement ratio' law (*Yeh 2006)*. As per this law, it was proposed that the strength of a fully compacted concrete processed with specific type of aggregates at a given age of curing and at a prescribed temperature, is dependent primarily on water – cement ratio.

Actually, the strength of concrete depends indirectly on the pore structure of the matrix. The pores are inherent to cement based materials and mainly two types of pores exist, namely gel pores and capillary pores. The amount of water needed for desired workability at the time of mixing is often far in excess than that required for hydration of cementitious materials. This excess water, which does not take part in hydration reaction results, in the formation of capillary pores. Thus, higher water-to-binder ratio leads to the formation of more number of capillary pores. Hence it is said that the water-to-binder ratio is the most important factor that controls pore size distribution, packing density and thereby strength and durability of concrete, and is thus chosen as a parameter for this investigation.

Three different water-to-binder ratios varying from high (0.45) to medium (0.35) and low (0.25) are used to ensure wide variations in strength. While water-to-binder ratio of 0.25 corresponds to high strength concrete, 0.35 and 0.45 corresponds to moderately high strength concrete and normal strength concrete, respectively. Mixes with water-to-binder ratio of more than 0.45 are less commonly used with silica fume from the durability view point and are therefore, not considered in this study.

3.2.2. Mineral Admixtures

Hydrated cement paste contains approximately 70 percent C-S-H gel, 20 percent calcium hydroxide, 7 percent sulphoaluminate and 3 percent of secondary phases (*Oner et al 2005)*. The calcium hydroxide, which is formed as a result of the hydration process, affects the quality of concrete by forming cavities due to its high solubility in water and low strength. On the other hand, the mineral admixtures have a positive effect on the quality of concrete as they bind with calcium hydroxide, transforming it into secondary C-S-H gel, thereby causing the transformation of larger pores into finer pores as a result of pozzolanic reaction. The reactions are explained as below.

$$Hydration\mathrm{Re}action: \quad Cement(C_3S, C_2S) + H_2O \;\rightarrow\; C-S-H + Ca(OH)_2 \ldots (3.1)$$

$$Pozzolanic\ \mathrm{Re}action: \quad Ca(OH)_2 + SiO_2 \;\rightarrow\; C-S-H \qquad \ldots (3.2)$$

Amongst the mineral admixtures, silica fume is considered to be most efficient in contributing towards both early age as well as later age properties of concrete. Therefore, its use as a partial replacement of cement is a parameter considered in the experiment design.

However, silica fume comes under the category of costly materials. Especially in India, it is imported and is expensive. It is thought that using silica fume alone in the system may not be as economical as using another admixture like fly ash, which is abundantly available in India and is generally inexpensive. It is produced as a by product of combustion of pulverized coal in thermal power plants and hence is treated as a waste material. Fly ash alone in the concrete system does not contribute towards early age strength and requires longer curing periods to have more beneficial effect. On the other hand, the pozzolanic reaction with silica fume occurs more rapidly than fly ash due to the extreme fineness and higher portion of reactive silica in silica fume *(Bagel 1998)*.

Considering the positive effects of both the mineral admixtures, in the study undertaken, silica fume and fly ash have been used in combination to see their combined effect on improvement in both early and later age properties.

It is reported that normal replacement levels of cement by silica fume range from 5 percent to 10 percent *(ACI Committee Report 234 1996).* Also, beyond 10 percent replacement level, the mix tends to become unworkable *(Bayasi et al 1993)*. Thus, two levels of silica fume, i.e. 5 percent and 10 percent, as partial replacement of cement, are chosen in the experimental program. In addition, the levels of fly ash replacement are so chosen such that the maximum total cement replacement is up to 30 percent; as the replacement level higher than 30 percent come under the category of high volume fly ash concrete. The designation of mixes on the basis of chosen levels of admixture replacement in the experimental programme is summarized in Fig. 3.1.

In the mix designation, the first alphabet M stands for mix; the numeral following M represents the water-to-binder ratio (1, 2 and 3 are used for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively); the alphabets following the water-to-binder ratio, that is B or T, represent whether admixtures are used as binary or ternary combinations. The alphabet B represents the mix in which one of the mineral admixtures, either silica fume or fly ash, is used with cement as the cementitious material and T represents the mix containing a combination of cement and both silica fume and fly ash as mineral admixtures. In the binary mixes, the alphabet followed by 'B' represents whether silica fume (S) or fly ash (F) is used as partial replacement of cement and in the ternary mixes, alphabet followed by 'T' represents a combination of silica fume and fly ash (C). The percentage of mineral admixtures used for the various combinations are further shown in Fig. 3.1. Thus, M2TC1 corresponds to the ternary mix having water-to-binder ratio of 0.35 with 5% of silica fume and 15% of fly ash, used as replacement of cement.

3.2.3. Curing Conditions

It is well known that the hydration of cement and cementitious materials is not instantaneous and takes place over a period of time. Therefore, age is another factor that controls both strength and durability of concrete. The age of concrete is selected as a parameter in the investigation. The strength development studies are carried out at the seven curing ages of 1 day, 3, 7, 14, 28, 56 and 90 days. The curing age is extended beyond 28 days (as is the normal practice) because it is known that in mineral admixture concrete, there can be significant strength gain in the long run *(Yogendran and Langan 1991)*.

Over the past several decades, numerous failures of concrete structures during construction due to accelerated construction schedules have emphasized the early age strength gain of concrete *(Kim et al 2007)* and the importance of minimum days of curing for concrete *(Ozer and Qzkul 2004).* In the standards, the minimum curing periods under certain weather conditions are specified. However, the curing practices recommended in codes refer to either OPC concrete or the blended cement concrete in general. Most of the standards recommend increase in initial curing days for the blended cements *(IS 456: 2000, BS 8110: Part 1: 1985, ACI 308-92).* Many investigators *(Manmohan and Mehta 1981; Marsh et al 1985)* believe that a curing period of about 28 to 90 days is required for pozzolanic cement concrete specimens to attain properties superior to that of plain cement concrete. It is due to the fact that the pozzolanic reaction is highly dependent on good curing practice. However, the behaviour of all the blended cements may not be same. For instance, the mineral composition of silica fume is not the same as that of fly ash. Therefore, the curing days required for silica fume concrete may not be same as that for fly ash concrete. The system becomes even more complicated when a combination of OPC, silica fume and fly ash is used. Therefore, there is a need to investigate the effect of curing regimes on binary as well as ternary systems.

Along with this, it is well known that curing practice not only plays an important role in the development of strength of concrete, but also plays an equally important role in improving the durability through segmentation of capillary pores. Thus, the minimum number of curing days should not be selected for strength development alone, rather due consideration should be given to both strength and impermeability characteristics.

In order to know the influence of the type of curing practice on the resultant properties of concrete and to find out the minimum number of curing days required for mineral admixture concrete; curing condition is taken as a parameter in the study. The concrete specimens are subjected to five different curing regimes as summarized in Table 3.1. The performance evaluation is carried out in terms of mechanical properties which include compressive strength and tensile strength, and durability characteristics by conducting impermeability tests for five different curing conditions.

3.2.4. Super-Plasticizer Dosage

As is already mentioned, strength of concrete is inversely related to the size of pores. Agglomerated system has larger pores as compared to well-dispersed system. The use of super-plasticizers ensures proper dispersion of particles resulting in smaller pores. Hydrated cement particles have the tendency to form flocks that entrap water inside them thus reducing the availability of water for workability. The molecules of chemical admixtures that are anionic in nature, if present, get adsorbed on to the grains of cement. It results in anionic repulsion of cement particles. This repulsion of cement particles release the trapped water within the cement flocks and increase fluidity of the system. With the increase in fluidity, more surface area of cement gets exposed to water that enhances the hydration process and results in more gel formation *(Rixom and Mailavaganam 1986)*. Therefore, in order to attain fully dispersed system, optimum dose of super-plasticizer is used as an additional parameter in the investigation. The optimum dosage of super-plasticizer is determined through preliminary investigations that are presented later in this chapter.

3.2.5. Aggressive Media

At present, the durability of concrete is controlled almost exclusively by specifying certain requirements for concrete composition, casting and compaction procedures, curing conditions and most importantly, by standard compressive strength. This approach very often yields unsatisfactory results. Though it may give some indication of potential durability of concrete, such as resistance to carbonation, it cannot be taken as a general criteria because the standard compressive strength of a concrete cube is the mean value of the property of an entire cross section, where as concrete durability is governed primarily by the properties of the concrete skin *(Kropp et al 1998)*.

Although strength of concrete can be used as a reference for concrete durability because the strength of concrete specimen may reflect closely the properties of concrete skin at a later age, it is generally accepted that concrete durability is governed to a large extent by its resistance to the penetration of aggressive media. Therefore, the concrete made from some select mixes is also investigated for its resistance to penetration of aggressive salts. The aggressive salt attack is studied under three categories; Acid attack, Sulfate attack and Chloride ingress, each of which is discussed in the following sections.

3.2.5.1. Acid Attack

Concrete containing Portland cement is highly alkaline and is not resistant to attack by strong acids or compounds that may convert into acids *(Neville 2004 a).* Acids usually originate from industrial processes where concrete is employed for retaining structures. Also, for natural exposure conditions, the attack of mineral acid may occur when the natural water contains excessive amount of carbon dioxide, or in the form of acid rain which consists mainly of sulfuric acid and nitric acid. Acid attack represents a worrying topic of increasing significance, owing to the spread of damage of concrete structures all over the world due to acids. This unfavorable situation is a consequence of two factors:

1. The spreading of sources of acidic media coming into contact with concrete structures due to growing industrialization.
2. The universal alkalinity of cement based materials conditioning their high sensitivity and vulnerability in acidic environment *(Zivica and Bajza 2001)*

In the present investigation, the resistance of blended concrete is studied when subjected to three different acids, namely sulfuric acid, hydrochloric acid and nitric acid. The aggressiveness of acids is normally judged according to their pH, the attack being called severe if pH is below 5.5. However, it is established that concentration of these acids is more reliable parameter that its pH *(Monteny et al 2000)*. Therefore, in the present investigation, concentration of the acids is kept constant. The pH of all the solutions is found to vary between 2.5 to 3. The details of the solutions are given in Table 3.2. Sulfuric acid and hydrochloric acid are taken because in these solutions, in addition to acid attack, the sulfate or chloride attack also takes place simultaneously. On the other hand, nitric acid is studied because NO_x comprise of large portion of the air pollutant found in urban environments which originate from automobile exhausts. With water particles in the air atmosphere, they may form aerosols, fogs and acid rain. The pH of this rain can be as low as 3 *(Zivica and Bajza 2002)*.

3.2.5.2. Sulfate Attack

Sulfate attack is reported to be a major cause of damage to concrete for over a century now (*Ganjian and Pouya 2005).* Till today, research related to the effect of sulfate ions on the performance of concrete is in progress. Such a long and continuous research is motivated by the following factors:

1. Modification of physico - chemical characteristics of Portland cement during the last four decades *(Al Amoudi 2002)*
2. Increase in the use of blended materials with Portland cement to improve the concrete durability
3. The controversy on the influence of cement content and cement composition on sulfate attack.

Sulfates are normally found in the form of sodium sulfate, potassium sulfate, magnesium sulfate and calcium sulfate. These salts are highly soluble in water. Sulfates react with various phases of hydrated cement paste causing expansion, cracking and disruption.

In the present study, an attempt is made to investigate the effect of mineral admixtures on sulfate attack. Sulfate attack is influenced by the type of cations associated with sulfate ions and several authors have focused on its effect. Previous studies on sulfate attack are conducted mainly by using sodium sulfate, magnesium sulfate and calcium sulfate solutions *(Neville 2004 b, Lawrence 1990)*. However, due to limited solubility of calcium sulfate at normal temperature (approximately 1400 mg/l sulfate ions), sulfate attack is normally ascribable to the presence of magnesium sulfate and sodium sulfate salts *(Hossain and Lachemi 2006)*. Therefore, two sulfate salts, i.e. sodium sulfate and magnesium sulfate are chosen for studying the sulfate attack. The strength of the salt used is 5% for both the salts. The details of the solutions used are given in Table 3.2.

3.2.5.3. Chloride Ingress

Chloride ingress is a kind of physical attack on concrete. Its primary action is the corrosion of steel reinforcement and only as a consequence of corrosion of reinforcement, deterioration of surrounding concrete occurs. In the present study, the corrosion of steel is not investigated. Instead, the emphasis is laid on the mechanism of transport of chloride ions through concrete cover towards the steel reinforcement. The damaging effect of two chloride chemicals, namely sodium chloride and calcium chloride is studied. The reason for taking these two chemicals is to investigate the influence of the type of cation on the transport mechanism of chloride ions into concrete, which is supported by other researchers also *(Al-Hussain et al 1990; Wang et al 2006)*. The details of the solutions are given in Table 3.2.

3.3. MATERIALS

Same sets of materials are used throughout the investigation for casting of specimens. Relevant tests in accordance with the Indian Standard codes of practice are conducted to determine the physical properties of materials used in the study. The details of the materials along with their properties are presented in the subsequent sections.

3.3.1. Cement

Although all materials that go into concrete mix are essential, cement is the most important material and is a delicate link in the chain. Although it constitutes only 20 percent of the volume of concrete mix, but it is the most active portion of the binding medium and is also the only scientifically controlled ingredient of concrete.

Ordinary Portland Cement (43 Grade) confirming to IS 8112:1989 and ASTM C 150-94 is used throughout the investigation. Cement of same brand was obtained from local market and was stored in airtight drums when not in use to minimize the effect of weathering. Tests were conducted for each batch of cement procured. The physical properties of cement tested in laboratory are listed in Table 3.3. The chemical composition of the cement as supplied by the manufacturer is given in Table 3.4.

3.3.2. Mineral Admixtures

Mineral admixtures are the pozzolanic materials that are added to obtain specific engineering properties of cement paste or concrete. These are incorporated into mortar or concrete either through blended cements or are directly added to concrete at the time of mixing. In the present investigation, condensed silica fume and fly ash are used as mineral admixtures and are added along with cement at the time of mixing. The properties of these mineral admixtures are described below.

3.3.2.1. Condensed Silica Fume

Electric arc furnaces used in the manufacture of ferrosilicon or silicon metal release silica fume as a by-product. The fume, which has a high content of very fine spherical particles of amorphous silicon dioxide, is collected by filtering the gases escaping from the furnaces.

Elkem brand of silica fume is used in the present investigation. Chemical composition and physical properties of silica fume are given in Table 3.5. From the Table, it can be observed that silica fume is composed primarily of silica (SiO_2), although, it also contains some amount of other compounds as well. It can be assumed that silica fume is practically active silica and the rest is inert. Silica fume obtained from a single source is used throughout the investigation.

3.3.2.2. Fly Ash

Fly ash is a by-product of combustion of pulverized coal in thermal power plants. It is removed by the dust collection system as a fine particle residue from the combustion of gases before they are discharged into the atmosphere. Fly ash particles are typically spherical, ranging in diameter from less than 1μm up to 150 μm, the majority being less than 45 μm. More than 85 per cent of most fly ashes comprise of chemical compounds and glasses formed from the elements like silicon, aluminum, iron, calcium and magnesium.

For the present investigation, a good quality fly ash collected from the sixth hopper of Guru Gobind Singh Thermal Power Plant at Ropar is used. The physical and chemical properties of fly ash used are provided in Table 3.6. The fly ash used is a Class F fly ash confirming to standards laid in IS 3812: 1981.

3.3.3. Aggregates

Aggregates are relatively inert coarse particles. Not only do they impart bulk to concrete, but they also provide better durability than hydrated cement paste alone. The coarse aggregates are used primarily for the purpose of providing bulk to the concrete. On the other hand, the most important function of fine aggregates is to assist in producing workable and uniform concrete mix. The fine aggregates also assist the cement paste to hold the coarse aggregates in suspension. This action promotes plasticity in the concrete mix and prevents segregation of the paste and coarse aggregates during the transportation of concrete. The aggregates form three-quarter of the volume of concrete and hence their quality is of considerable importance.

3.3.3.1. Fine Aggregates

Throughout the present study, locally available riverbed sand confirming to IS 383: 1970 and BS 882:1992 is used. The properties of fine aggregates used are given in Tables 3.7 and 3.8. The fine aggregates confirm to Zone II as per IS 383: 1970. The fine aggregates used were washed and removed of any silt content followed by drying for twenty – four hours in an oven. The oven-dried aggregates are used for casting of cubes for each type of concrete mix.

3.3.3.2. Coarse Aggregates

The aggregates that are retained on 4.75 mm sieve are termed as coarse aggregates. The nominal size of aggregates used in present study is 10 mm. The properties of coarse aggregates used are given in Table 3.9. The coarse aggregates too were washed and removed of any silt and then dried for twenty- four hours in an oven. The oven-dried aggregates are then used for casting of specimens for each type of concrete mix. The volume of water in each mix was adjusted to compensate for the water absorption of coarse aggregates and fine aggregates.

3.3.4. Water

Potable laboratory tap water is used throughout the investigation for the preparation of specimens. The source of tap water is ground water.

3.3.5. Super-Plasticizer

Super-plasticizers are high range water reducers that are used to make the mix workable at lower water-to-binder ratios.

Several commercially available super-plasticizers are investigated through a preliminary test scheme to select the most compatible and suitable super-plasticizer. The four super-plasticizers investigated are naphthalene formaldehyde condensate named Complast SP 430; a melamine formaldehyde condensate named Sikament 600; a sodium lignosulphate named Complast P211; and Sturcturo 100 which is naphthalene based super-plasticizer with a poly-carboxylic group. Vee-bee time and slump tests are used for determining the suitability of super-plasticizer from the workability point of view. The test procedure adopted to get the optimum dosage is described in the subsequent sections.

Amongst four brands of super-plasticizers tested, Structro 100 is selected and used throughout the investigation. Structro 100 is based on carboxylic ether polymeric group. This group maintains the electrostatic charge on the cement particles and prevents flocculation by adsorption on the surface of cement particles *(Giaccio and Zerbino 2002).* It is a light yellow coloured liquid complying with requirements of IS 9103: 1979, BS 5075: Part 3: 1985 and ASTM – C494 Type F. The specific gravity of super-plasticizer is 1.2 and solid content is 40% by mass.

3.4. SPECIMEN PREPARATIONS AND CASTING

Prior to specimen preparations, it is necessary to determine the mix proportions and an optimum dosage of selected super-plasticizer for desired workability as mentioned in the previous section. The optimum dosage corresponds to the saturation point at which nearly complete dispersion of the cementitious particles is expected. This dosage is determined by using a combination of vee-bee time test and slump cone test.

3.4.1. Mix Proportions

Three control mixes (with no mineral admixtures) at water-to-binder ratios of 0.45, 0.35 and 0.25 are prepared. The concrete mix proportions are obtained by using DoE (British) Mix design. To fix the mix proportions, the water content is first adjusted for the mid water-to-binder ratio, i.e. 0.35, according to British Practice corresponding to 0 mm to 10 mm slump. Keeping in mind that natural fine aggregates and crushed coarse aggregates are used together, a water content value of 160 kg/m^3 is obtained from the appropriate table. With the water-to-binder ratio and water content known for the control mix, the total aggregate content is determined form the knowledge of specific gravity of aggregates. The percentage of fine aggregates is then determined from the British Practice (DoE) curves depending on the water-to-binder ratio, maximum size of the aggregates and grading of fine aggregates. The water content for water-to-binder ratio of 0.25 is reduced to 130 kg/m^3 to limit the cement content and the water content for water-to-binder ratio of 0.45 is increased to 190 kg/m^3 to limit the super-plasticizer content. The water contents of control mixes are finally adjusted by a trial and error procedure to obtain a final slump of 200 ± 20 mm with optimal dosage of super-plasticizers. Accordingly, total aggregate content is calculated as mentioned earlier and fine to coarse aggregate ratios are determined using British curves. Without disturbing either the water-to-binder ratio or proportions of aggregates of the respective control mix, other mixes are obtained by varying quantity of mineral admixtures from 0 percent to 30 percent as replacement of cement, used either in a binary or a ternary combination. The mix details of control mixes are listed in Table 3.10.

3.4.2. Determination of Optimum Super-Plasticizer Dosage

Silica fume, fly ash and super-plasticizer are used in the present investigation to obtain superior mechanical and durability properties, as well as to achieve high workability in its fresh state at low water-to-binder ratios. In order to predict concrete workability, and hence to find out optimum super-plasticizer dosage for a required workability accurately, the tests are directly conducted on concrete. One of the most commonly used methods for measuring concrete workability, i.e. slump cone test, together with Vee-bee test are adopted in the current study. Both the tests are performed simultaneously in order to achieve a correlation between the two.

The following procedure is adopted for mixing the constituents for workability studies:

- All the mix ingredients in the required proportions are measured.
- Coarse aggregates and the fine aggregates are placed in the mixing drum and then the mixer is rotated at the slow speed of about 140 rev./min. for 1 minute. In the mean time, the cementitious materials (Portland cement, silica fume and fly ash) are mixed together separately in another container.
- The cemetitious materials are then put in the mixing drum and the resultant mixture is dry mixed for one minute with the mixer operating at slow speed followed by addition of half of the total water content during the next one minute mixing.
- The remaining water along with super-plasticizer is then added and mixed for 1.5 minutes at slow speed. (Super-plasticizer is taken as percentage by mass of cementitious material, which includes cement, silica fume and fly ash, if any present). Water content of super-plasticizer is taken into account when calculating the total water content of the mix *(Duval et al 1998)*.
- The mixer is stopped and the material is scraped from the sides of the mixer and then further mixing is continued for 2 minutes or till a uniform and homogeneous mix is achieved at high speed. The prepared mix is used for obtaining Vee – bee time and slump value.

In order to first decide on the type of super-plasticizer best suited for the work, the trials are carried out on the control mix (no silica fume and fly ash) at the water-to-binder ratio of 0.25. Out of the four super-plasticizers tried, Structro 100 is found to exhibit maximum slump and minimum Vee-bee time and hence the same is selected and is used throughout. After that, the trials are carried out extensively for all the mixes at water-to-binder ratio of 0.45. At this water-binder ratio, some mixes are found to be sufficiently workable even without super-plasticizers as visibly observed and as confirmed by the values of slump and Vee-bee time. Therefore, the mix could be prepared without super-plasticizer addition. However, as mentioned in Section 3.2, degree of dispersion of cementitious material is taken as a factor governing pore size distribution and hence strength and durability aspects, and to avoid variability due to partial dispersion, complete dispersion through super-plasticizer addition is adopted in the experimental scheme. Therefore in order to ensure complete dispersion, optimum super-plasticizer dose is determined for these mixes as well.

Also, for the water-to-binder ratio of 0.25, the mix without super-plasticizer is found to be quite stiff as observed visually and therefore is not considered. The trial was done even for the mix at water-to-binder ratio of 0.2, without addition of silica fume or fly ash. However, the slump and Vee-bee time was not adequate even with the super-plasticizer dosage higher than permissible maximum dose of 3 percent as recommended by the manufacturer. Thus, lowest water-binder ratio that could be used with the present super-plasticizer is kept at 0.25 and the same is adopted in the experimental scheme as lowest water-binder ratio.

In this way, the trials are done for all 24 mixes at water-binder ratios of 0.45, 0.35 and 0.25 with various combinations of silica fume and fly ash. For each mix, the super-plasticizer dosage is given step increments and the corresponding Vee-bee time and slump are noted. The saturation point is obtained from the slump verses super-plasticizer dosage curves; which is taken as that value of super-plasticizer beyond which the addition of more super-plasticizer will not increase slump. In other words, super-plasticizer will have no further plasticizing effect after this dosage. Three determinations of slump and Vee-bee time are made for each sample and the mean value is taken. It is worth mentioning at this stage that for the selected dose of super-plasticizer, no segregation is observed at any stage.

The results of these tests are presented in Figs. 3.2 to 3.7 where slump is plotted against super-plasticizer dosage and in Fig. 3.8 where optimum super-plasticizer dosage is plotted against water-binder ratio. The nomenclature used in these figures is given in Fig 3.1. The relation between the super-plasticizer dosage and the type of mineral admixture used is discussed in the following sections.

3.4.2.1. Super-Plasticizer Dosage and Slump for Binary Mixes

The results of variation of slump with super-plasticizer dosage for binary mixes are presented in Figs. 3.2 to 3.4 for the three series of water-to-binder ratios studied. Normally, for all mixes, with an increase in super-plasticizer dosage, the value of slump increases initially and then with further increase in dosage, the slump either remains constant or starts decreasing, indicating the saturation point. For binary mixes containing silica fume as mineral admixture, at the same water-to-binder ratio, with increase in silica fume content in concrete, the value of slump decreases and hence the optimum super-plasticizer dosage increases, which is clear from the rightward shift in the curves containing silica fume (Figs. 3.2 to 3.4). This can be attributed to high specific surface of silica fume with an average particle size of 0.1µm. However, this is not the sole factor affecting the increase in super-plasticizer demand for silica fume mixture. Along with the high specific surface area, the particles of silica fume are chemically highly reactive and have affinity for multilayer adsorption of super-plasticizer molecules, which is also supported by other researchers *(Park et al 2005, Nehdi et al 1998).* As a result, with increase in silica fume percentage, the quantity of available super-plasticizers in the concrete system for dispersion decreases leading to steep increase in the super-plasticizer demand to maintain required workability. The same type of behaviour is observed for the entire range of water-to-binder ratios with an exception for water-to-binder ratio of 0.25. At this ratio, with the addition of 5% silica fume, the optimum dosage of super-plasticizer decreased by a small amount from 4% (for control mix) to 3.75%. This reverse trend can be explained by considering the dispersion action of flocculated cement particles by silica fume particles in combination with super-plasticizer. Actually, the effectiveness of super-plasticizer is enhanced in the presence of silica fume. Similar observations are made in some previous studies also *(Duval and Kadri 1998; Yogendran et al 1987).*

The binary mixes with fly ash as the mineral admixture is observed to have just the opposite effect upon fresh properties of concrete in terms of workability and optimum dosage of super-plasticizer required as compared to the effect of silica fume. With incorporation of fly ash, the curve of slump verses super-plasticizer dosage shift towards left compared to the control mix for all water-to-binder ratios studied, indicting decrease in water demand and hence a decrease in the optimum percentage of super-plasticizer required. The reduction in water demand of concrete caused by the presence of fly ash is ascribed to its spherical shape, which reduces the frictional forces among the angular particles of OPC, called ball – bearing effect *(Termkhajornkit et al 2001, Park et al 2005).* These spherical particles easily roll over one another, reducing inter-particle friction. The spherical shape also minimizes the surface to volume ratio of particles, resulting in low fluid demand. Also, due to the electrical charges, the fine fly ash particles become adsorbed on the surface of cement particles, which thus become deflocculated, reducing the water demand. In other way, the effect of fly ash can be considered similar to the action of super-plasticizer.

3.4.2.2. Super-Plasticizer Dosage and Slump for Ternary Mixes

While silica fume tends to increase the optimal super-plasticizer dosage, fly ash, on the other hand, acts in a reverse way. Thus, by using both in combination, beneficial effect of fly ash on fluidity can be used to compensate the loss of slump with silica fume addition. As evident from Figs. 3.5 to 3.7, when fly ash is used in combination with silica fume, the optimum super-plasticizer dosage determined is lower in comparison to the value obtained in the corresponding mixes having only silica fume. Further, for the same silica fume content, increasing fly ash content from 15% to 20% resulted in a shift of slump verses super-plasticizer dosage curve towards left indicating the positive influence of fly ash on optimum super-plasticizer dosage in ternary mixes. The trend is found to be just reverse while increasing silica fume content for same fly ash percentage. Among the ternary mixes, mix TC2 is found to require least super-plasticizer dosage while TC3 require highest optimum super-plasticizer dosage for all the three water-to-binder ratios.

3.4.2.3. Relation Between Water-to-Binder Ratio and Optimum Super-Plasticizer Dosage

Fig. 3.8 shows the results of optimum super-plasticizer dosage obtained for all mixes at various water-to-binder ratios. From the figure, it is observed that as the water-to-binder ratio decreases, the optimum dosage of super-plasticizer increases. With the decrease in water-to-binder ratio, more number of super-plasticizer molecules are required for adsorption on the surface of cement and mineral admixture particles in order to increase the fluidity of the mix. The optimum dosage increases sharply as the water-to-binder ratio is decreased from 0.35 to 0.25 as compared to the shift from 0.45 to 0.35. For the control mix, the optimum super-plasticizer dosage increases from 1.25% to 4% as the water-to-binder ratio decreases from 0.35 to 0.25 as compared to the change from 0.2% to 1.25% with the decrease in water-to-binder ratio from 0.45 to 0.35. This is because at very low water – binder ratio, cement particles are very close and to overcome inter particle friction and inter particle forces of attraction, higher optimum dose of super-plasticizer is required.

The optimum super-plasticizer dosage values and the corresponding slump values are presented in Table 3.11. Although the slump values for optimum dosage of super-plasticizer are in close range i.e. 200 ± 16 mm, some systematic variation of these values with mineral admixture content can be observed. With the increase in silica fume content the maximum slump obtained reduces, whereas the maximum slump increases with fly ash addition in binary mixes. An exception to this behavior is observed in the case of mix with 0.25 water-to-binder ratio and 5% silica fume content. In ternary mixes, the effects of silica fume and fly ash on maximum slump are similar to those observed for binary mixes.

3.4.2.4. Relationship between Slump and Vee-Bee Time

For the mixes with medium workability, Vee-bee time is also measured along with slump in order to formulate a relation between the two for mineral admixture concrete. Fig. 3.9 shows the graph for slump versus Vee-bee time. In the graph, the green line shows the approximate relationship between slump and Vee-bee time for the normal OPC concrete without using super-plasticizers *(Neville 2004 a)* and the blue line is the best fit obtained for the test results in the present study. The marked shift of the present curve for concrete containing mineral admixtures and super-plasticizers from the existing curve for normal concrete can be observed from the graph. For higher values of Vee –bee time, the amount of slump required is almost same from both the curves. However, when the Vee – bee time is lesser than 5 seconds, the difference in the values of slumps obtained from the two curves differ in the range of 20 mm to 50 mm. Thus, it can be said that for equal Vee-bee time, the mixes with mineral admixtures exhibit 20 mm to 50 mm higher slump than the mix containing Portland cement only. This shift in the curve can be due to the effect of cohesive nature of the mix with silica fume, fly ash and super-plasticizers.

3.4.3. Casting of Specimens

For the different tests performed, the shape, size and number of specimens prepared are presented in Table 3.12. The Table also contains the information regarding the number of curing conditions adopted, the testing age and the number of replicates cast for each test.

For casting any mix proportion, the mixing of all the ingredients is done in the manner similar to the one described earlier for workability tests. All the moulds are properly oiled before casting of specimens. The mould is filled in three layers. Each layer is compacted on the vibration table with fixed revolutions per minute. The top surface is properly finished by means of a float. After casting, the moulds are stored undisturbed for 24 hours and are kept covered with a plastic sheet to prevent the loss of hydration water due to evaporation. The specimens are demoulded after 24 hours. However, for mixes prepared at water-to-binder ratio of 0.25, the specimens are demoulded only after 48 hours because the high dose of super-plasticizers used delayed the initial setting of the mix.

3.4.4. Curing Process

After demoulding, all specimens (except those meant for curing regime R2) are transferred carefully to water baths maintained at the reference curing temperature of 27 ± 2°C. The temperature controlled water baths has heating elements, thermostats and pumps (for circulation of water) to keep the temperature at desired level (Plate 3.1). The temperature of water in the tank is kept within this range for the entire period of curing. For curing regime R2, the specimens are to be air cured. Therefore the specimens are kept in the atmosphere having relative humidity varying from 50 ± 10% percent and with temperature in the range of 27 ± 5°C.

3.5. TEST DESCRIPTION

This section gives a brief description about the principle and procedure of various tests performed during the investigation.

3.5.1. Compressive Strength Test

This test is performed on the cubical specimens as per IS 516: 1959. At the required age of testing, the cubes are taken out from the curing tank and cleaned with cloth to wipe out excess water from the surface in order to bring them to saturated surface dry condition. If, according to the curing condition, the cubes are already in the dry condition, they are tested as such. These specimens are then placed on the automatic compression-testing machine (3000 KN Capacity) in such a way that it is tested at right angles to the as cast position. The compressive load is applied through the hydraulic jack at a constant rate of 140 kg/cm^2/min till failure. The average failure stress of six cubes is considered as the representative compressive strength of the mix. The automatic compression testing machine used for measurement of compressive strength is shown in Plates 3.2 and 3.3.

3.5.2. Tensile Strength Tests

Although concrete is not normally designed for tension, the knowledge of tensile strength often plays a vital role in concrete making. In concrete, cracks can propagate very easily in tension and the cracking of concrete due to its tensile stresses being exceeded may cause serious serviceability and durability problems *(Bhanja and Sengupta 2005; Choi and Yuan 2005)*. Strength in tension is important both for reinforced and un-reinforced concrete structures *(Neville 2004 a).* There are two commonly used methods to find strength in tension, viz. flexure strength test and split tensile strength test. Both these tests are performed in the present investigation.

3.5.2.1. Flexure Strength Test

For this test, plain concrete beams of size 150 × 150 × 700 mm are cast and tested as per IS 516: 1959. On the testing age, the specimen is placed on two rollers that are 600 mm apart. The two point load is then applied on the uppermost surface as cast in the mould, by means of steel rollers placed in such a way that the distance of each roller from nearest support remains one – third of the simply supported span, i.e. nearly 200 mm (as shown in Plate 3.4). The load is increased continuously, without shock, at a rate of 400 kg/min. until failure and the maximum load applied at failure is recorded. The flexure strength of the specimen (expressed as modulus of rupture) is then calculated as follows:

$$f_r = \frac{PL}{bd^2} \qquad if \;\; a > 200mm$$

$$\ldots (3.1)$$

$$f_r = \frac{3Pa}{bd^2} \qquad if \;\; a > 170mm \; but < 200mm$$

The specimen is rejected if ‘a’ < 170 mm.

where a = The distance between the line of fracture and the nearest support (mm)

b = Measured width of specimen (mm)

d = Depth of specimen (mm)

L = Length of span on which the specimen is supported (mm)

P = Maximum load applied to the specimen (N)

In this way, the average of three values is taken as the representative modulus of rupture.

3.5.2.2. Split Tensile Strength Test

Split tensile strength test is well known indirect test used for determining tensile strength of concrete. This test is performed along with flexure strength test in order to establish the relation between the two. Split tensile strength test is simpler to perform and gives more uniform results than other tests. This test is performed as per IS 5816: 1970 and ASTM C-496. In this test, a cylindrical specimen (150 mm diameter and 300 mm height) is taken and placed with its axis horizontal between the platens of compression testing machine. The compressive line load is applied along the opposite generators of concrete cylinder. Due to the applied line loading, a fairly uniform tensile stress is introduced over nearly two – third of the loaded diameter. The magnitude of this tensile stress (acting in the direction perpendicular to the line of action of applied compression) is given by:

$$f_{sp} = \frac{2P}{\pi DL} \qquad \ldots (3.2)$$

where P = Applied load at failure (N)

D = Diameter of cylinder (mm)

L = Length of cylinder (mm)

In this way, the average of six values is taken as the representative split tensile strength of concrete. The position of specimen and the type of failure in split tensile test is shown in Plates 3.5 and 3.6.

3.5.3. Non Destructive Tests

At present, the investigation of non-destructive testing techniques is a very popular subject. Among the available non-destructive methods, rebound hammer and ultrasonic pulse velocity tests are the most commonly used non-destructive techniques adopted for evaluating the quality of in-situ concrete structures. In this study, these two are performed on the specimens cast for compressive strength studies prior to the destructive compressive strength test in order to assess the quality of concrete. An effort is also made to establish a combined relationship between the non-destructive techniques and compressive strength. The testing procedures followed for the non-destructive tests are described as under.

3.5.3.1. Rebound Hammer Test

The rebound hammer test is performed as per the procedure described in IS 13311: Part II – 1992. The objective of performing rebound hammer test is to:

1. Assess the uniformity of concrete
2. Assess the quality of concrete in relation to standard concrete
3. Establish a relation between the rebound index and the compressive strength.

Rebound hammer test is based on the principle that the rebound of an elastic mass depends on the hardness of the surface against which the mass impringes. The energy absorbed by the concrete is related to its strength.

The rebound hammer test is performed on the surface perpendicular to the cast surface of the cubical specimens. The surface is prepared by the abrasive stone so that the test surface is ground smooth. A grid of size 30 mm × 30 mm is then formed on the prepared surface. In this way the grid is formed on the four faces of the cubical specimen. The specimen is kept between the two platens on the compression-testing machine and a fixed load of magnitude approximately $7N/mm^2$ is then applied to the specimen. A fixed amount of energy is applied by striking the hammer perpendicular to the test surface. After impact, the rebound number is noted. In this way, observation is taken at each point on the grid (as shown in Plate 3.7), making it 64 readings for each specimen. Average of these readings, after deleting outliers, is taken as the rebound index for this specimen. The average of six specimens is taken as the representative rebound index for each condition.

3.5.3.2. Ultrasonic Pulse Velocity Test

The ultrasonic pulse velocity test is performed as per the procedure laid out in IS 13311: Part I – 1992. The ultrasonic pulse velocity test is based on the principle that the ultrasonic pulse, generated by a transducer, when induced into concrete undergoes reflections and is then finally detected by the receiving transducer. Since the distance between the generating transducer and the receiving transducer remains same, the velocity of wave depends only on time required by the wave to travel through concrete. If the concrete is homogeneous, dense and uniform, lesser time will be taken by pulse to travel, thereby giving more velocity. Therefore, a comparative higher velocity means better quality.

The test is performed as per standards laid down by IS 13311 (Part 1): 1992. Direct transmission method is adopted for testing. The transducer used has a natural frequency of 56 KHz. The test is performed on cubic surfaces normal to the cast position. Therefore, four surfaces are available for each specimen. Two faces are used for getting one value of ultrasonic pulse velocity by direct transmission giving, in all, two values for each sample. To ensure that the ultrasonic pulses generated at the transmitting transducer pass into the concrete and are then detected by the receiving transducer, petroleum jelly is used as a couplant between concrete and face of each transducer. The observations are made on six specimens and the mean of the observed velocities is taken as the representative ultrasonic pulse velocity value. The equipment used for conducting ultrasonic pulse velocity test is shown in Plate 3.8.

3.5.4. Water Impermeability Test

Most deterioration processes have two stages. Initially, aggressive fluids (water, solution etc.) penetrate through the capillary pore structure of the concrete to reaction sites. This penetration is followed by the actual chemical or physical deterioration reactions.

To access concrete durability during the first stage, tests that measure transport rates in concrete are required. The transport rate, normally called permeability of concrete, is measured in terms of flow of water through the concrete specimen. However, there is a problem with the permeability test: in good quality concrete, there is no flow of water through concrete even after some days also.

In the present investigation, since mineral admixtures like silica fume and fly ash are used, they make the pore structure refined by reducing the size of pores. It is expected that the water permeability tests might not give any data for comparison of mixes. Therefore, water impermeability test is performed instead of water permeability test. The test is performed as per the German Standard DIN 1048 (Part 5).

For performing the test, 150 mm cubical specimens are cast similar to the procedure adopted for casting specimens for strength tests. The specimens are subjected to all the five curing regimes and the test is carried out at the age of 90 days. For conducting the test, the concrete specimens are exposed to a water pressure of 0.5 N/mm^2 acting normal to the mould filling direction, for a period of three days. Three cell apparatus is used for performing the test, i.e. three specimens are subjected to the said pressure at the same time (as shown in Plate 3.9). The pressure is kept constant throughout the test. At the end of three days, the pressure is released and the specimens are split down the center with the face which was exposed to water facing down. After about ten minutes, the maximum depth of penetration in the direction of cube thickness is measured on each of the split halves in mm. The mean of the maximum depth of penetration obtained from the three specimens tested is taken as the test result.

3.5.5. Durability Tests

Although prescriptive specifications of concrete served the industry reasonably well in the past, the current effort is in moving from prescriptive to performance based specifications in order to use the available construction material more innovatively. While compressive strength of concrete is a good indicator of its load resistance, it is not a major indicator of performance of concrete called durability. Thus in the present work, some of the durability studies are also conducted in which the specimens are subjected to a certain percentage of aggressive solutions for some period and the loss in performance is monitored.

The durability studies are started only after finalizing the best ternary and binary mixes and the most appropriate curing regime for these mixes. It is found that the curing regime R3 is the most appropriate curing regime, in which, the specimens are cured in water tank maintained at temperature of 27 ± 2°C for 7 days followed by continuous air curing in the lab environment at around 27 ± 5°C and 50 ± 10% RH till the age of 90 days. After subjecting the specimens to the most appropriate curing regime for three months, the specimens are kept in the respective aggressive solutions for a period of up to one year. The testing techniques that are followed for acid attack, sulfate attack and chloride ingress, respectively, are explained in the succeeding sections.

3.5.5.1. Acid attack

In order to evaluate acid corrosion resistance of the prepared mixes, the specimens are tested in three aggressive chemical environments. These are simulated by using the following chemicals: 1% sulfuric acid (H_2SO_4), 1% hydrochloric acid (HCl), and 1% nitric acid (HNO_3). The value of pH obtained by using the above mentioned concentration of acids come under the category of strong chemical attack as per DIN EN 206 Standard. The solution is renewed on monthly basis in order to maintain uniform concentration and pH throughout the testing age. The test program concludes after a period of 48 weeks. The tests are completed in triplicate to confirm reproducibility of the test results. The tanks used for storing the specimens in various acids are shown in Plates 3.10 and 3.11.

The weight loss of specimens is monitored initially at 1 week interval till 4 weeks, then at an interval of 2 weeks till 8 weeks and then once every 4 weeks till the end of testing age of 48 weeks. The weight is measured using balance with 0.5 gram sensitivity. At the time of weight measurement, the cubes are rinsed with tap water and brushed gently with wire brush to remove loose surface debris and then dried for 24 hours to constant weight and are then weighed. After weighing, the cubes are returned to the acid channel. The weight loss of material (WL) is determined as follows:

$$WL = \frac{W_r - W_s}{W_r} \times 100 \qquad \text{… (3.3)}$$

where W_r is the average initial weight in grams of three specimen before immersion in the acid solution (after the end of initial curing regime) and W_s is the average weight in grams of the specimens after it is immersed in acid for the required time.

Mass loss is a simple traditional test measurement in acid attack tests. However, mass change results could depend on sample size and cement type and are also influenced by the way of treating the reaction products and decomposed cement paste on samples in a test *(Chang et al 2005)*. Therefore, along with weight loss test, compressive strength is also measured. It is considered to be a more reliable measure to judge the performance of concrete subjected to acid attack. Compressive strength is monitored at the end of 8, 16, 24, 32, 40 and 48 weeks of exposure and then compressive strength loss (CSL) is calculated as follows:

$$CSL = \frac{f_{cr} - f_{cs}}{f_{cr}} \times 100 \qquad \text{… (3.4)}$$

where f_{cr} is the reference compressive strength of specimen before immersion in the acid solution in MPa and f_{cs} is the average compressive strength of the specimens after immersion in acid solutions for the required time.

3.5.5.2. Sulfate Attack

After the common initial curing regime, the specimens are stored in two different solutions containing 5% of sodium sulfate and 5% of magnesium sulfate, respectively. The above exposure conditions represent very severe sulfate exposure conditions. The cube specimens are fully submerged in the test solutions and the concentration of the solution is adjusted on monthly basis throughout the testing age. In order to intensify the degradation process, the specimens are subjected to monthly cycles of wetting and drying. Each cycle starts with two days of drying, then submerging them in containers with the appropriate type of solution and leaving them in the solution for 5 days. After 5 days, the specimens are removed from the containers and are left to dry in the laboratory for next 2 days and then again submerging them in the solution for another 5 days. After the second immersion, the specimens are left to dry for 2 days followed by submersion for again 12 days. The last immersion period is kept as 12 days in order to ensure that the specimens are in saturated state before measurements. The solutions used for the immersion tests are renewed every four weeks to minimize the increase in pH due to the leaching of hydroxide ions from the specimens.

The deterioration of specimens is investigated at the end of 2, 4, 6, 8, 10 and 12 cycles of exposure by measuring compressive strength loss which is calculated as follows:

$$CSL \quad = \quad \frac{f_{cr} - f_{cs}}{f_{cr}} \times 100 \qquad \ldots (3.5)$$

where f_{cr} is the reference compressive strength of specimen before immersion in the sulfate solution, in MPa (five days prior to the end of initial curing regime, the specimens are immersed in water and at the end of 90 days, the specimens are taken out and their initial weight, compressive strength and ultrasonic pulse velocity are measured and are considered as the reference values); and f_{cs} is the average compressive strength of the specimens after immersion in sulfate solutions, in MPa. At each test age, the compressive strength of three specimens stored in test solution is determined and the average of these values is taken as the representative compressive strength.

Prior to compressive strength tests, the cube specimens are visually examined for any signs of deterioration in the form of cracking, spalling, disintegration etc. Then the ultrasonic pulse velocity is measured for each specimen. For measuring weight loss, the specimens are cleaned gently to remove loose particles and then weighted. The weight loss of material (WL) is determined as follows:

$$WL \quad = \quad \frac{W_r - W_s}{W_r} \times 100 \qquad \ldots (3.6)$$

where W_r is the average initial weight of three specimen before immersion in the sulfate solution and W_s is the average weight of the specimens immersed in sulfate solutions for required time, in grams.

3.5.5.3. Chloride Ingress

At the end of initial curing regime of 90 days, the cubical specimens are sealed on all sides except the testing surface in order to ensure unidirectional chloride penetration into the specimen. The seal is provided with the help of three coats of acrylic paint. On the testing surface, a 30 mm dyke is made with cut out pieces of glass to allow for ponding as shown in Plate 3.12. Two different ponding solutions, one containing 5% sodium chloride and other having 5% calcium chloride respectively are used. In order to intensify the degradation process, the specimens are subjected to weekly cycles of wetting and drying. Each cycle starts with two days of drying, then the required solution is put in the dyke for next 5 days. This weekly sequence is continued for 48 weeks that is equivalent to nearly one year of exposure.

At the end of 48 weeks, a core of diameter 50 mm is taken out from the centre of the cube with the help of diamond core cutter as shown in Plates 3.13 to 3.16. The core is further cut into thin slices from the surface to the centre of core as shown in Fig. 3.10. The concrete slices obtained are dried and then ground into a thin powder and passed through 150µm sieve. This fine powder is collected in polythin bags as shown in Plate 3.17 for further chemical analysis.

The powder so collected is used to determine free chloride and total chloride content at various depths of the specimen. Both free chlorides and total chlorides are found in order to obtain a general relationship between the free chloride and total chloride content in concrete for various types of blended concretes. It also gives an idea of chloride binding capacity of concrete. Actually, chlorides occur in concrete both in free or uncombined form as well as bound form, in which they are physically bound to cement hydration products through adsorption or chemically bound in the form of Friedel's salt. Although, free chlorides are generally believed to be responsible for the initiation of corrosion *(Thangavel and Rangaswamy 1998)*, the chloride threshold value necessary to initiate corrosion of steel bars in concrete is generally provided in terms of total chlorides *(Alonso et al 2000; Mohammed and Hamada 2003)*. Therefore, the knowledge of both free and total chloride ions is important to have an idea about the chloride binding capacity of concrete.

The concentration of chlorides at a given depth is determined through potentiometric titration with 0.1M silver nitrate ($AgNO_3$) solution using Metrohm 798 MPT Titrano automatic titrator as shown in Fig. 3.11 and Plate 3.18. The steps involved in determining chloride content is shown schematically from Plates 3.19 and 3.22. The chloride concentration is computed from the inflection point of a potential vs titration volume plot. For determining free chloride content, 3 grams of the powdered concrete sample is taken and is transferred to 100 ml beaker. 50 ml of distilled water is added in the beaker. The sample is thoroughly mixed by mixing for 15 minutes with the magnetic stirrer with hot plate. After 15 minutes of stirring, the solution is filtered using Whatmann No. 1 filter paper. The filtered water is placed on 798 MPT Titrano. The electrode is inserted into the beaker and titration is started. The chloride concentration is computed from the inflection point of a potential vs titrant volume plot. For finding total chlorides, nitric acid (6N) is used in place of distilled water and the same procedure is repeated.

The chloride content of the concrete sample is calculated using the following expression:

$$\%\ Chloride = \frac{35.453\,V_s\,N_s}{W} \qquad \dots (3.7)$$

where V_s is the volume of $AgNO_3$ used in milliliters to neutralize chloride, N_s is the normality of $AgNO_3$ and W is the weight of powder sample. This test is also conducted in triplets and the average of three values is taken as the representative chloride concentration at the required depth. After obtaining chloride content at various levels, chloride profile is made for each mix in terms of chloride content by percentage of concrete mass.

3.6. INFERENCES ON FRESH PROPERTIES OF CONCRETE

From the results on the variation of slump with super-plasticizer dosage for all mixes, it is established that the super-plasticizer dosage has a saturation point beyond which the value of slump do not increase with the further increase in super-plasticizer dosage.

Regarding the role of mineral admixtures on workability of concrete, it is observed that, at the same water-to-binder ratio, with increase in silica fume content in concrete, the value of slump decreases and hence the optimum super-plasticizer dosage increases. It can be attributed to high specific surface of silica fume with an average particle size of 0.1μm and to higher reactivity of silica fume particles and affinity for multilayer adsorption of super-plasticizer molecules. On the other hand, with incorporation of fly ash, optimum percentage of super-plasticizer required decreases. The reduction in water demand of concrete caused by the presence of fly ash is ascribed to its spherical shape, which reduces the frictional forces among the angular particles of cement, called ball – bearing effect.

When silica fume and fly ash are used in combination in ternary mixes, silica fume tends to increase the optimal super-plasticizer dosage and fly ash tends to decrease the same. The overall benefit of using fly ash in combination with silica fume is that the optimum super-plasticizer dosage required is lower in comparison with the corresponding mixes having only silica fume.

Regarding the effect of water-to-binder ratio on optimum super-plasticizer dosage, it is observed that as the water-to-binder ratio decreases, the optimum dosage of super-plasticizer increases. With the decrease in water-to-binder ratio, more number of super-plasticizer molecules are required for adsorption on the surface of cement and mineral admixture particles to increase the fluidity of the mix. Further, the optimum dosage increases sharply as the water-to-binder ratio is decreased from 0.35 to 0.25 as compared to the dosage required when the shift in water-to-binder ratio is from 0.45 to 0.35. This is because at very low water – binder ratio, cement particles are very close and to overcome inter particle friction and inter particle forces of attraction, higher optimum dose of super-plasticizer is required.

From the curve that is developed between vee-bee time and slump, it is observed that for equal vee-bee time, the mixes with admixtures require 20 mm to 50 mm higher slump than the mix containing Portland cement only.

Table 3.1. Summary of curing regimes adopted

S.No.	Curing Regime	Description	Remarks
1.	R1	Continuous water curing at temperature of 27 ± 2°C	Ideal curing
2.	R2	Continuous air curing in the lab environment at around 27 ± 5°C and 50 ± 10% RH	Can occur in worst case
3.	R3	Initial 7 days of water curing followed by air drying (as in curing regime R2)	Realistic curing practice for OPC concrete
4.	R4	Initial 28 days of water curing followed by air drying (as in curing regime R2)	Curing practice adopted for pozzolanic concrete in research
5.	R5	Initial 14 days of water curing followed by wetting and drying cycles of 7 days duration	Wetting and drying exposure

Table 3.2. Details of the storage solution

Type of attack	Chemical Used	Strength (Percent)
Acid Attack	HCl	1
	H_2SO_4	1
	HNO_3	1
Sulphate Attack	Na_2SO_4	5
	$MgSO_4$	5
Chloride Attack	NaCl	5
	$CaCl_2$	5

Table 3.3. Physical properties of 43 Grade ordinary Portland cement

S.No.	Characteristics	Results obtained	Requirements as per IS: 8112 – 1989
1.	Normal consistency (%)	30 – 32	
2.	Setting time		
	(i) Initial setting time	120 - 150 minutes	Minimum 30 min.
	(ii) Final setting time	230 - 265 minutes	Maximum 600 min.
3.	Specific gravity (by specific gravity bottle)	3.12 - 3.15	
4.	Soundness (by Le-Chatelier's method)	1.5 - 2.0 mm expansion	Maximum 10 mm
5.	Fineness (percentage retained on 90 μ sieve)	3.0 - 5.0 percent	Maximum 10%
6.	Compressive strength		
	(i) 3 days	26 – 27.5 MPa	Minimum 23 MPa
	(ii) 7 days	34 – 36.5 MPa	Minimum 33 MPa
	(iii) 28 days	45 – 47.5 MPa	Minimum 43 MPa

Table 3.4. Chemical composition and some physical properties of Cement

S.No.	Constituent	Weight (percent)
1.	Calcium oxide (CaO)	61.7
2.	Silica (SiO_2)	22.4
3.	Aluminum oxide (Al_2O_3)	5.93
4.	Iron oxide (Fe_2O_3)	4.91
5.	Total sulfur (SO_3)	2.28
6.	Magnesium oxide (MgO)	1.5
7.	Potassium oxide (K_2O)	0.65
8.	Available alkalis as sodium oxide (Na_2O)	0.122
9.	Loss on ignition	1.27
10.	Insoluble Residue	4.52
11.	Blaine fineness (m^2/kg)	287.8
12.	Density (kg/m^3)	3150

Table 3.5. Chemical and physical properties of silica fume

S.No.	Constituent	Weight (percent)
1.	Calcium oxide (CaO)	0.5
2.	Silica (SiO_2)	90.7
3.	Aluminum oxide (Al_2O_3)	0.68
4.	Iron oxide (Fe_2O_3)	2.2
5.	Total sulfur (SO_3)	-
6.	Magnesium oxide (MgO)	1.47
7.	Potassium oxide (K_2O)	0.9
8.	Total alkalis as sodium oxide (Na_2O)	0.86
9.	Loss on ignition	2.5
10.	Insoluble Residue	-
11.	Density (kg/m^3)	650
12.	Specific surface (m^2/kg) by nitrogen adsorption	21,000
13.	Mean particle diameter (μm)	0.1
14.	Specific gravity	2.24
15.	Accelerated pozzolanic activity index with OPC at 7 days	102%

Table 3.6. Chemical and physical properties of fly ash

S. No.	Constituent	Weight (percent)
1.	Loss on ignition	2.15
2.	Silica (SiO_2)	56.8
3.	Aluminum oxide (Al_2O_3)	25.8
4.	Iron Oxide (Fe_2O_3)	6.43
5.	Calcium Oxide (CaO)	1.7
6.	Magnesium Oxide (MgO)	0.6
7.	Total Sulfur as sulfur trioxide (SO_3)	1.4
8.	K_2O	0.79
9.	Available alkalis as sodium oxide (Na_2O)	0.36
10.	Insoluble residue	84.9
11.	Loss on ignition	2.15
12.	Specific gravity	2.42
13.	Specific surface: Blain (m^2/kg)	250
14.	Colour	Grey

Table 3.7. Sieve analysis of river bed sand

Weight of sample taken: 1.0 kg

IS sieve size	Weight retained, gm	Percentage retained	Cumulative percentage retained	Percentage passing
4.75 mm	50.5	5.05	5.05	94.95
2.36 mm	45	4.5	9.55	90.45
1.18 mm	80.5	8.05	17.6	82.4
600 micron	270	27	44.6	55.4
300 micron	355.5	35.55	80.15	19.85
150 micron	154.5	15.45	95.16	4.84
Pan	44	4.4	-----	-----
		Total	251.9	

Fineness Modulus 2.519

Table 3.8. Physical properties of fine aggregates

S. No.	Property	Observed Values
1.	Unit mass	1.692 kg/m^3
2.	Specific gravity	2.54
3.	Percentage absorption	1.95 per cent

Table 3.9. Properties of coarse aggregates

S.No.	Property	Result
1.	Unit mass (kg/m^3)	1.68 kg/m^3
2.	Specific gravity	2.64
3.	Percentage absorption	1.12 percent
4.	Sieve Analysis	Cumulative percentage retained (%)
	20 mm	0
	10 mm	2.5
	4.75 mm	92.8

Table 3.10. Mix proportions for control mix

S.No.	Mix designation	Water binder ratio	Mix proportions (kg/m^3)			
			Cement	Aggregates		Water
				Fine	Coarse	
1.	M1	0.45	422	557	1183	190
2.	M2	0.35	457	524	1283	160
3.	M3	0.25	520	521	1340	130

Table 3.11. Fresh properties of mixes

Mix type	**W/B**	**Notation**	**MA (% replacement of cement)**		**Optimum SP dosage (wt. % of binder)**	**Slump (mm)**
			SF	**FA**		
Control mixes	0.45	M1	-	-	0.2	205
	0.35	M2	-	-	1.25	211
	0.25	M3	-	-	4	184
Binary mixes	0.45	M1BS1	5	-	0.3	194
		M1BS2	10	-	0.7	192
		M1BF1	-	30	0.1	215
	0.35	M2BS1	5	-	1.5	204
		M2BS2	10	-	2	193
		M2BF1	-	30	0.5	216
	0.25	M3BS1	5	-	3.75	196
		M3BS2	10	-	4.25	191
		M3BF1	-	30	2	212
Ternary mixes	0.45	M1TC1	5	15	0.1	198
		M1TC2	5	20	0.1	202
		M1TC3	10	15	0.4	201
		M1TC4	10	20	0.3	211
	0.35	M2TC1	5	15	1	207
		M2TC2	5	20	0.75	213
		M2TC3	10	15	1.5	201
		M2TC4	10	20	1.25	208
	0.25	M3TC1	5	15	3.25	205
		M3TC2	5	20	2.75	209
		M3TC3	10	15	3.5	197
		M3TC4	10	20	3.25	199

Table 3.12. Test description

S. No.	Test	Specimen Size	No. of Curing Regimes	Testing age	Replicates
1.	Compressive Strength	150 mm Cube	5	1, 3, 7, 14, 28, 56, 90 days	6
2.	Flexure strength	Prisms (150mm ×150mm × 700mm)	5	7, 28, 56, 90 days	3
3.	Split Tensile strength	Cylinders (150mm × 300mm)	5	7, 28, 56, 90 days	6
4.	Non Destructive Tests (Rebound Hammer and Ultrasonic Pulse Velocity Test)	Specimens cast for compressive strength	5	1, 3, 7, 14, 28, 56, 90 days	6
5.	Water Impermeability test	150 mm cube	5	90 days	3
6.	Salt attack (a) Sulfate (b) Acid	 150 mm cube 150 mm cube	 1 1	After 1 year in aggressive solution	 3 3
7.	Chloride penetration profile	150 mm cube (Ultimately powder from different depths)	1	After 1 year in aggressive solution	3

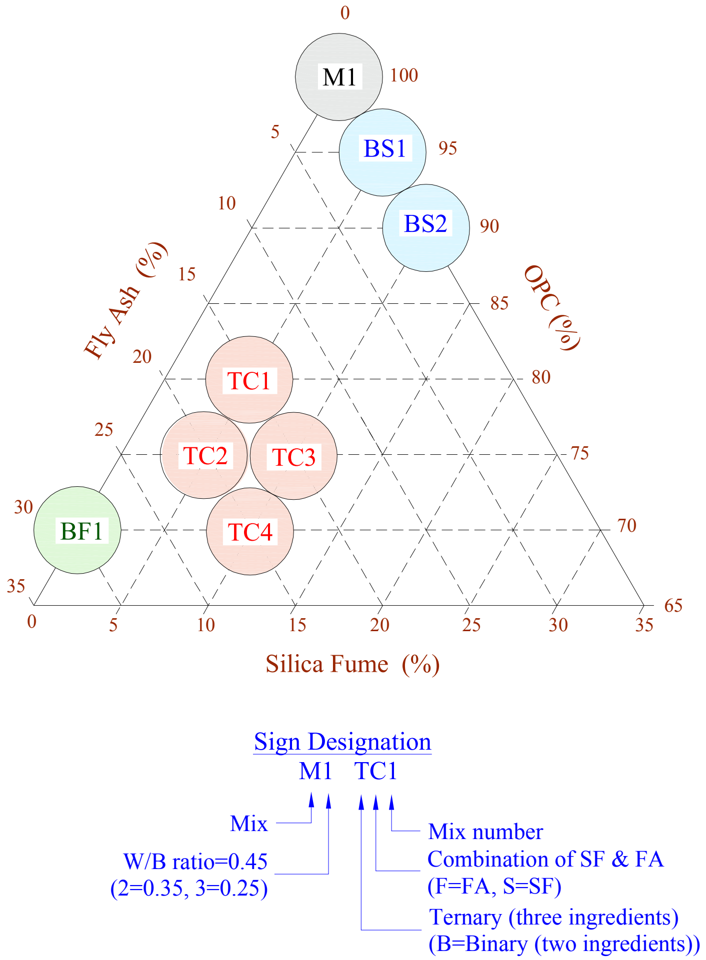


Fig. 3.1. Details of mix design adopted in the study

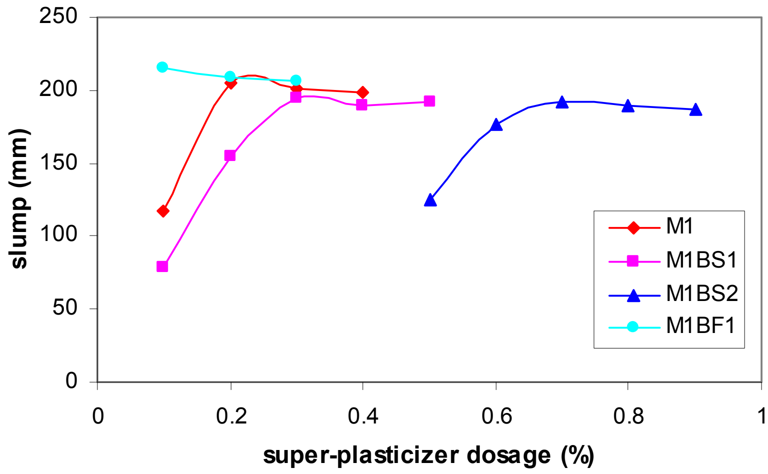


Fig. 3.2. Super-plasticizer dosage v/s slump for control and binary mixes at water-to-binder ratio of 0.45

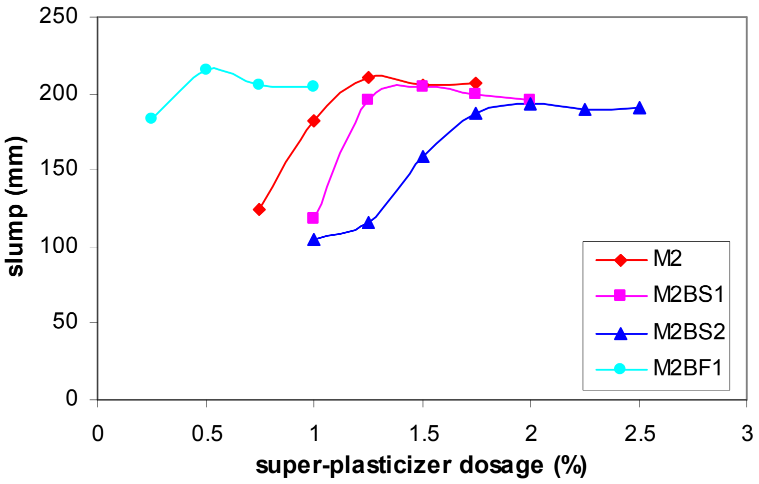


Fig. 3.3. Super-plasticizer dosage v/s slump for control and binary mixes at water-to-binder ratio of 0.35

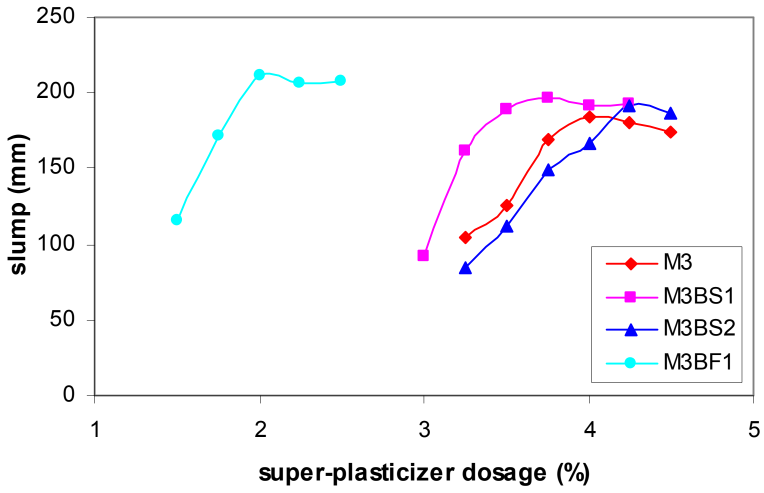


Fig. 3.4. Super-plasticizer dosage v/s slump for control and binary mixes at water-to-binder ratio of 0.25

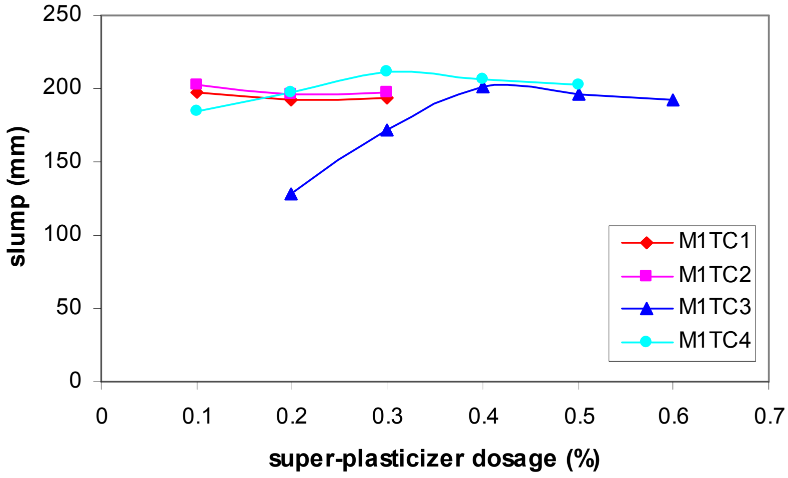


Fig. 3.5. Super-plasticizer dosage v/s slump for ternary mixes at water-to-binder ratio of 0.45

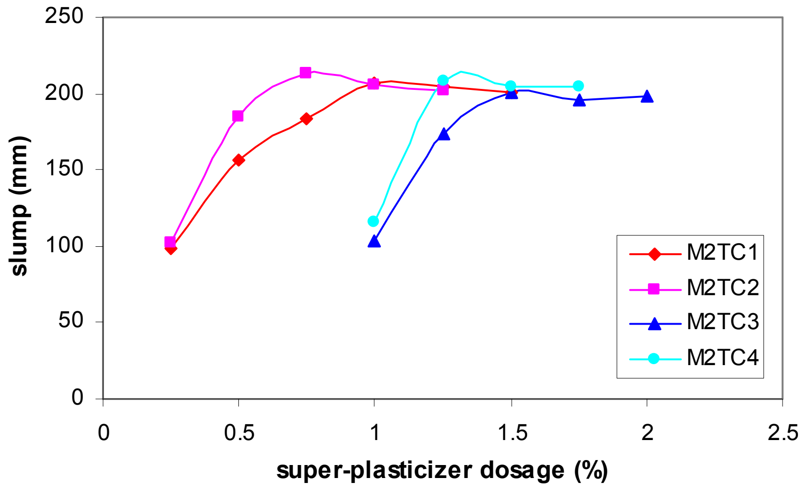


Fig. 3.6. Super-plasticizer dosage v/s slump for ternary mixes at water-to-binder ratio of 0.35

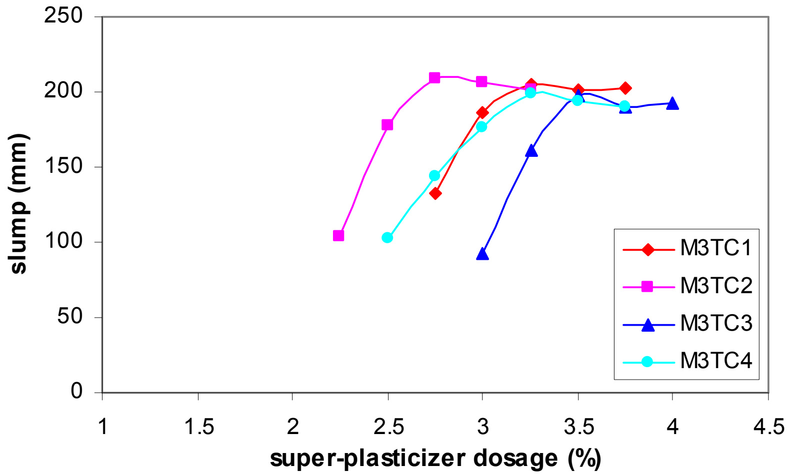


Fig. 3.7. Super-plasticizer dosage v/s slump for ternary mixes at water-to-binder ratio of 0.25

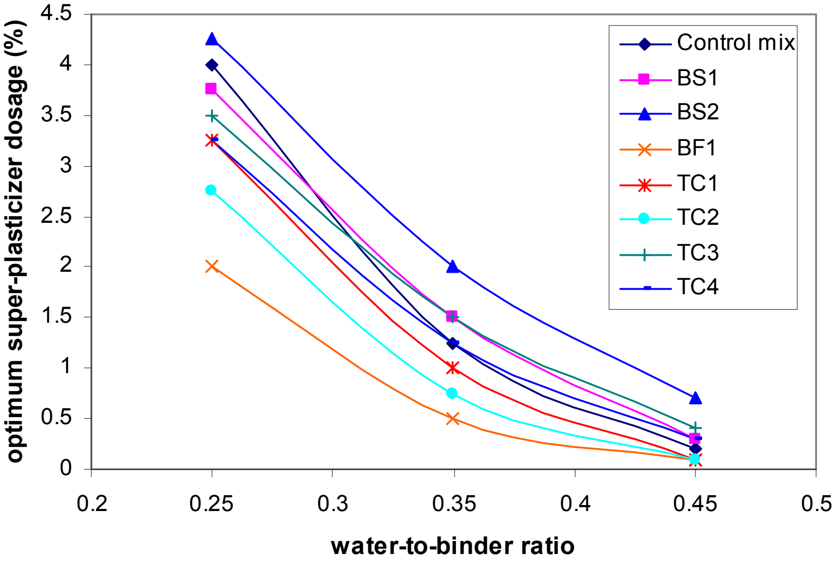


Fig. 3.8. Relation between water-to-binder ratio and optimum super-plasticizer dosage

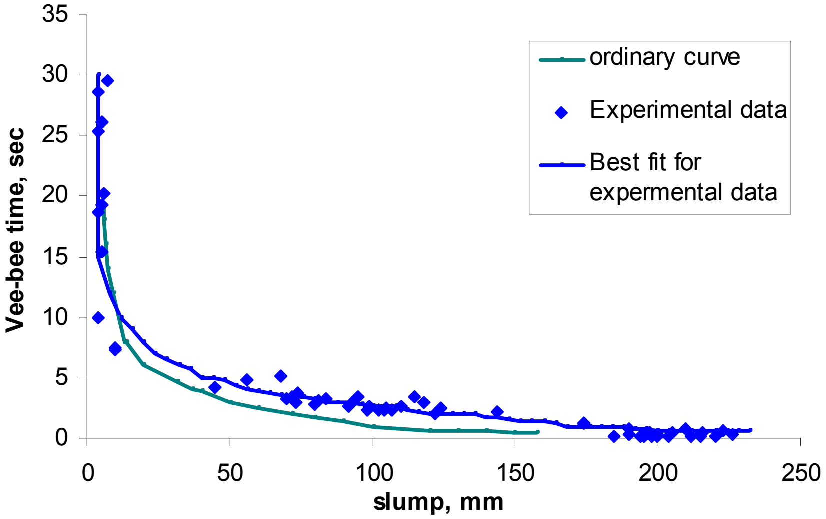


Fig. 3.9 Relationship between slump and Vee - bee time

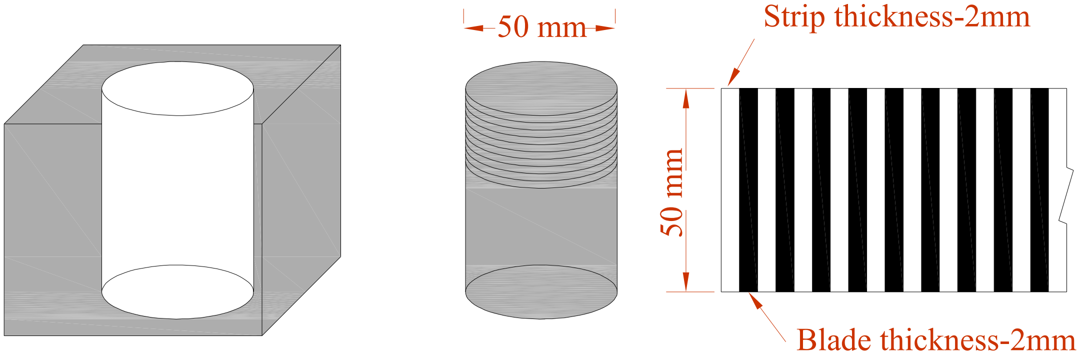


Fig. 3.10: Process of taking strips for chloride analysis along depth

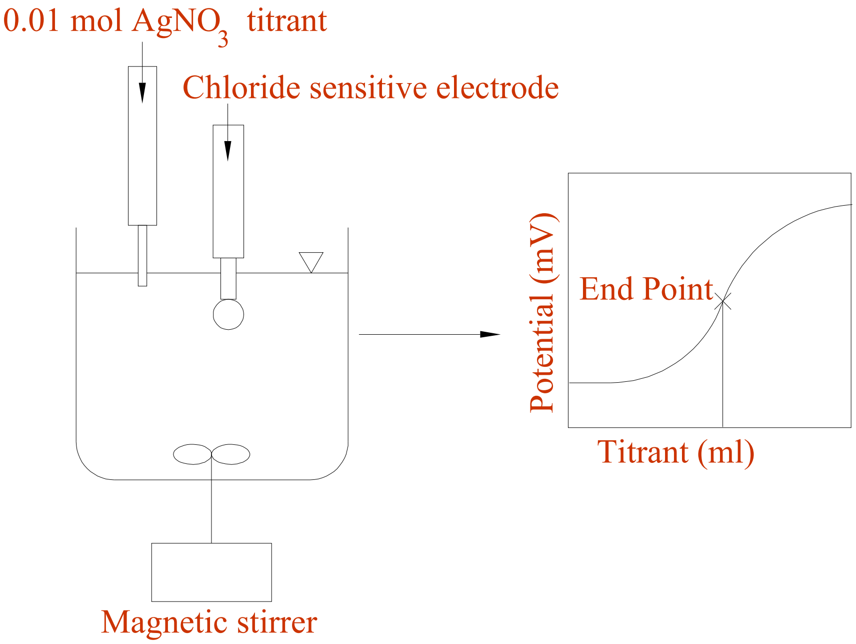


Fig. 3.11: Working principle of Auto-titrator

Plate 3.1. Temperature controlled curing tank

Plate 3.2. Automatic compression testing machine

Plate 3.3. Compression test in progress

Plate 3.4. Typical arrangement for flexure test

Plate 3.5. Split tensile test on cylindrical specimens in progress

Plate 3.6. Failure patterns in split tensile test

Plate 3.7. Rebound hammer test in progress

Plate 3.8. Ultrasonic pulse velocity test in progress

Plate 3.9. Apparatus for water impermeability test

Plate 3.10. Tanks containing aggressive solutions

Plate 3.11. Cubes put in the aggressive solution

Plate 3.12. Dykes prepared at the top of the specimens for ponding chloride solution

Plate 3.13. Positioning of diamond core cutter for taking cores

Plate 3.14. Core cutting in progress

Plate 3.15. Core taken from the cube

Plate 3.16. Typical cores used for chloride analysis at various depths

Plate 3.17. Powder concrete samples collected from various depths of cores for chemical analysis

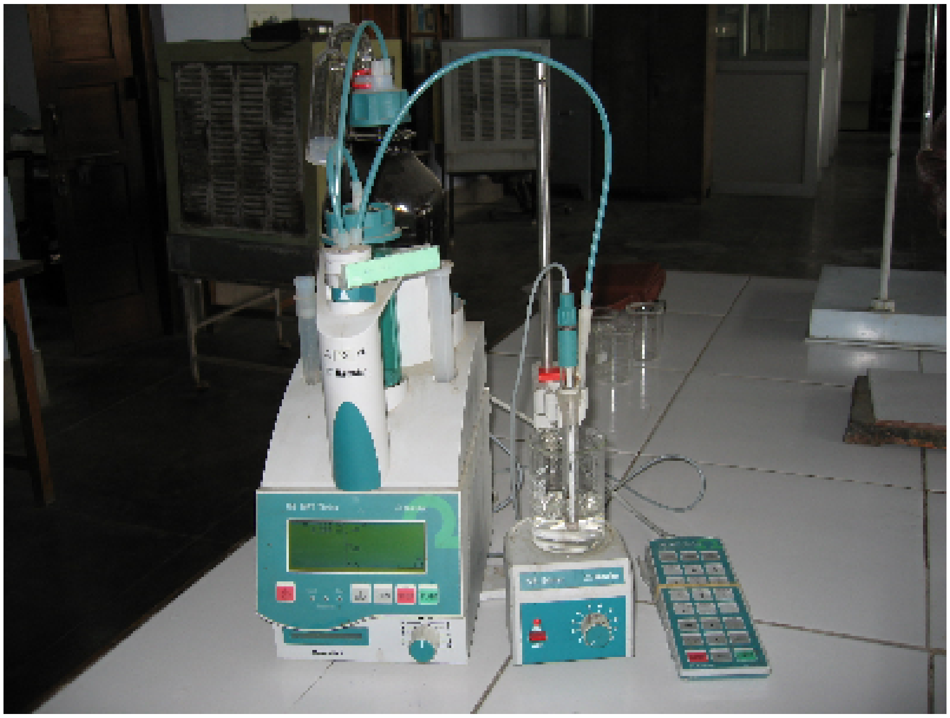


Plate 3.18. Metrohm DMS 98 Titrano automatic titrator for potentiometer titration

Plate 3.19. Collection of 3 gram sample for chloride analysis

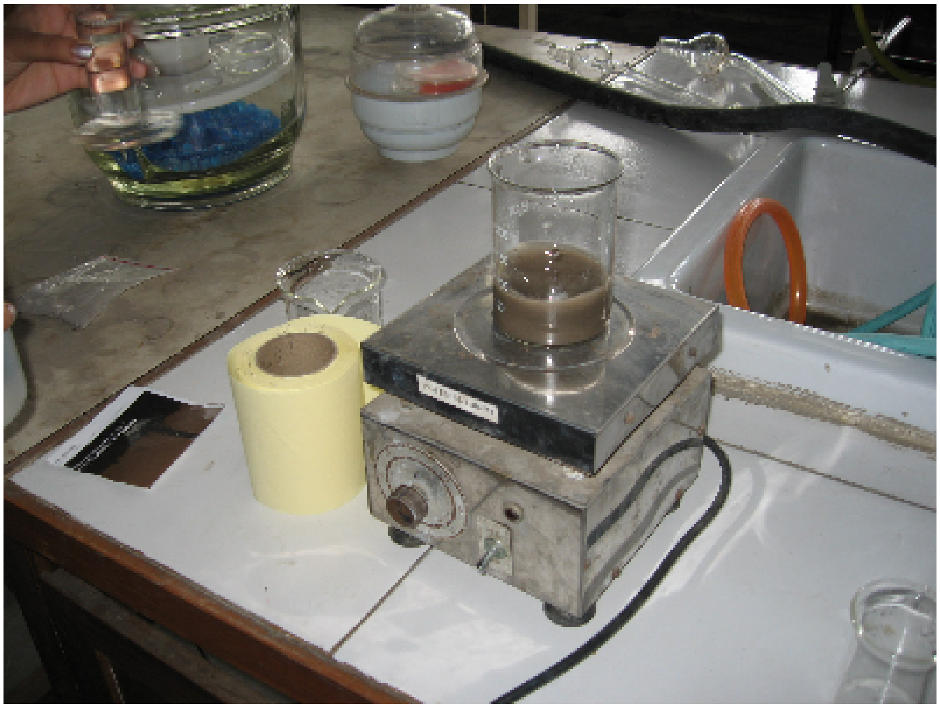


Plate 3.20. Stirring the powder in 50 ml of water or acid on hot plate for 15 minutes

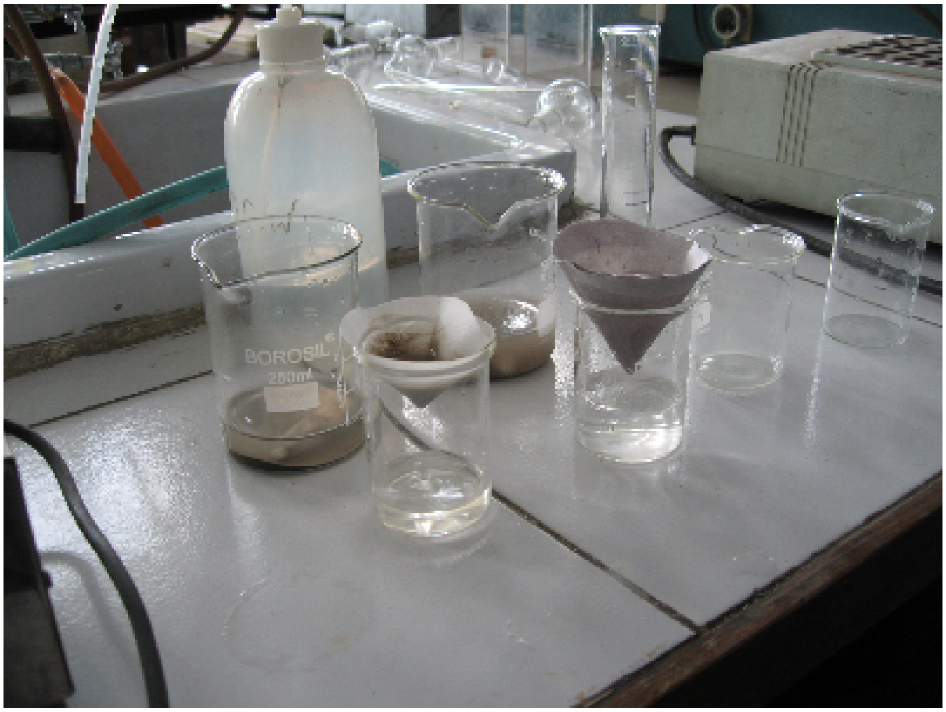


Plate 3.21. Filtering of samples after stirring

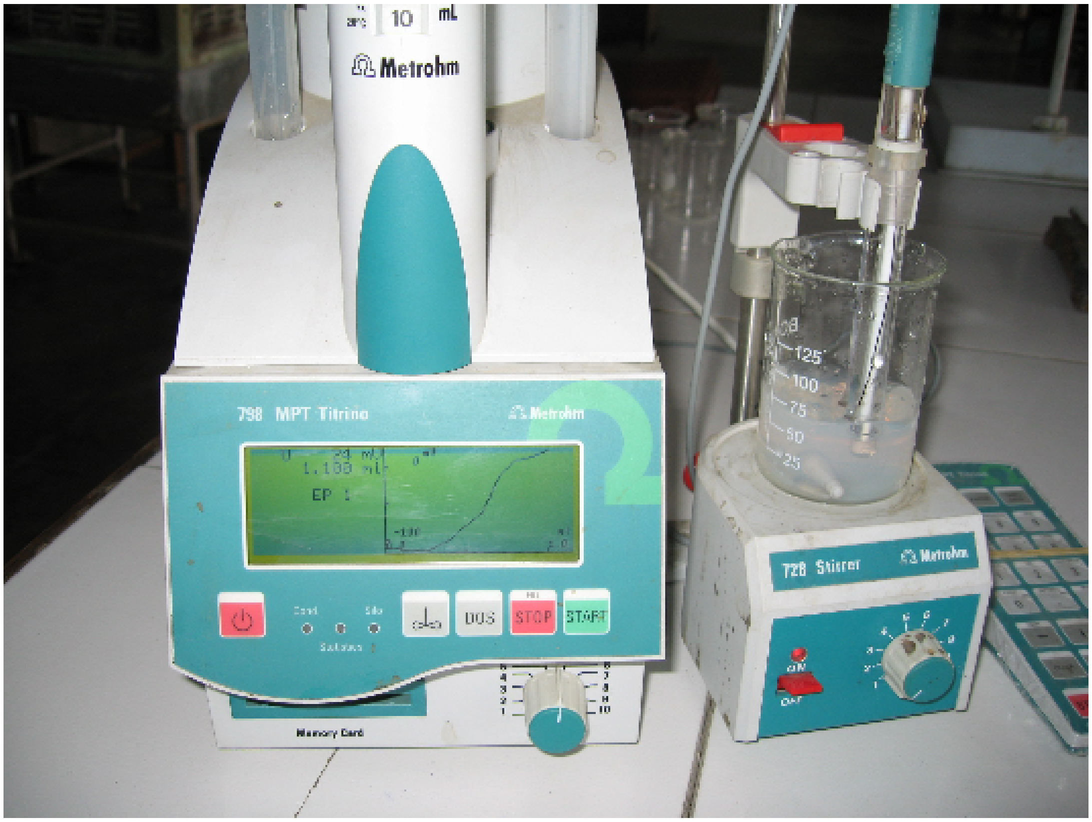


Plate 3.22. Typical potential vs titration volume plot for obtaining end point

CHAPTER 4

STRENGTH ASPECTS OF TESTED CONCRETE

4.1. GENERAL

Strength of concrete is considered as its most valuable property because it usually gives an overall picture of quality of concrete. Moreover, strength of concrete is almost invariably a vital element of structural design and is specified for compliance purposes. The objective of the first part of the study is to examine the effect of various parameters on the strength development of mineral admixture concrete. The parameters that are varied for the investigation include water-to-binder ratio, percentage replacement of mineral admixtures, curing age, curing regimes etc. The aim is to select the most suitable mix in terms of strength development, impermeability characteristics and economical aspects. Along with this, the selection of the most beneficial curing regime is carried out.

In the present chapter, the strength aspects of various mixes are discussed thoroughly to include the effect of all the parameters on strength development of concrete. The above discussion is followed by prediction models for the relationship of different strengths among one another. Further, the observations made from the non-destructive testing are presented followed by their combined relationship with the compressive strength.

4.2. COMPRESSIVE STRENGTH OF CONCRETE

The compressive strength of concrete depends on water-to-binder ratio, type and amount of mineral admixture used as replacement of cement, curing regime adopted and the curing age. The data obtained after conducting compressive strength tests on various mixes, when subjected to different curing regimes are presented in Figs. 4.1 to 4.3 for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. The effect of individual parameters is systematically presented in the following sections.

4.2.1. Effect of Water-to-Binder Ratio

It is observed from Figures 4.1 to 4.3 that with the decrease in water-to-binder ratio, the compressive strength increases for all mixes. It is an obvious observation as per Abrams law. In order to further evaluate the relative importance of pozzolanic admixtures and water-to-binder ratio, a compressive strength development graph of the binary mixes containing only silica fume as the pozzolanic material is drawn at all water-to-binder ratios as shown in Fig. 4.4. It is observed from the figure that the effect of water-to-binder ratio is more pronounced than the effect of increase in the percentage of pozzolanic material.

4.2.2. Effect of Mineral Admixtures

Looking at the binary mixes containing either silica fume or fly ash alone; it can be observed that the addition of silica fume produces an increase in strength while addition of fly ash results in a decrease in strength for all water-to-binder ratios. The better performance of silica fume concrete can be attributed to the improvement in bond between the hydrated cement matrix and aggregate. This is due to the combined effect of secondary pozzolanic reaction and extremely fine silica fume particles *(Bagel 1998; Hassan et al 2000; Jaturapitakkul 2004).* Among silica fume concrete mixes also, the compressive strength increases as the percentage replacement of cement by silica fume is increased from 5% to 10%, for all water-to-binder ratios. However the percentage rise is higher at water-to-binder ratio of 0.45 (21.3% and 44% for 5% and 10% silica fume respectively) and reduces as water-to-binder ratio is decreased. The respective values of percentage rise are 19.3% and 31.6% at 0.35 water-to-binder ratio and 17.4% and 21.5% at 0.25 water-to-binder ratios. This slow down can be due to lack of water in the mix at lower water-to-binder ratios since self-desiccation of specimens may have taken place and due to dense microstructure of hydrated cement that makes it further difficult for water to penetrate from outside towards the unhydrated remnants. This trend is observed by other researchers as well *(Langan et al 2002).* Along with this, it is observed from Fig. 4.4 that the relative increase in strength is very sharp at early ages (between 3 days to 14 days) and then it reduces and reaches at a almost constant value. It indicates that the effect of silica fume on compressive strength is more significant at the early ages. The percentage increase in strength at 1, 3, 7, 14, 28, 56 and 90 days of curing age is 49%, 46%, 51.5%, 27%, 29%, 22%, 21.3% and 66%, 80.5%, 54.5%, 54%, 42%, 44%; at 5% and 10% replacement levels of silica fume respectively at 0.45 water binder ratio. The corresponding values at 0.35 water-binder ratio are 32.4%, 30%, 25%, 24%, 21%, 19.3% and 53%, 55%, 46.2%, 40.8%, 34.2%, 32%, 31.6%; and at water-to-binder ratio of 0.25 are 21.9%, 19%, 17%, 23%, 18%, 17.4%, 17.4% and 41%, 32%, 23%, 29%, 23.4%, 21.6%, 21.5% respectively.

The behaviour of fly ash concrete is different from silica fume concrete as it exhibits a reduction in compressive strength as compared to the control mix, although the strength of the mix increases with the decrease in the water-to-binder ratio (Fig. 4.5). However, the contribution of fly ash in concrete mixes prepared at lower water-to-binder ratios is greater than those prepared at higher water-to-binder ratios. For instance, at 90 days, fly ash concrete mix is observed to achieve 97.8% of compressive strength of the control mix at water-to-binder ratio of 0.25 as compared to the corresponding mixes at water-to-binder ratios of 0.35 and 0.45 which achieved 94.6% and 90.2% respectively of the strength of the reference OPC concrete. The similar trend is observed by Lam et al in their previous research *(Lam et al 1998)*. In order to analyze the strength development of fly ash concrete with age, a graph between the relative strength ratio, which is the ratio of compressive strength of fly ash concrete to the compressive strength of corresponding control mix, and curing age is prepared as shown in Fig. 4.6. It can be observed from the figure that the fly ash mixes have lowest compressive strength at early ages and achieves almost similar strength to OPC mix at 90 days. Fly ash contributes little to strength at early ages. The relative strength is just 7.2% in average at 3 days, which increases to the value of above 90% after 28 days of curing period. This observation is consistent with the results of other studies as well *(Lam et al 1998)*.

The combination of silica fume and fly ash leads to increase in compressive strength as compared to control mix at all water-to-binder ratios in most of the cases. Fig. 4.7 shows the relative strength achieved by all the ternary mixes as compared to respective control mixes for all water-to-binder ratios. The combination of 5% silica fume, 15% fly ash and 80% cement is observed to perform best among the four combinations studied for all water-to-binder ratios. This combination produces an increase in strength of about 17%, 14.4% and 13% over the control mix at water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. The strength produced is almost similar to the strength of the binary mix having 5% silica fume and 95% cement.

It is also noticed that replacing cement by percentage greater than 20% tends to lower the efficiency of mineral admixtures. Mixes TC2 and TC3 that contains 25% of mineral admixtures, as replacement of cement, do not show significant increase in strength and in TC4 mix, the ultimate strength decreases, although only marginally, showing that with further increase in replacement of cement, the strength is adversely affected. It can be understood from the stoichiometric equations of hydration reaction as explained below.

The major compounds of cement hydration are tri-calcium silicate (C_3S), di-calcium silicate (C_2S), tri-calcium aluminate (C_3A) and tetra-calcium alumino ferrite (C_4AF). Compound compositions of commercially available ordinary Portland cement varies depending on the feeding of raw materials during manufacturing processes. However, one can assume that normal compound composition is 54.5% C_3S, 19.5% C_2S, 9.5% C_3A and 9% C_4AF. In addition to the main compounds, there exist minor compounds such as MgO, TiO_2, Mn_2O_3, K_2O and Na_2O, all together taken as 7.5%. If C grams of cement is taken, then C_3S, C_2S, C_3A, C_4AF and minor compounds can be taken as 0.545C, 0.195C, 0.095C, 0.09C and 0.075C respectively. These compounds react with water and form products of hydration, which in turn produce firm and hard mass.

It is well known that out of the four main compounds of cement, only C_2S and C_3S produces calcium hydroxide (CH) and C_4AF consumes CH during hydration reaction. Further, 100 grams of C_2S and C_3S produces 22 grams and 49 grams of CH respectively and C_4AF consumes 30.45 grams of CH *(Neville 2004 a).* The stoichiometric equations for C grams of cement can be written as:

$$0.545\,C + 0.1308\,H \rightarrow 0.4087\,C_3S_2H_3 + 0.26705\,CH \qquad \ldots (4.1)$$

$$0.195\,C + 0.0409\,H \rightarrow 0.19305\,C_3S_2H_3 + 0.0429\,CH \qquad \ldots (4.2)$$

$$0.095\,C + 0.038\,H \rightarrow 0.133\,C_3AH_6 \qquad \ldots (4.3)$$

$$0.09\,C + 0.0274\,CH + 0.033\,H \rightarrow 0.150\,C_6AFH_{12} \qquad \ldots (4.4)$$

The hydration product is the summation of hydration products produced by four major compounds and calcium hydroxide liberated during hydration. From the above equations, it can be seen that C grams of cement produces 0.885 C grams of C-S-H and 0.2825 C grams of CH on complete hydration.

As already stated in Chapter 3, silica fume is composed of primarily SiO_2 and the other constituents are present in very low concentration and they can be treated as inert. Chemical reaction in the hydration of pozzolanic cementitious system is given below

$$2S + 3CH \rightarrow C_3S_2H_3 \qquad \ldots (4.5)$$

Considering the atomic mass of all the elements involved, one can find that 1 gram of silica fume would react with 1.851 grams of calcium hydroxide to provide 2.851 grams of C-S-H gel. Since 1.85 grams of calcium hydroxide reacts with 1 gram of silica, then 0.2825 C grams of calcium hydroxide would react with 0.2825/1.85 C grams i.e. 0.1525 grams of silica. Therefore, maximum silica that would react with calcium hydroxide is 15.25% of cement content. It means, the stoichiometric upper limit of silica fume is 15.25%. Similarly, it can be found that 1 gram of fly ash reacts with nearly 1.11 gram of calcium hydroxide to produce C-S-H gel. Since 1.11 grams of calcium hydroxide reacts with 1 gram of fly ash, then 0.2825 C grams of calcium hydroxide would react with 0.2825/1.11 C grams i.e. 0.2524 grams of fly ash. Therefore, maximum fly ash content that would react with calcium hydroxide is 25.24% of cement content. It concludes that the stoichiometric upper limit of fly ash is 25.24%.

Now, for a mix containing mineral admixtures, if the amount of calcium hydroxide produced by the hydration reaction is more than the amount that can be consumed by the pozzolanic material present in the mix, the reaction is said to be pozzolanic product controlled; and if the calcium hydroxide produced is less than the amount required by the pozzolanic material, the reaction is said to be lime controlled *(Patil 2006)*. In Table 4.1, all binary and ternary mixes at all the three water-to-binder ratios are analyzed for the amount of calcium hydroxide consumed by them. From the Table, it can be seen that the amount of calcium hydroxide consumed by BS1 and BS2 is very less as compared to calcium hydroxide produced by hydration of cement, thus making the secondary hydration reaction mineral admixture controlled. In all other mixes, amount of CH produced by cement is less than the amount required by the mineral admixtures present in the mix. Therefore, in all these mixes, the reaction is lime controlled, which indicates that the full potential of mineral admixture is not used and is lying unreacted in the matrix. Looking at the column (VI) of Table 4.1, it can be seen that for all water-to-binder ratios, TC1 mix has least imbalance of CH produced by cement and consumed by mineral admixtures. Therefore, theoretically, this mix is the most optimum in terms of the usage of mineral admixtures and in terms of strength development by secondary hydration reaction.

4.2.3. Effect of Curing Regimes

In order to extensively study the effect of curing regimes on the strength development of concrete, all the mixes are subjected to five different curing regimes, as described in Chapter 3. The results are presented in Figures 4.1 to 4.3. It is a common observation from the figures that air cured specimens gain the lowest strength for all mixes and at all ages. In general, compressive strength of concrete is found to increase with increase in initial water curing period. This general trend has some exceptions in the case of OPC and silica fume concrete mixes. These mixes exhibit higher strengths at 56 and 90 days when initially water cured for 28 days (R4 curing condition) as compared to the corresponding continuously submerged specimens (R1 curing condition). The higher strength of partial dried specimens can be attributed to the increase in secondary forces between the surfaces of cement gel *(Popovics 1986; Tan and Gjorvl 1996; Hassan et al 2000; Ramezanianpour and Malhotra 1995)* and also to the reduction in disjoining pressure due to drying *(Ozer and Qzkul 2004).*

In order to judge whether the effect of curing regime is same at all water-to-binder ratios or not for all the mixes, compressive strength development of OPC concrete prepared at three water-to-binder ratios and subjected to water curing and air-drying regimes are compared. For this, compressive strength of the control concrete is plotted against age (log scale) for the two curing regimes. From Fig. 4.8, it can be seen that the average difference between the strength curves of continuously water cured and air cured specimens is smaller at higher water-cement ratios and this difference widens as the water-to-binder ratio is reduced, indicating the importance of early curing in lower water-binder ratio concretes.

Similarly, comparing the influence of curing conditions on OPC concrete and pozzolanic concrete, it is observed that the average difference between compressive strength at two extreme curing conditions, continuously air cured and continuously water cured, is smaller for OPC concretes than that for pozzolanic concretes indicating that mineral admixture concrete is more sensitive to inadequate curing than OPC concrete, as indicated previously by other researchers as well *(Ozer and Qzkul 2004; Toutanji and Bayasi 1999; Ramezanianpour and Malhotra 1995).* This can be attributed to the lack of development of hydration and pozzolanic reactions to produce a dense microstructure and the extensive shrinkage cracking which may have developed due to air curing as is indicated by other researchers *(Termkhajornkit et al 2001; Toutanji and Bayasi 1999; Lam et al 1998; Guneyisi at al 2005).*

Of all the concrete mixes, fly ash concrete is worst affected by the air-curing regime. The decrease in strength is as high as 44.2% as compared to the moist curing regime for water-to-binder ratio of 0.25. The strength level is low even for the specimens that are moist cured for initial 7 days (reduction in strength is 30.3%, 24% and 21% respectively at water-to-binder ratios of 0.25, 0.35 and 0.45). The reduction is attributed to the fact that specimens are cured for a short period of time and fly ash undergoes slow pozzolanic reaction that requires continuous wet curing and favorable curing temperature for longer duration for proper development of strength *(Toutanji et al 2004)*.

In order to judge the performance of mixes prepared with mineral admixtures under various curing regimes, relative to the corresponding OPC concrete mix, relative strength bar charts are made for these mixes and are presented in Figs. 4.9 to 4.13. In these charts, percentage increase or decrease in strength with respect to the corresponding control mix under different curing conditions is plotted against the mix type. From these charts, it can be seen that continuous water curing is the best curing practice for mineral admixture concrete, as the relative rise in strength is highest in this curing regime. However, relative rise in strength decreases with decrease in water-to-binder ratio. Among binary mixes, silica fume concrete mixes are observed to perform best for all water-to-binder ratios and among ternary mixes, TC1, which is contains combination of 5% silica fume and 15% fly ash, achieve best results.

Relative fall of strength is maximum in the case of air-cured specimens, concluding that continuous air curing is worst curing regime. Silica fume concrete still manages to have relative increase in strength as compared to control mix. This increase in strength is attributed to early hydration process of silica fume concrete. All the mixes having fly ash attain lesser strength than the corresponding control mix. In this case also, among the ternary combinations, TC1 mix gives the best results.

Regarding the effect of wetting drying cycles after initial 14 days of water curing, it can be seen that this condition does not have any major effect on compressive strength of concrete. The relative strength performance does not show a definite trend under all water-to-binder ratios and thus needs further investigation by testing specimens after longer exposure durations.

4.3. COMPRESSIVE STRENGTH DEVELOPMENT ANALYSIS

The strength development of mixes is analyzed by using the following equation.

$$f_c = aLn(t) + b \qquad \ldots (4.6)$$

where f_c is the compressive strength of concrete at t days, *a* and *b* are constants. This type of equation has been used earlier by many researchers *(Ozer and Ozkul 2004; Popovics 1986; Neville 2004 a).*

In this equation, constant *a* represents the rate of strength gain of concrete and therefore even a small change in the value of *a* may lead to large change in compressive strength at later ages. Constant *b* represents the effect of other factors on compressive strength. The plots of compressive strength with the logarithm of time for all the mixes and for all curing regimes are shown in Figs. 4.14 to 4.21. The values of constants are then obtained by using the least square method. The values of *a* and *b* obtained from the figures are presented in Tables 4.2 to 4.4 for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. The correlation coefficients obtained are quite high, and ranges from 0.91 to 0.99 for all the mixes.

It is observed from the Tables that the rate of strength gain (i.e. constant *a*) is less sensitive to curing regime at higher water-to-binder ratios and becomes more and more sensitive as the water-to-binder ratio is decreased. Also, the rate of strength gain is more sensitive for mixes containing fly ash confirming that fly ash concrete is more affected by the curing practice adopted.

Constant *b,* which represents the effect of other factors on compressive strength, is found to be nearly independent of the curing regime. However, the value of *b* varies significantly with water-to-binder ratio and the type and proportioning of the pozzolanic materials. It increases with the decrease in water-to-binder ratio. By plotting values of *b* against water-to-binder ratio for all the curing regimes, it is observed that the variation can be easily expressed in the parabolic form for all the mixes (Fig. 4.22). The modified equation can thus be written as:

$$f_c = aLn(t) + c + d(w/b) - e(w/b)^2 \qquad \dots (4.7)$$

where c, d and e are constants that vary with binder type and are given in Table 4.5. It may be noted that *b* represents compressive strength at t equals to 1, i.e. at 1 day. In most cases, e is greater than d indicating that one day strength reduces with the increase in water-to-binder ratio.

Further, the minimum time required by the pozzolanic concrete to reach the strength level of continuously water-cured specimens of the control mix prepared by OPC is examined. For doing this, continuously submerged 28 days moist cured OPC concrete is considered as the reference and corresponding strength as the reference strength. Using equation 4.6**,** the number of days required to attain this reference strength for all the mixes are calculated for two curing regimes, namely continuously submerged curing regime (R1) and 7 days of initial water curing regime (R3). These values are given in Table 4.6. Table 4.6 shows that the desired 28 days strength level of the OPC concrete can be reached much early for silica fume concretes and for TC1 mix. On the other hand, fly ash concrete mixes take much longer time to attain the desired strength level. The time taken is very large if the curing regime of 7 days water curing is adopted. This indicates that 7 days of initial water curing is not sufficient for concrete mixes having only fly ash as the pozzolanic material. Also, the lack of early strength development, which is a characteristic of fly ash blended concrete, is not exhibited by silica fume concrete, rather 5% to 10% addition of silica fume enhances the early strength development even when the initial moist curing is restricted to 7 days. Moreover, for fly ash concrete (up to 15%), incorporation of small amount of silica fume (up to 5%)

overcomes deficiency of early strength development in fly ash concrete even when the initial moist curing is restricted to 7 days.

This inference can also be drawn by considering reference strength as the 28 days strength for the control concrete, with initial water curing of 7 days, corresponding to curing regime R3. Thus there is no need for increasing the number of initial moist curing days in structures when either silica fume is incorporated alone in concrete up to 10% or silica fume up to 5% is incorporated in fly ash concrete containing up to 15% fly ash. In other words, 7 days of water curing is sufficient for these mixes and curing concrete for more than 7 days will not provide any benefit in terms of strength or in terms of number of days required to reach the given strength level.

4.4. ECONOMIC CONSIDERATIONS

It is understood that silica fume in concrete enhances strength although it results in consumption of higher amount of super-plasticizer for achieving required workability. Since both silica fume and super-plasticizers are costly, therefore using only silica fume as mineral admixture may not be economically best. Fly ash, on the other hand, reduces super-plasticizer dosage and increases slump to a slight extent. Reduction in super-plasticizer dosage combined with the lesser cost of fly ash makes concrete ultimately economical, but it reduces the strength.

Therefore, in order to achieve economy and desired strength, a combination of silica fume and fly ash can be used. For example, a cost comparison can be made between the best ternary mix TC1 and the mix having the same strength as TC1 but containing only silica fume. The silica fume content of such a mix is obtained by simple linear interpolation of strength between the control mix and the mix containing 5% silica fume. For the cost analysis the following costs of ingredients are considered:

- Cement: Rs. 4/kg (U$ 0.08/kg)
- Silica fume: Rs. 30/kg (U$ 0.6/kg)
- Super-plasticizer: Rs. 150/kg (U$ 3/kg)

Table 4.7 represents the cost comparison per cubic meter of concrete between binary mixes with only silica fume as mineral admixture and corresponding ternary mix having a combination of silica fume and fly ash, for similar strength at different water-to-binder ratios. From the Table, it is observed that with the use of silica fume and fly ash together in the system, the concrete can be made cheaper by 13%, 16% and 12% for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively as compared to the system that uses only silica fume as a mineral admixture.

Also, if the cost comparison between binary mix containing only fly ash as the mineral admixture and the ternary mix having a combination of silica fume and fly ash is made, it can be said that the binary mixes with fly ash will require more number of curing days to reach the strength level of ternary mixes and that will increase the curing cost and the number of days for which the structure cannot be occupied. It will ultimately lead to the overall cost of the project. The ternary mixes will be economical due to the reduction in cost incurred on curing.

It is worth mentioning here that the cost analysis that is performed in this work is just the 'first time cost analysis'. For the realistic cost analysis, life cycle cost must be calculated for each mix and compared. Life cycle cost analysis is an engineering economic cost analysis tool useful in comparing the relative merit of competing project alternatives. It is defined as a process for evaluating the total economic worth of a usable project segment by analyzing initial costs and discounted future costs (such as maintenance, reconstruction, rehabilitation, restoring costs) over the life of the project segment. The repair and maintenance cost depends on the service life prediction models. However, the reliable deterioration models are not available for mineral admixture concrete and a lot of additional data is required for creating such a model. Therefore, the cost analysis is done for initial costs only. Life cycle cost analysis will be taken as the scope for future work.

4.5. FLEXURAL STRENGTH TEST RESULTS

For all the concrete mixes, flexural strengths are determined at the end of 7 days, 28 days, 56 days and 90 days and are presented in Figs. 4.23 to 4.30. The effect of various parameters on flexural strength of concrete is discussed in the following sections.

4.5.1. Effect of Mineral Admixtures

Fig. 4.31 to 4.35 shows the percentage variation of 90 days flexural strength of mineral admixture concrete prepared at different water-to-binder ratios with respect to their corresponding mix with no mineral additive, under all five curing regimes respectively. It is observed that for all mixes, the trend of rise in flexural strength is similar to the pattern of compressive strength development. However, the presence of mineral admixtures has a more pronounced effect on flexural strength than their effect on compressive strength. For instance, the performance of fly ash concrete in terms of flexural strength is better than their performance in terms of compressive strength. Comparing Fig. 4.31 for flexural strength with the corresponding graph for compressive strength (Fig. 4.9), it can be seen that the addition of 30% fly ash causes decrease in compressive strength relative to the control mix by 9.8%, 5.4% and 2.2% respectively for water-to-binder ratios of 0.45, 0.35 and 0.25. The respective values for relative flexure strength are –0.84%, -0.66% and +0.71%. Also, when the combination of 10% silica fume and 20% fly ash is used in the mixes (TC3), all the mixes show an increase in flexural strength with respect to control mix, while the relative compressive strength of these mixes is observed to decrease as compared to the respective control mix. The higher tensile strength of mineral admixture concrete can be attributed to the improved interfacial bond between the paste and the aggregate. It is observed by other researchers also that the improvement of interfacial bond is less effective on enhancing the cube compressive strength than the tensile strength because the cubical specimens have a lower height-to-width ratio and are more influenced by the end restrain effects *(Lam et al 1998)*.

4.5.2. Effect of Curing Regimes

In order to analyze whether the curing regimes affect both compressive strength and tensile strength in a similar way, relative 90 days strength plots of the control mixes for both compressive strength and flexure strength are made for the worst curing practice, that is, R2 curing regime as shown in Fig. 4.36. It can be observed from the figure that the adverse curing regime affects flexural strength more than the compressive strength of specimens. For instance, the percentage fall in flexural strength of control mix in air-cured specimens with respect to water curing is 24%, 30.6% and 35.6% at water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. The corresponding fall in the values of compressive strength are 15.6%, 18.3% and 25%**.** It means flexural strength is more sensitive to adverse curing. Actually, adverse curing results in micro shrinkage cracking which affects flexural strength more prominently than compressive strength *(Lam et al 1998; Toutanji and Bayasi 1999).* The same trend is observed in the relative strength plots of the control mixes for compressive and flexure strengths when the mixes are subjected to R3 curing regime in which initial water curing of 7 days is provided to the specimens followed by subjecting them to air-drying (Fig. 4.37). Even the specimens that have 28 days of initial water curing (R4 curing regime) exhibit behaviour opposite to that shown in compressive strength. In compressive strength development results, it is observed that after 28 days of curing, the specimens have higher strength than the corresponding specimens that are cured till the testing age (R1 curing regime). In the flexural strength results, it is seen that the specimens which are water cured for initial 28 days followed by air drying till the testing age has lower modulus of rupture than the similar specimens tested in wet condition. This difference can be due to the tensile stresses induced by restrained shrinkage prior to the application of load, which induces tension in the extreme fibers. The percentage loss is more in the case of silica fume concrete as compared to the control mix indicating that silica fume concrete has more of micro shrinkage cracking.

Wetting and drying cycles also affect the flexural strength more severely than the compressive strength. The final flexural strength attained at the end of 90 days under wet–dry cycles is even lesser than the value attained by the specimens that are water cured for just 7 days. Such a great fall in strength can be due to micro cracks development both by the reversal of water gradient in every wetting drying cycle and the shrinkage cracks that develop due to non uniform drying *(Yurtdas et al 2006; Barlett and Macgregor 1994).* It means drying induced micro cracking weakens the material that is not visible in compressive strength results but is indicated in flexural strength results of concrete. Some researchers even say that this micro cracking increases the permeability and therefore plays an important role in durability of concrete structures *(Burlion et al 2003).*

In order to analyze whether the minimum curing days established by compressive strength studies are sufficient for even flexural strength development of the mixes, strength development at 7, 28, 56 and 90 days are plotted for all the mixes under R3 curing regime as shown in Figs. 4.38 to 4.40 for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. Further, a horizontal line is drawn in the figures corresponding to the 28 days flexural strength of the control mix under R3 curing regime and is taken as the reference strength. It can be seen that at water-to-binder ratios of 0.45 and 0.35, silica fume mixes and TC1 mix reach this reference strength easily even when initial 7 days water curing is adopted. Thus, it can be inferred that, when consideration is flexural strength, 7 days of initial water curing is sufficient for silica fume mixes and ternary mixes containing up to 15% fly ash in combination with 5% silica fume. At water-to-binder ratio of 0.25, flexure strength of all the mixes (including control mix) decreases with time if the initial water curing of 7 days is provided, which further confirms that the sensitivity of the mixes towards water curing increases with the decrease in water-to-binder ratio.

4.6. SPLIT TENSILE STRENGTH RESULTS

For all the concrete mixes, split tensile strength is determined at the end of 7 days, 28 days, 56 days and 90 days and the test results are shown in Figs. 4.41 to 4.48. From figures, it is observed that generally the strength development pattern for split tensile strength is similar to that of flexure strength development. The effect of various parameters, mainly mineral admixtures and curing regimes adopted, on split tensile strength of concrete is discussed in the following sections.

4.6.1. Effect of Mineral Admixtures

The split tensile strength development pattern is similar to compressive strength development for all the mixes. This trend is also observed by *Wiegrink et al (1996)* in their research work. However, there are some variations from this general trend. Firstly, it is noted that the effect of addition of fly ash on cube compressive strength is more severe than the effect on split tensile strength (Fig. 4.49). The results show about 9.8% decrease in compressive strength with the addition of 30% fly ash to a mix at water-to-binder ratio of 0.45, but only 2% decrease in split tensile strength at the same water-to-binder ratio. The percentage decrease in split tensile strength and compressive strength is 2.7% and 5.4% at water-to-binder ratio of 0.35 and 2.2% and 1.5% at water-to-binder ratio of 0.25 respectively. The lesser decrease in the split tensile strength of fly ash concrete can be due to the improvement in the interfacial bond between the paste and the aggregate, which is less effective in cube compressive strength *(Lam et al 1998)*.

4.6.2. Effect of Curing Regimes

Like flexure strength, split tensile strength is observed to be more sensitive to air curing as compared to the compressive strength. The percentage decrease in tensile strength of almost all mixes under the air curing regime as compared to water curing regime is higher than the corresponding decrease in compressive strength. For instance, ultimate relative split tensile strength loss of the control mixes at all the three water-to-binder ratios under water-curing regime vis-à-vis air curing regime is determined and plotted in Fig. 4.50. For comparison, corresponding compressive strength loss and flexure strength loss for the same mixes are also plotted in the same figure. It is observed that the split tensile strength loss is greater than the compressive strength loss for all water-to-binder ratios. It is possibly due to the effect of non-uniform shrinkage on the specimens that affects the split tensile strength *(Neville 2004 a)*. However, the percentage decrease in split tensile strength is lesser than the corresponding decrease in flexure strength. It can be explained from the fact that in split tensile test, the failure occurs away from the place where micro cracks are formed and in the flexure strength test, the failure occurs in the zone of micro cracks.

Regarding wetting and drying curing regime (R5), a typical feature that is observed in this regime is that the split tensile strength of specimens either decreases with the number of wetting / drying cycles or increases at a very slow rate. Ultimately 90 days split tensile strength of the specimens subjected to wetting / drying is lesser than the corresponding strength of the specimens cured for 7 days. This shows that the wetting / drying cycles have the detrimental effect on concrete strength which is not visible in the compressive strength studies. As has already been explained in flexure strength studies, the reason for decrease in tensile strength of concrete with the increase in wetting / drying cycles is the formation of micro cracks due to frequent reversal of water gradient.

In order to analyze whether the minimum curing days established by compressive strength studies is sufficient for split tensile strength development of the mixes, strength development of all the mixes under R3 curing regime is plotted in the Figs. 4.51 to 4.53 for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. Further, a horizontal line is drawn in the figures corresponding to the 28 days spilt tensile strength of the control mix under R3 curing regime and is taken as the reference strength. It can be seen that the silica fume mixes and TC1 mix reach this reference strength easily even when initial 7 days water curing is adopted. Thus it can be inferred that, when consideration is split tensile strength, 7 days of initial water curing is sufficient for silica fume and ternary mixes containing up to 15% fly ash in combination with 5% silica fume.

4.7. RELATIONSHIP BETWEEN TENSILE AND COMPRESSIVE STRENGTH

4.7.1. General

Usually concrete is specified through its compressive strength and it is customary to relate tensile strength of concrete to the compressive strength *(Choi and Yuan 2005).* As has been mentioned in the literature review, in most of the previous studies, tensile strength has been related to compressive strength by a general power function without accounting for age, water-to-binder ratio etc. Some studies such as the one reported by *Zain et al (2002)* tried to relate tensile strength to water-to-binder ratio and the age of concrete apart from compressive strength. They developed separate relations for each individual factor and no combined model is proposed. Besides, no earlier study has taken into consideration, the effect of curing practice on the tensile strength. The present investigation is aimed to develop mathematical models for the combined relation between tensile strength, compressive strength, water-to-binder ratio, concrete age and the initial water curing conditions for concrete containing mineral admixtures. The developed models are further validated with the available data from literature having compressive strength ranging from 1MPa to 118 MPa.

4.7.2. Model Development

Both tensile strength and compressive strength of concrete are governed by its porosity and pore sizes, and therefore the relationship between the two is obvious. However, influence of porosity and pore sizes on tensile strength and compressive strength of concrete are not same. Therefore, the relationship between these two strengths will involve other factors as well. The porosity and pore sizes are further dependent on the water-to-binder ratio, age of concrete and initial curing regime adopted. Thus, it is expected that a realistic relationship between compressive strength and tensile strength may also involve parameters such as water-to-binder ratio, concrete age and initial curing regime. Hence, the general form of the relation can be represented as: $f_t = f(f_c, W/B, t, R)$; where f_t is the tensile strength of concrete in MPa (either split tensile strength or flexural strength), f_c is the cube compressive strength of concrete in MPa, W/B is the water-to-binder ratio, t is the concrete age at the time of testing in days, R is the curing regime adopted for the specimens.

From review of available literature, it is observed that individually, all parameters are related to the tensile strength through their power functions. Thus assuming power functions for all factors in the combined model, including the curing regime, which was not considered in any of the earlier models, the combined relation can be expressed as:

$$f_t = A\,(f_c)^p\ (W/B)^q\ t^r\ R^s \qquad \ldots (4.8)$$

where A, p, q, r and s are the constants of equation. This equation can also be re-written as:

$$Log f_t = Log A + p\,Log(f_c) + q\,Log(W/B) + r\,Log t + s\,Log R \qquad \ldots (4.9)$$

Therefore, the combined relation can be developed through a multiple linear regression analysis of the data obtained experimentally. Using the constants obtained through the multiple regression analysis carried out using the experimental data generated, the following combined relationship between the mentioned factors and split tensile strength is obtained:

$$f_{st} = 0.39\,(f_c)^{0.55}\,(W/B)^{0.09}\left(\frac{t}{28}\right)^{-0.03}(1+t_R)^{0.06} \qquad \ldots (4.10)$$

where f_{st} is the split tensile strength of concrete in MPa , t is the age of concrete at the time of testing of concrete in days, t_R is the number of days till which initial water curing is provided to the specimens.

The coefficient of determination for this multiple linear regression analysis is 0.954. The standard errors of estimation of the constants A, p, q, r and s are 0.019, 0.03, 0.02, 0.004 and 0.003 respectively.

Similarly, through multiple linear regression analysis of the experimental data following expression for flexure strength is also obtained

$$f_r = 0.56\,(f_c)^{0.55}\,(W/B)^{0.14}\left(\frac{t}{28}\right)^{-0.08}(1+t_R)^{0.07} \qquad \ldots (4.11)$$

where f_r is the flexure strength of concrete in MPa.

The coefficient of determination for the model developed by multiple linear regression analysis is 0.985. The standard errors of estimation of the constants A, p, q, r and s are 0.02, 0.033, 0.023, 0.005 and 0.003 respectively. It shows the accuracy of the obtained relationship is high.

4.7.3. Validation of the Models

In order to check the accuracy of the proposed model on a much more wider level, apart from the experimental results, data is collected from the literature with varying characteristics of cement, water-to-binder ratio, type of supplementary cementitious materials used, testing age and the number of days till which initial water curing is provided, and the size and shape of specimens used for testing. The brief variability of the data is presented in Tables 4.8 and 4.9 for split tensile strength and flexural strength respectively. In all 615 data points are collected for split tensile strength and 440 data points are available for flexure strength. All the available data points are plotted in Figures 4.54 and 4.55 respectively for split tensile strength and flexure strength. The accuracy of the proposed model is further compared with other existing power function relations. Since some of the earlier models refers to standard cylinder results for concrete compressive strength while some other models use cube compressive strength, thus for the available data, cube strengths are converted into equivalent cylinder strength and vice versa, wherever required according to the need of the model. The conversion factor used is $f_{cu} = 1.25\ f_{cy}$; where 'cu' and 'cy' represent cube strength and cylinder strength respectively *(Neville 2004 a).*

For checking the accuracy of the obtained model, two techniques are used:

1. Integral absolute error index (IAE) that has been used by other researchers to evaluate the goodness of fit of the proposed model *(Oluokun et al 1991; Arioglu et al 2006; Gardener 1990; Oluokun 1991).* It measures the relative deviation of data from the proposed model and can be computed by using the following equation:

$$IAE = \sum \frac{\left[(O_i - P_i)^2\right]^{1/2}}{\sum O_i} \times 100 \qquad \ldots (4.12)$$

   where O_i is the observed value from the experiments, P_i is the predicted value from the regression analysis. For acceptable model, the value of IAE should be in the range of 0 percent to 10 percent. When comparing different equations, the equation with the least IAE is the best fit. This approach is used in the present work as well to evaluate the reliability of all the models.

2. Average ratio of observed and predicted values $(O/P)_{avg}$ is the another tool that has been used in the present work to evaluate the reliability of the models *(Zain et al 2002).* The accuracy of the model is judged on the basis of closeness of the obtained average to unity.

The value of IAE and $(O/P)_{avg}$ for split tensile strength and flexure strength for all the models are presented in Tables 4.10 and 4.11 respectively. It can be observed from Table 4.10 that the values of IAE and $(O/P)_{avg}$ for split tensile strength corresponding to the proposed model are 7.64 and 0.971 respectively. A comparison of the IAE index value of all the models reveals that the index value of the proposed model is by far the lowest among all, indicating the highest reliability of the model. While comparing

$(O/P)_{avg}$ values, it can be observed that the value corresponding to the proposed model is sufficiently close to unity. It must be stated here that IAE index deals with absolute deviation of predicted value from the experimental ones. Therefore, lower value of IAE index indicates lower spread of the deviation about zero. The index $(O/P)_{avg}$, on the other hand, deals with the average of ratios of observed value to predicted value and therefore fails to recognize the true spread of these ratios about unity, as in the average, values drastically lower than unity can be compensated by drastically higher values. Therefore, validation of models through IAE index is far more reliable than the other index. The observed values of both these indices confirm the high reliability and accuracy of prediction of the proposed model as compared to all other models and the model can be used for a wide range of concrete strengths. Further, the present model takes into consideration most of the variables that affect the relation between compressive strength and tensile strength. The models that were developed earlier for normal strength OPC concrete, such as the ones proposed by *Gardner (1990), Gardner et al (1988), Oluokan et al (1991), Oluokun (1991), Raphael (1984)* etc., are not suitable for wide range of strengths and for concrete containing mineral admixtures as is clear from very large values of IAE for these models. This finding is in agreement with various other researchers *(Zain et al 2002; Arioglu et al 2006; Marzouk and Chen 1995; Li and Ansari 2000).*

Similarly, it can be observed from Table 4.11 that the values of IAE and $(O/P)_{avg}$ for flexure strength corresponding to the proposed model are 7.75 and 1.03 respectively and is the best amongst all the models in terms of both the indices. In fact, all other available models have IAE index greater than 10, which is the upper limit for the model to be reliable.

4.8. NON - DESTRUCTIVE TEST RESULTS

Non-destructive methods of investigation such as ultrasonic measurements are often proposed for evaluating the state of concrete structures already in use. However, the conclusions that evolved over years about correlation between velocity of ultrasonic waves and compressive strength of cement materials is that some additional properties have to be measured, for example, hammer rebound index, hardness etc. *(Neville 2004)*.

In the present study, ultrasonic pulse velocity and rebound number are investigated along with the compressive strength in order to obtain the combined relation between the three. The results are presented hereunder:

4.8.1. Ultrasonic Pulse Velocity Test

Prior to destructive compressive strength tests, ultrasonic pulse velocity and rebound number is measured on cubical specimens for all mixes under five different curing regimes. The ultrasonic pulse velocity test is performed as per standards laid down by IS 13311 (Part 1): 1992. Direct transmission method is adopted for testing. The test is performed on cubic surfaces normal to the cast position. In this way, test is conducted on six specimens and the average of the readings is taken as the representative pulse velocity. To ensure the uniform saturation level, all the specimens are submerged in water for 24 hours prior to the test. The values of ultrasonic pulse velocity obtained at different ages are plotted in Figs. 4.56 to 4.63. The effects of various parameters on pulse velocity are discussed in the following sections.

4.8.1.1. Effect of Mineral Admixtures

As can be seen from the figures, with the addition of silica fume, the ultrasonic pulse velocity values increases as compared to the corresponding control mix. However, the increase in the ultrasonic pulse velocity due to silica fume replacement is much lower than that of compressive strength. The increase in ultrasonic pulse velocity value ranges from 1.3% to 4% as against the increase in compressive strength values in the range of 12% to 45% with the addition of silica fume. Similarly with the addition of fly ash, the ultrasonic pulse velocity decreases as compared to the control mix but the reduction in ultrasonic pulse velocity value is much lower than that of the compressive strength. Similar remarks can also made for the concrete mix made with the combination of silica fume and fly ash.

Secondly, it is observed, that in most of the cases, ultrasonic pulse velocity takes a shorter time to reach a plateau value after which the increase in velocity with time is very less when compared to the increase in compressive strength. The similar observation is also made by *Demirboga et al (2004)* while studying the behaviour of high volume mineral admixture concrete.

4.8.1.2. Effect of Curing Regimes

Ultrasonic pulse velocity values are calculated for all the five curing conditions. The lower values of ultrasonic pulse velocity for air cured specimens are in pattern with the strength results that indicate adverse effect of air curing on the properties of concrete. The ultrasonic pulse velocity values are lower by as much as around 1000 m/s for the air cured specimens as compared to corresponding water cured specimens. In the R4 curing condition, in which the specimens are water cured for initial 28 days, the velocity obtained has lower value than the specimens under water curing. It is opposed to the compressive strength results that are higher under R4 curing as compared to R1 curing regime. The reason for it can be the decrease in the moisture content in R4 curing after 28 days that leads to decrease in ultrasonic pulse velocity value.

In R5 curing regime, the velocity values start decreasing after wetting / drying cycles. This is similar to the observation made in flexure strength tests. It can be due to the formation of micro cracks and it shows that ultrasonic pulse velocity test can give some indications about the development of micro cracks by the reversal of water gradient.

4.8.2. Rebound Hammer Test

The rebound hammer is considered to be the most useful test for rapidly surveying large areas of similar type of concrete in the construction *(Qasrawi 2000)*. However *Neville (2004 a)*, while presenting the benefits of using rebound hammer in concrete, stated that the test *all alone* is not a strength test and the exaggerated claims of its use as a replacement for compression test should not be accepted. In order to obtain a combined relationship between ultrasonic pulse velocity, rebound number and compressive strength, rebound hammer test is conducted on all the specimens meant for compressive strength studies and the results are plotted in Figs. 4.64 to 4.71. The effect of various parameters on rebound number is discussed in the following sections.

4.8.2.1. Effect of Mineral Admixtures

The increase or decrease in rebound number with the addition of mineral admixtures follows almost the same trend as their effect on compressive strength. However, the increase / decrease is lesser in the case of rebound number than the compressive strength; but the trend is more prominently reflected than the corresponding effect on ultrasonic pulse velocity.

4.8.2.2. Effect of Curing Regimes

By looking at the rebound number for all the curing regimes, it seems that the effect of curing regime on rebound number is similar to the effect on compressive strength. Under R4 curing condition, the rebound number is higher than the corresponding value of water cured specimens. This confirms that the moisture content of concrete affects the rebound number which is a measure of surface hardness; lower moisture content tends to increase the rebound number of all the mixes. This conclusion was also obtained by Willetts (1958) while studying the effect of moisture content of concrete on the results of rebound hammer test and is reported by *Neville (2004 a).*

In the case of R5 curing regime, in most of the specimens, the rebound number keeps on increasing in repeated wetting / drying cycles though the increase is at a very low pace. This result is opposite to that obtained from split tensile strength test, flexural strength test and ultrasonic pulse velocity test. It shows that the rebound hammer test is not much affected by micro cracks developed in concrete.

4.8.3. Relation between Compressive Strength, Rebound Number and Pulse Velocity

The objective of this section is to obtain correlation between compressive strength, rebound number and pulse velocity for wide range of strength. For this purpose, the values of rebound index and the pulse velocity are correlated to the compressive strength separately, as well as in combination. The purpose of correlating compressive strength to each of the non-destructive parameter separately is to obtain the type of function that represents relationship in a best way. For obtaining the relationship, all results, for all mixtures under different curing regimes and ages, are treated together. For each relationship, the independent variable refers to non-destructive parameters and the dependent variable refers to the established cube strength.

In Fig. 4.72 pulse velocity versus compressive strength is plotted while Fig. 4.73 represents a plot between rebound number and compressive strength. It is clear from the figures that the regression curve represented by the power function fits best for the data points obtained. The regression curve can be represented by:

$$f_{cs} = p\, x^{q} \qquad \ldots (4.13)$$

where f_{cs} is the estimated compressive strength in MPa, x is the non-destructive parameter used, p *and* q are coefficients obtained by using least-square method. The analytical relations for ultrasonic pulse velocity is:

$$f_{cs} = 3 \times 10^{-14}\ V^{4.24} \qquad \ldots (4.14)$$

Where V is the ultrasonic pulse velocity of the mix in m/s. The exponent in the equation 4.14 is close to 4, which is similar to the value that can be obtained by considering the theoretical relationship between ultrasonic pulse velocity and modulus of elasticity and further between modulus of elasticity and compressive strength *(Qasrawi 2000; Pascale et al 2003; IS 456: 2000).*

Similarly, the analytical relationship between rebound number and compressive strength is:

$$f_{cs} = 0.9114\ N^{1.194} \qquad \ldots (4.15)$$

where N is the rebound number of the mix. The exponent of equation 4.15 is close to unity, indicating near linear relationship between compressive strength and rebound number.

Looking at the individual relationship, it can be concluded that power functions can be adopted for obtaining the combined relationship. Therefore, the following form of the relationship is adopted:

$$f_{cs} = p\, V^{q}\ N^{r} \qquad \ldots (4.16)$$

The values of $p, q \; and \; r$ is obtained with the help of multiple linear regression technique, explained in Section 4.7.2 that is used for development of relation between compressive strength and tensile strength. The combined model obtained is

$$f_{cs} = 5.57 \times 10^{-5} \; V^{0.779} \; N^{1.34} \qquad \ldots (4.17)$$

In order to establish the reliability of the developed model, integral absolute error (IAE), as discussed in Section 4.7.3, is calculated for the model. For acceptable model, the value of IAE should be in the range of 0 percent to 10 percent. The value of IAE for the present model is 9.8%. Therefore, it can be said that the present model can be accepted to estimate the compressive strength of concrete from non-destructive measurements. Also, from Fig. 4.74, it can be seen that the value of regression co-efficient between estimated compressive strength and measured strength is 0.91, which is acceptable.

4.9. INFERENCES ON STRENGTH ASPECTS

The first part of the present research focused on studying the effect of silica fume and fly ash, either in binary mix or in ternary mix, on strength of concrete and to determine how curing conditions affect concrete strength. Based on the results obtained, the following inferences are drawn:

In the binary mixes containing either silica fume or fly ash, the addition of silica fume leads to increase in compressive strength of the mix, while the addition of fly ash tends to decrease the strength of resultant concrete. The combination of silica fume and fly ash leads to increase in compressive strength as compared with the corresponding control mix at all the water-to-binder ratios studied. Among the four ternary combinations studied, the mix containing 5% silica fume, 15% fly ash and 80% cement is observed to perform best at all water-to-binder ratios. The final strength achieved by this combination is almost similar to the strength of the binary mix containing 5% of silica fume and 95% cement. It is further observed that there is some maximum percentage of mineral admixtures that can be used as replacement of cement, beyond which the value of strength starts decreasing with further increase in replacement percentage. This maximum replacement level can be explained on the basis of stoichiometric equations of cement.

On the basis of stoichiometric equations, it is inferred that initially the secondary hydration reaction is pozzolanic material controlled. But as the amount of mineral admixture used is increased, the reaction starts shifting from pozzolanic material controlled to lime controlled. In the ternary mixes, full potential of mineral admixture is not utilized when the percentage replacement of silica fume and fly ash increases beyond 20%.

In order to judge the importance of curing practices adopted on mineral admixture concrete, the strength studies are carried out for five different curing regimes, varying from continuous water cured to air cured regime. It is observed that the continuous air curing is the worst curing regime for all mixes and should never be adopted as the curing practice for construction. Comparing the effect of curing practices adopted on strength of both OPC concrete and mineral admixture concrete, it is observed that the pozzolanic concretes are more adversely affected by poor curing practices than OPC concrete. For totally submerged curing condition, strength gaining rates of OPC concrete is lower than mineral admixture concrete. However, the trend becomes opposite for air curing condition.

In order to judge the minimum number of curing days that are required for all mixes, compressive strength development is analyzed. From the analysis, it is concluded that for silica fume concrete and for a ternary combination, 7 days of initial water curing is both necessary and sufficient to explore the pozzolanic activity and for reaching the desirable strength level. However, for mixes having larger percentage of fly ash, a long initial moist curing period is necessary to fully benefit from the addition of these supplementary cementitious materials. Replacing cement by percentage greater than 20% tends to lower the efficiency of mineral admixtures. Also, among the two strength development constants, a and b, b represents the compressive strength at one day and is found to be independent of initial water curing regime adopted but depends on water-to-binder ratio of the mix.

Comparing the economic benefits of all the mixes, it is observed that the overall economy can be achieved by using silica fume and fly ash in combination. For the same strength level, use of some percentage of fly ash in silica fume concrete helps in reducing the amount of cement required and amount of super-plasticizer required for achieving desired workability, thus making the mix economical. Comparing the economy of fly ash concrete and the ternary concrete, it can be said that the use of small amount of silica fume in fly ash concrete helps in reducing the number of curing days required to obtain a desired strength level, thus reducing the cost incurred on curing, leading to overall economy of the project.

The compressive strength studies are followed by tensile strength studies for all mixes under variable curing regimes. It is observed that the effect of incorporation of mineral admixtures is more pronounced on tensile strength development results than the compressive strength development trends. Also, the detrimental effect of adverse curing regime is more pronounced in tensile strength studied. For instance, the tensile strength of all mixes decreases due to wet and dry exposure although it is not reflected in compressive strength studies. Regarding the minimum curing days required on the basis of tensile strength studies, it is found that 7 days of water curing is sufficient for the silica fume concrete mixes to reach the desired tensile strength level.

Using the data of compressive strength and tensile strength (flexure and split tensile strength), mathematical model relating tensile strength and compressive strength based on other parameters like water-to-binder ratio, concrete age and curing conditions, is developed by multiple linear regression technique. Based on the error analysis, the proposed model is found to be reasonably accurate when checked either by Integral absolute error (IAE) index or the average value of the experimental/observed ratio $(O/P)_{avg}$. The developed model is found to be applicable to all kinds of concrete ranging from immature to fully developed concrete regardless of mix proportions and shape and size of specimens used for testing.

Along with the strength studies, non destructive parameters, viz ultrasonic pulse velocity and rebound number are also measured on the specimens meant for destructive compressive strength studies in order to obtain a combined relationship between compressive strength, ultrasonic pulse velocity and rebound number. The relation between the three parameters has been developed for the strength range of 20 MPa to 112 MPa. The obtained relation is further validated by integral absolute error index is found to be acceptable.

Table 4.1. Stoichiometry of hydration reaction for all mixes

Water-to-binder ratio (I)	Mix Type (II)	Cement content (kg) (III)	Maximum CH Liberated (kg) (IV)	CH that can be consumed by mineral admixtures (kg) (V)		Amount of CH left/required (VI)	Limiting parameter for pozzolanic reaction (VII)
				SF	FA		
0.45 (cement content per meter cube of mix = 422 kg)	M1BS1	401.0	113.3	39.1	-	74.2 /--	Pozzolana
	M1BS2	379.8	107.3	78.1	-	29.2 /--	Pozzolana
	M1BF1	295.4	83.5	-	140.5	-- /57	Lime
	M1TC1	337.6	95.4	39.1	70.3	-- /14	Lime
	M1TC2	316.5	89.4	39.1	93.7	-- /43.4	Lime
	M1TC3	316.5	89.4	78.1	70.3	-- /58.9	Lime
	M1TC4	295.4	83.5	78.1	93.7	-- /88.3	Lime
0.35 (cement content per meter cube of mix = 457 kg)	M2BS1	434.2	122.7	42.3	-	80.4/--	Pozzolana
	M2BS2	411.3	116.2	84.6	-	31.6/--	Pozzolana
	M2BF1	319.9	90.4	-	152	-- /61.8	Lime
	M2TC1	365.6	103.3	42.3	76.1	-- /15.1	Lime
	M2TC2	342.8	96.8	42.3	101.5	-- /47	Lime
	M2TC3	342.8	96.8	84.6	76.1	-- /63.9	Lime
	M2TC4	319.9	90.4	84.6	101.5	-- /95.7	Lime
0.25 (cement content per meter cube of mix = 520 kg)	M3BS1	494	139.6	48.1	-	91.5 /--	Pozzolana
	M3BS2	468	132.2	96.3	-	35.9 /--	Pozzolana
	M3BF1	364	102.8	-	173.2	-- /70.4	Lime
	M3TC1	416	117.5	48.1	86.6	-- /17.2	Lime
	M3TC2	390	110.2	48.1	115.4	-- /53.3	Lime
	M3TC3	390	110.2	96.3	86.6	-- /72.7	Lime
	M3TC4	364	102.8	96.3	115.4	-- /108.9	Lime

CH = calcium hydroxide, SF = silica fume, FL = fly ash

Table 4.2. Regression coefficients for different mixes at water-to-binder ratio of 0.45

Mixes	**Regression coefficients**	**Curing Regimes**				
		R1	**R2**	**R3**	**R4**	**R5**
M1	*a*	*8.5*	*6.9*	*8.0*	*9.0*	*8.1*
	b	*9.3*	*9.2*	*9.8*	*8.7*	*9.8*
M1BS1	*a*	9.5	*7.4*	*9.0*	*9.8*	*9.4*
	b	16.5	*15.7*	*17.1*	*15.9*	*16.5*
M1BS2	*a*	11.3	*8.6*	*10.3*	*11.8*	*10.6*
	b	19.2	*17.8*	*20.3*	*18.7*	*20.0*
M1BF1	*a*	8.1	4.7	6.1	7.6	6.9
	b	4.9	5.9	6.8	5.7	6.3
M1TC1	*a*	10.1	7.2	8.8	9.9	9.4
	b	9.4	7.9	10.6	9.8	10.3
M1TC2	*a*	9.8	6.6	8.6	9.5	8.8
	b	7.1	6.8	*8.4*	*7.5*	*8.3*
M1TC3	*a*	9.1	6.2	7.8	8.9	*8.0*
	b	11.8	9.3	12.8	12.0	*13.0*
M1TC4	*a*	8.7	5.3	7.2	8.3	*7.7*
	b	7.0	7.2	8.3	7.5	*8.1*

Table 4.3. Regression coefficients for different mixes at water-to-binder ratio of 0.35

Mixes	**Regression coefficients**	**Curing Regimes**				
		R1	**R2**	**R3**	**R4**	**R5**
M2	*a*	*10*	*7.1*	*8.9*	*10.4*	*9.3*
	b	*32.1*	*31.3*	*33.2*	*31.6*	*32.9*
M2BS1	*a*	10.8	*6.7*	*9.5*	*11.1*	*9.8*
	b	43.2	*40.2*	*44.3*	*42.8*	*44.4*
M2BS2	*a*	11.0	5.5	8.7	11.4	*9.8*
	b	52.1	48.8	53.8	51.6	*53.3*
M2BF1	*a*	11.3	5.2	7.1	10.2	9.1
	b	19.0	19.2	22.9	20.4	21.5
M2TC1	*a*	13.5	8.6	12.0	13.0	12.7
	b	24	23.7	25.7	24.7	25.2
M2TC2	*a*	13.6	8.3	10.9	12.9	11.5
	b	18.3	18.6	20.5	19.2	*20.4*
M2TC3	*a*	13.2	7.0	11.0	12.7	*11.6*
	b	21.5	23.8	23.4	22.1	*23.3*
M2TC4	*a*	12.1	7.4	9.0	11.1	*9.8*
	b	19.1	15.2	22.3	20.3	*21.6*

Table 4.4. Regression coefficients for different mixes at water-to-binder ratio of 0.25

Mixes	**Regression coefficients**	**Curing Regimes**				
		R1	**R2**	**R3**	**R4**	**R5**
M3	*a*	*12.6*	*7.1*	*10.9*	*12.9*	*11.7*
	b	*43.0*	*41.1*	*45.2*	*42.5*	*44.2*
M3BS1	*a*	14.4	*7.6*	*11.6*	*14.9*	*13.1*
	b	52.7	*48.9*	*55.4*	*51.9*	*54.5*
M3BS2	*a*	13.8	7.8	9.9	13.9	*12.3*
	b	60.4	46.1	63.7	59.6	*62*
M3BF1	*a*	15.8	6.4	7.6	13.8	12.3
	b	24.3	25.9	34.2	27.4	29.1
M3TC1	*a*	17.4	10.5	14.8	16.6	15.2
	b	31.9	28.1	35.4	33.2	35
M3TC2	*a*	18.0	10.1	13.9	16.7	14.6
	b	20.6	19.9	25.8	22.6	*25.4*
M3TC3	*a*	18.8	8.7	15.4	17.8	*15.7*
	b	18.0	25.1	22.5	19.5	*22.3*
M3TC4	*a*	17.9	8.4	13.0	16.2	*13.6*
	b	15.6	20.0	21.5	18.2	*21.4*

Table 4.5. Constants c, d and e

S.No.	***Mix***	***Constants***		
		c	***d***	***e***
1.	Control	20.6	240	587
2.	BS1	3.2	417	860
3.	BS2	23.6	645	1221
4.	BF1	16.8	137	359
5.	TC1	30.7	86	294
6.	TC2	0.3	193	388
7.	TC3	37.7	385	608
8.	TC4	49	457	735

Table 4.6. Time to reach the 28 day strength of corresponding control mix cured continuously in water

Mix	Time to reach 28 day strength of OPC (days)					
	W/B = 0.45		W/B = 0.35		W/B = 0.25	
	R1 curing	R3 curing	R1 curing	R3 curing	R1 curing	R3 curing
BS1	9.35	9.8	7.8	9.4	9.4	12.9
BS2	5.1	5.4	3.4	3.8	6.0	8.6
BF1	56.5	158.2	61.2	414.4	46.2	777.2
TC1	16.2	21.6	21.3	27.8	21.1	28.5
TC2	23.0	30.5	31.7	62.6	35.7	70.0
TC3	17.3	39.0	27.7	45.4	35.2	58.1
TC4	34.3	60.7	45.6	118.9	48.2	13.1

Table 4.7. Concrete cost per m^3

Water binder ratio	Mix	Material required per m^3 of mix (kg)				Cost (Rs)			Total cost (Rs)
		Cement	SF	FA	SP	Cement	SF	SP	
0.45	BS(4%)	405.3	16.9	-	1.18	1620	510	177	2310
	TC1	337.8	21.1	63.3	0.42	1350	635	63	2050
0.35	BS(3.8%)	439.7	17.4	-	6.58	1760	520	987	3275
	TC1	365.7	22.8	68.6	4.57	1465	685	685	2835
0.25	BS(3.8%)	500.2	19.8	-	19.81	2000	600	2970	5575
	TC1	416	26	78	16.9	1665	780	2535	4980

SF = silica fume, FL = fly ash, SP = super-plasticizer

Table 4.8. Description of data points used for checking the developed model for split tensile strength

Author	Strength Range (MPa)		Testing time (days)	W/B	Binder type	Shape of specimen for f_c	Other properties
	f_c	f_{st}					
Taylor et al (1996)	42 to 116	2.4 to 5.7	28	0.24 to 0.56	SF	Cube	Total binder content = 340 to 510 kg/m^{3}.
Lam et al (1998)	24 to 95	2.3 to 5.9	28 to 56	0.3 to 0.5	FA: 0% - 55%, SF: 0% - 5%	Cubes, cylinders	Coarse aggregates: granite, 10mm, 1086 – 1157 kg/m^{3},Total binder content = 400 to 500 kg/m^{3}. Fine aggregates = 536 to 724 kg/m^{3}.
Zain et al (2002)	41 to 118	3.6 to 6.5	28	0.22 to 0.55	OPC	Cylinders	
JianYong and Yan (2001)	63 to 104	3.8 to 6.14	3 to 28	0.26	GGBS:30%, SF: 10%	Cubes	Coarse aggregates: crushed limestone, 20mm, 1134 kg/m^{3}. Total binder content = 600 kg/m^{3}. Fine aggregates = 610 kg/m^{3}
Bhanja and Sengupta (2005)	47 to 94	3.8 to 6.6	28	0.26 to 0.42	SF: 0% - 25%	Cubes	Total binder content = 480 to 520 kg/m^{3}. Fine aggregates = 616 to 667 kg/m^{3}. Coarse aggregates = 1058 – 1146 kg/m^{3}
Kim et al (2007)	14 to 77	2 to 4.6	1 to 56	0.25	FA: 20%, SF: 0% - 20%, Metakaolin:0-20%		Coarse aggregates: 20mm, 891 – 915 kg/m^{3} Fine aggregates = 518 to 532 kg/m^{3}.
Zheng et al (2001)	11 to 70	1.1 to 4.2	3 to 28	0.39 to 0.8	PFA: 25%	Cubes	Coarse aggregates: granite, 20mm. Total binder content = 265 to 460 kg/m^{3}. Slump: 50 to 70 mm, HRWR: 0 to 3.63 L/m^{3}
Present study	20 to 112	1.91 to 5.98	7 to 90	0.25 to 0.45	SF: 0% - 10% FA: 0% - 30%	Cubes	Coarse aggregates: granite, 10mm, 1086 – 1157 kg/m^{3}, Total binder content = 400 to 500 kg/m^{3}. Fine aggregates = 536 to 724 kg/m^{3}.

Table 4.9. Description of data points used for checking the developed model for flexural strength

Author	Strength Range (MPa)		Testing time (days)	W/B	Binder type	Shape of specimen for f_c	Other properties
	f_c	f_r					
Taylor et al (1996)	42 to 116	2.4 to 5.7	28	0.24 to 0.56	SF	Cube	Total binder content = 340 to 510 kg/m$^{3.}$
Ujhelyi and Ibrahim (1991)	14 to 47	2.9 to 7.3	7 to 90	0.531	GGBS: 0% to 40%, Natural pozzolana: 0% to 40%	Cubes	Coarse aggregates: gravel, 16mm. Total binder content = 350 kg/m$^{3.}$ Mass of aggregates = 1806-1851 kg/m^3.
Khatib and Hibbert (2005)	33 to 65	2.7 to 6	90	0.5	OPC, GGBS: 0% to 80%, Metakaolin: 0% to 20%	Cubes	Coarse aggregates: 20mm. Total binder content = 325 kg/m$^{3.}$ Fine aggregates = 644 - 649 kg/m^3. Coarse aggregates = 1289 – 1298 kg/m^3.
Khatri et al (1995)	58 to 101	5.8 to 9.2	28 to 365	0.34, 0.35	OPC, high slag cement, slag cement, FA: 0% to 25%, SF: 0% to10%	Cylinders	Coarse aggregates: gravel, 20mm 10mm. Total binder content = 425 - 434 kg/m$^{3.}$ Fine aggregates = 708 - 744 kg/m^3. Coarse aggregates = 1082 – 1094 kg/m^3.
Douglas et al (1991)	41 to 48	4.8 to 6.3	7 to 14	0.34 to 0.50	GGBS	Cylinders	
Kim et al (2007)	14 to 77	2 to 4.6	1 to 56	0.25	FA: 20%, SF:0% to 20%, Metakaolin:0% to 20%		Coarse aggregates: 20mm. Fine aggregates = 518 to 532 kg/m^3. Coarse aggregates = 891 – 915 kg/m^3
Toutanji and Bayasi (1999)	32 to 44	1.7 to 5.8	35	0.41	SF: 0% to 30%	Cylinders	
Present study	20 to 112	2.08 to 8.08	7 to 90	0.25 to 0.45	SF: 0% to 10% FA: 0% to 30%	Cubes	Coarse aggregates: granite, 10mm. Total binder content = 400 to 500 kg/m$^{3.}$ Fine aggregates = 536 to 724 kg/m^3. Coarse aggregates = 1086 – 1157 kg/m^3

Table 4.10. Comparison of reliability of existing relations between compressive strength and split tensile strength

Source	Relationship	IAE (%)	$(O/P)_{avg}$	Remarks
Oluokan et al (1991)	$f_{st} = 0.206 f_{cy}^{\ 0.79}$	18.9	0.806	$f_c \leq 62\,MPa$
Iravani (1996)	$f_{st} = 0.57\sqrt{f_{cy}}$	10.44	0.950	
ACI 363R-84 (1993)	$f_{st} = 0.59\sqrt{f_{cy}}$	11.18	0.918	$21 \leq f_c \leq 83\,MPa$
ACI 318-99 (1999)	$f_{st} = 0.56\sqrt{f_{cy}}$	10.5	0.967	-
CEB-FIB (Arioglu et al 2006)	$f_{st} = 0.3 f_{cy}^{\ 2/3}$	9.67	0.951	$f_c < 83\,MPa$
Zain et al (2002)	$f_{st} = \dfrac{f_{cy}}{0.1 f_{cy} + 7.11}$	9.50	0.956	-
	$f_{st} = 0.54\sqrt{f_{cy}}\,(W/B)^{-0.07}$	10.61	0.933	
	$f_{st} = 0.59\sqrt{f_{cy}}\left(\dfrac{t}{t_{28}}\right)^{0.04}$	11.58	0.919	
Carino and Lew (1982)	$f_{st} = 0.272 f_{cy}^{\ 0.71}$	14.67	0.888	-
Bhanja and Sengupta (2005)	$f_{st} = 0.248 f_c^{\ 0.717}$	20.28	1.053	-
Ahmad and Shah (1985)	$f_{st} = 0.462 f_{cy}^{\ 0.55}$	9.65	0.967	$15 \leq f_c \leq 84\,MPa$
Raphael (1984)	$f_{st} = 0.313 f_{cy}^{\ 0.667}$	12.15	0.910	$f_c \leq 40\,MPa$
Arioglu (2006)	$f_{st} = 0.321 f_{cy}^{\ 0.661}$	12.23	0.908	$15 \leq f_c \leq 120\,MPa$
Arioglu et al (2006)	$\dfrac{f_{st}}{f_{cy}} = 0.387 f_{cy}^{\ -0.37}$	17.73	0.848	$4 \leq f_c \leq 120\,MPa$
Gardener et al (1988)	$f_{st} = 0.47 f_{cy}^{\ 0.59}$	21.7	0.814	$3 \leq f_c \leq 46\,MPa$ (Type I cement concretes
	$f_{st} = 0.46 f_{cy}^{\ 0.60}$	23.79	0.801	$13 \leq f_c \leq 72\,MPa$ (Type III cement concretes)
Gardener (1990)	$f_{st} = 0.34 f_{cy}^{\ 0.66}$	16.66	0.860	$4 \leq f_c \leq 57\,MPa$ (Best fit relationship)
	$f_{st} = 0.33 f_{cy}^{\ 2/3}$	16.35	0.864	$4 \leq f_c \leq 57\,MPa$ (Proposed relationship)
Current study	Equation (4.10)	7.51	0.971	OPC / MA concrete

Table 4.11. Comparison of reliability of existing relations between compressive strength and flexure strength

Source	Relationship	IAE (%)	$(O/P)_{avg}$	Remarks
ACI 363R-84 (1993)	$f_r = 0.94\sqrt{f_{cy}}$	21.5	0.818	$21 \le f_c \le 83\,MPa$
IS 456: 2000	$f_r = 0.7\sqrt{f_c}$	11.52	1.016	-
Bhanja and Sengupta (2005)	$f_r = 0.275 f_c^{0.81}$	36.57	0.754	-
Iravani (1996)	$f_r = 0.97\sqrt{f_{cy}}$	24.5	0.793	Silica fume concrete
Luther and Hansen (1990)	$f_r = 1.02\sqrt{f_{cy}}$	29.9	0.75	$51 \le f_c \le 107\,MPa$ Silica fume concrete
Current study	Equation (4.11)	7.75	1.03	For OPC / mineral admixture concretes

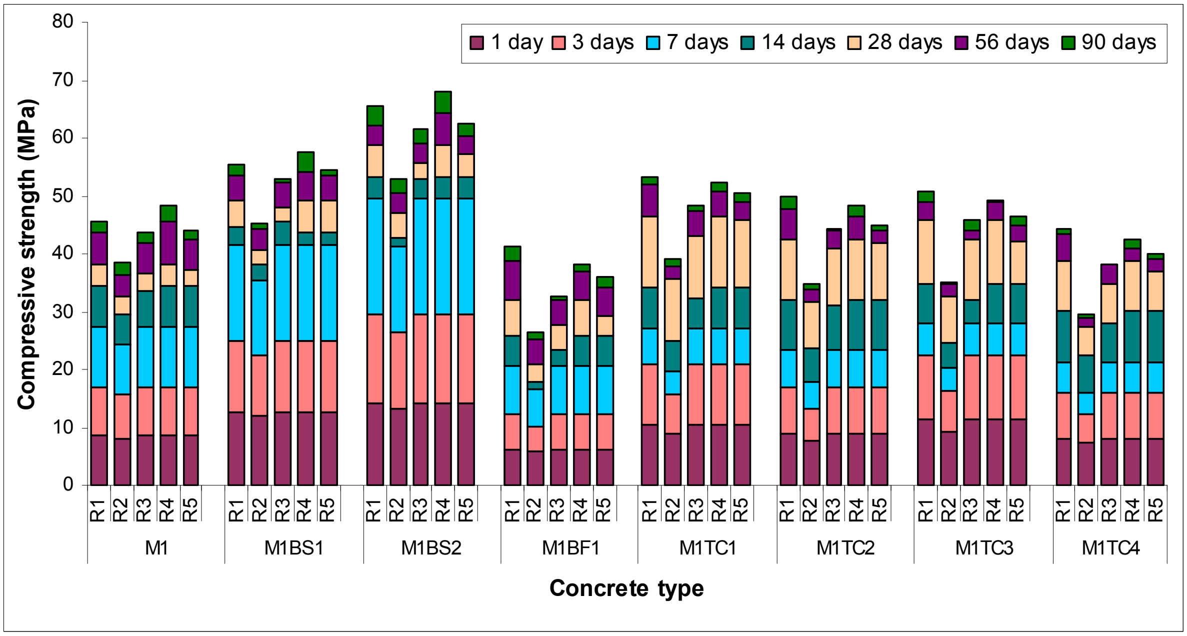


Fig. 4.1. Compressive strength development of mixes with 0.45 water-to-binder ratio

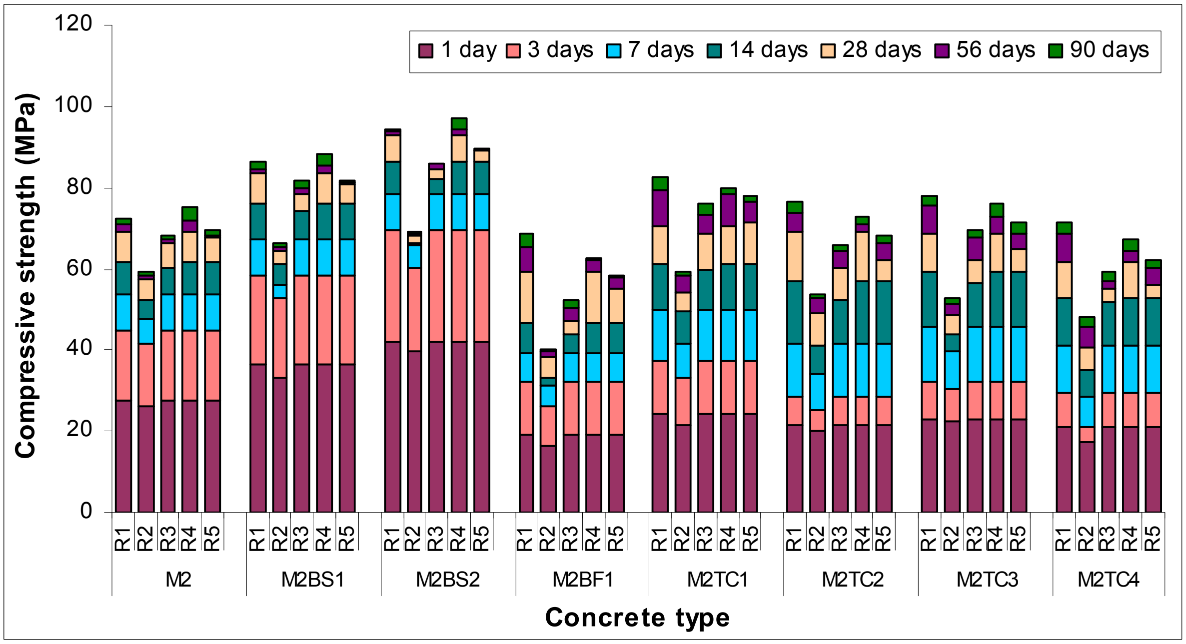


Fig. 4.2. Compressive strength development of mixes with 0.35 water-to-binder ratio

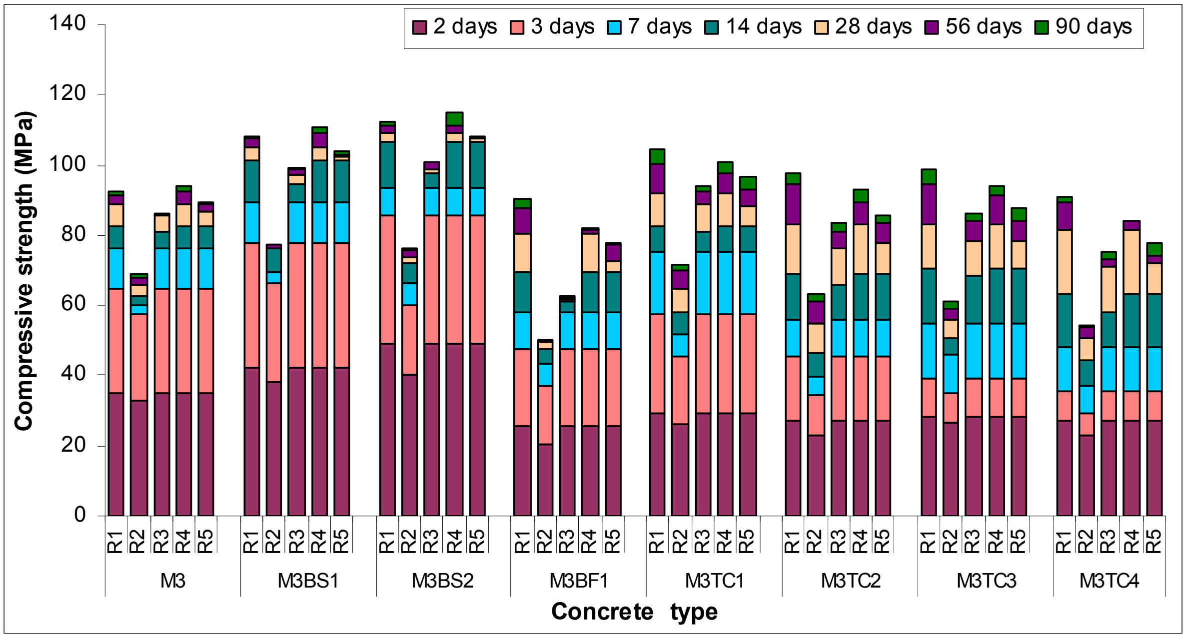


Fig. 4.3. Compressive strength development of mixes with 0.25 water-to-binder ratio

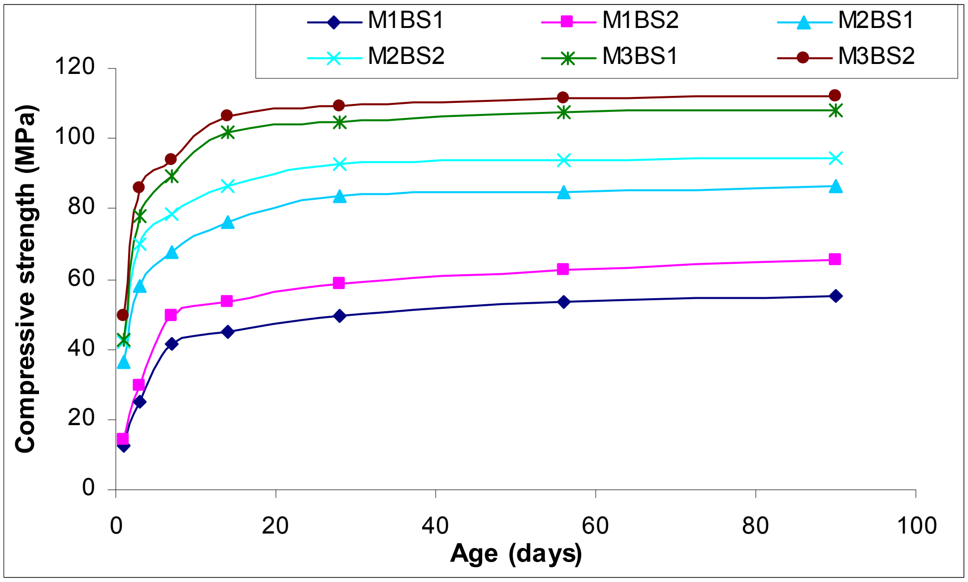


Fig. 4.4. Development of compressive strength for binary mixes with silica fume

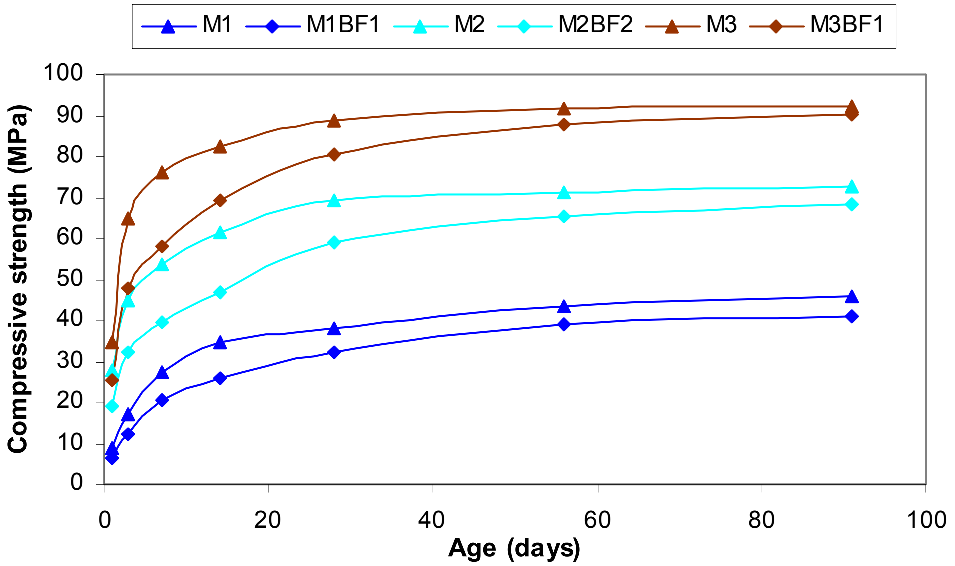


Fig. 4.5. Development of compressive strength for binary mixes with fly ash as compared with the corresponding control mixes

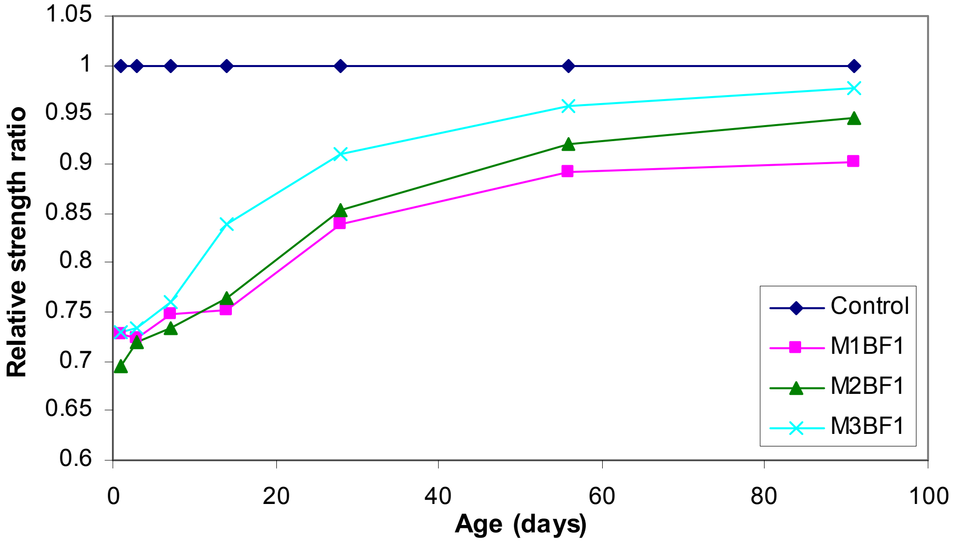


Fig. 4.6. Relative strength of fly ash concrete with respect to the control concrete

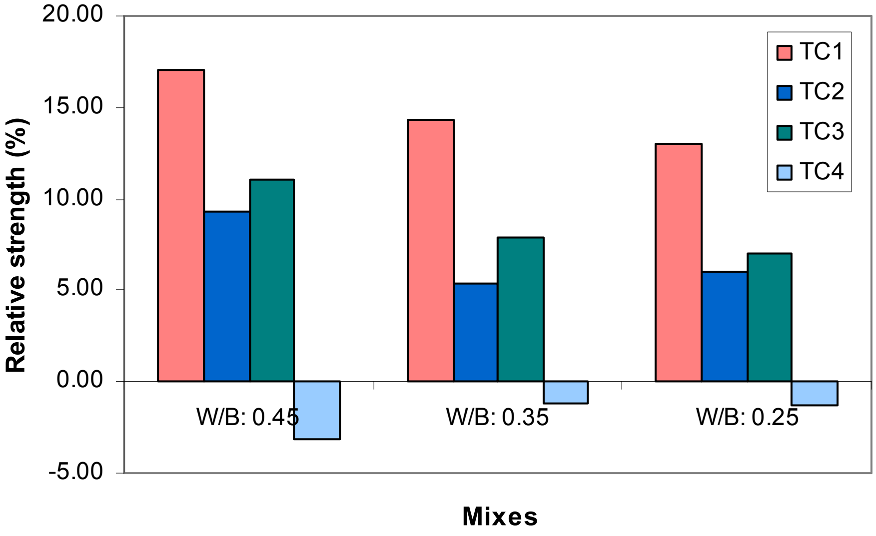


Fig. 4.7. Percentage change in strength of ternary mixes with respect to the corresponding control mix

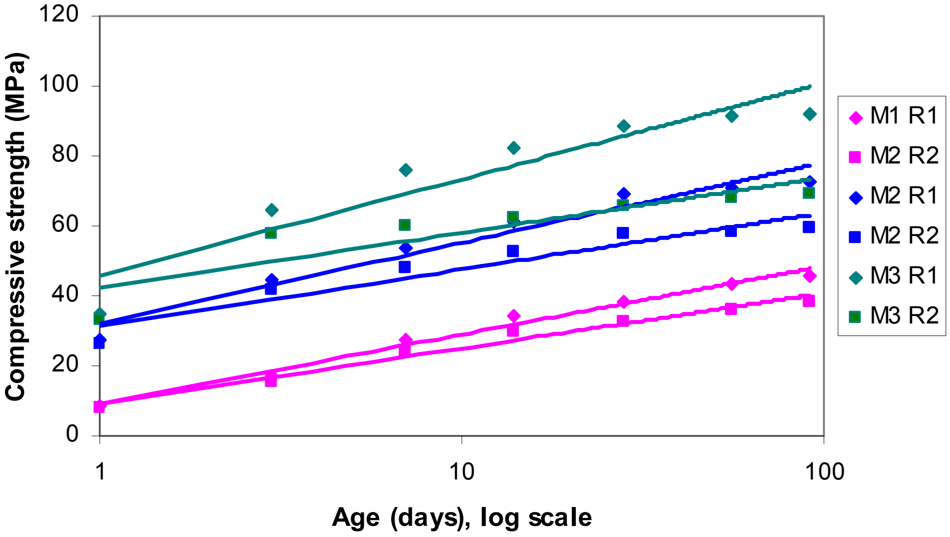


Fig. 4.8. Strength development of OPC concrete in water-curing and air-curing regimes

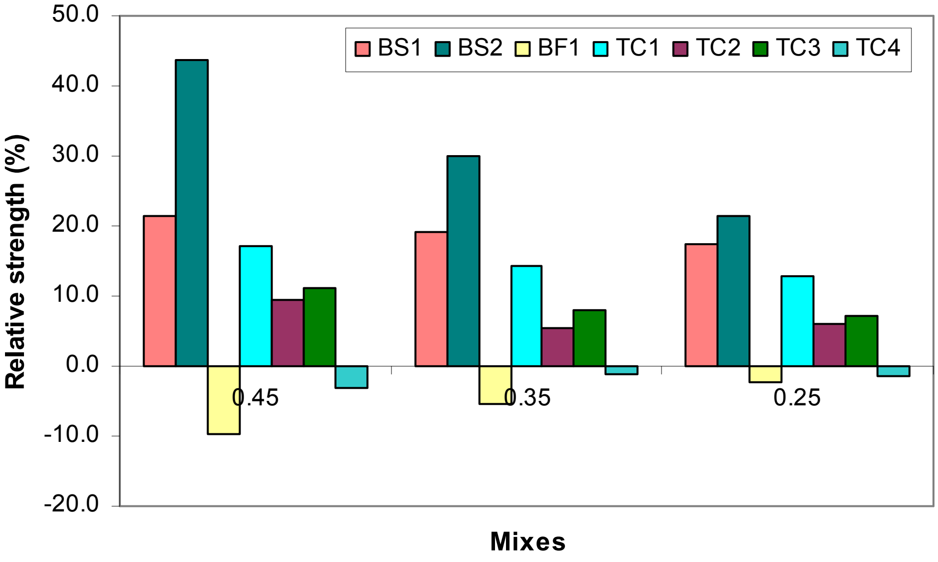


Fig. 4.9. Relative strength of mixes with respect to the corresponding control mix under R1 curing regime (water-curing)

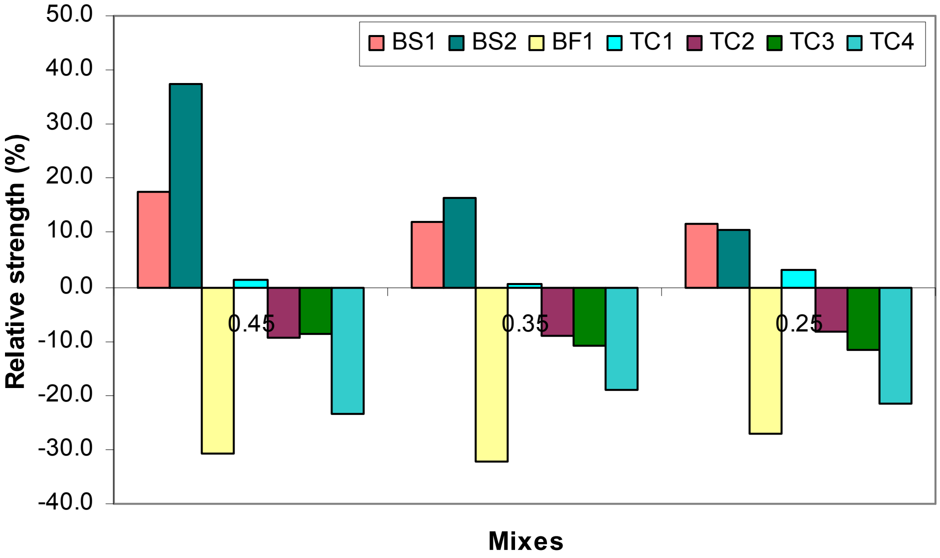


Fig. 4.10. Relative strength of mixes with respect to the corresponding control mix under R2 curing regime (air-curing)

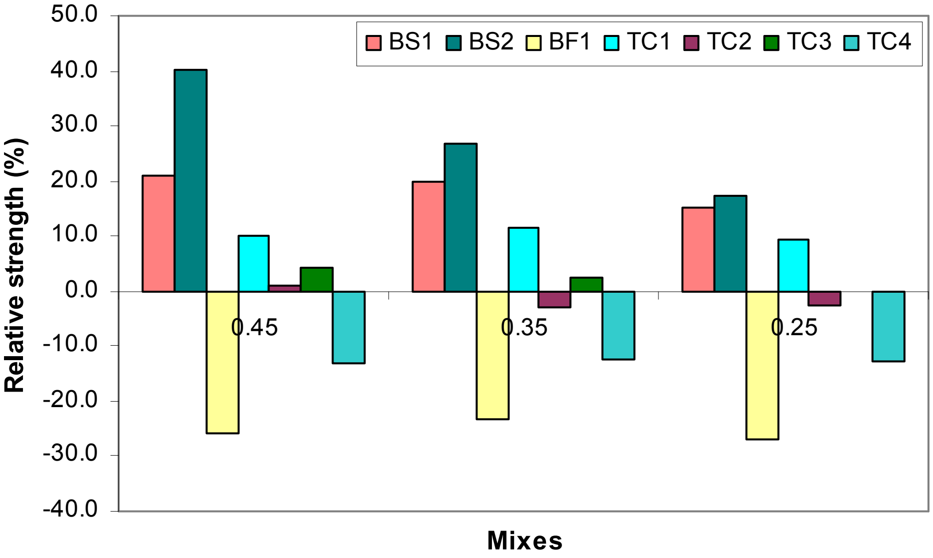


Fig. 4.11. Relative strength of mixes with respect to the corresponding control mix under R3 curing regime

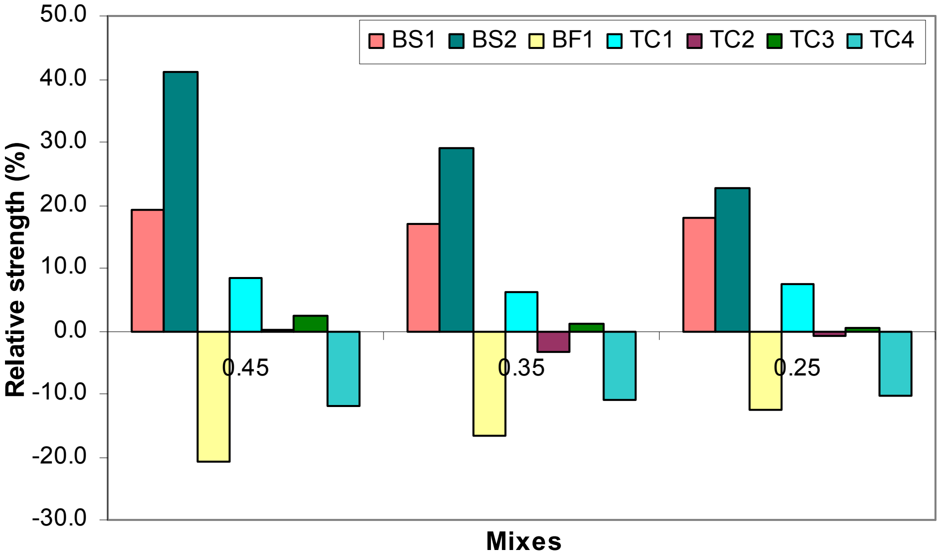


Fig. 4.12. Relative strength of mixes with respect to the corresponding control mix under R4 curing regime

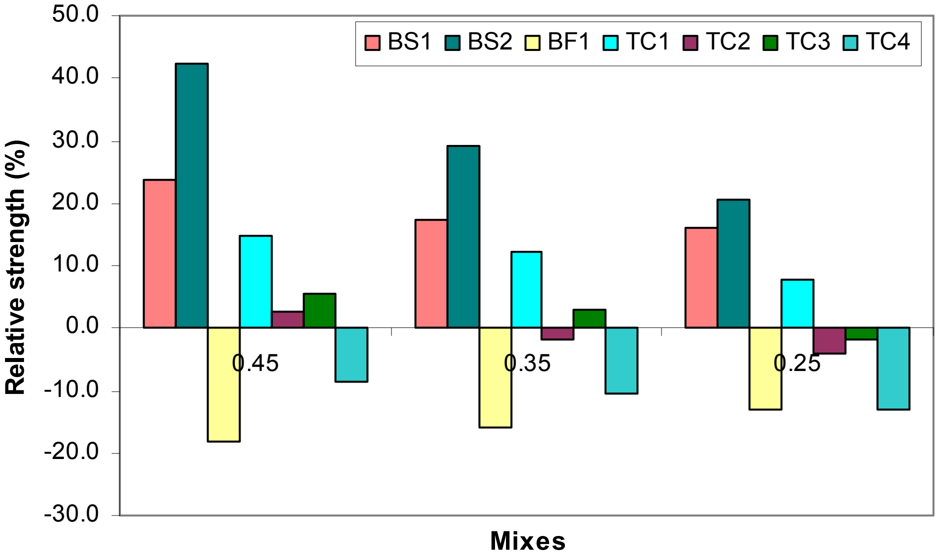
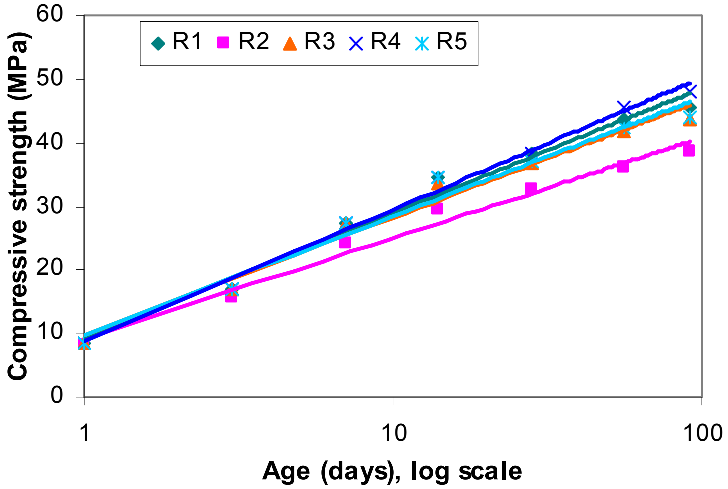
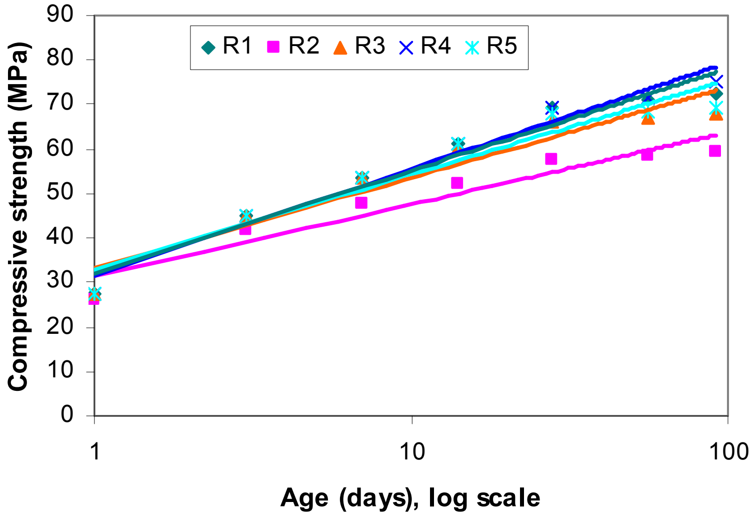


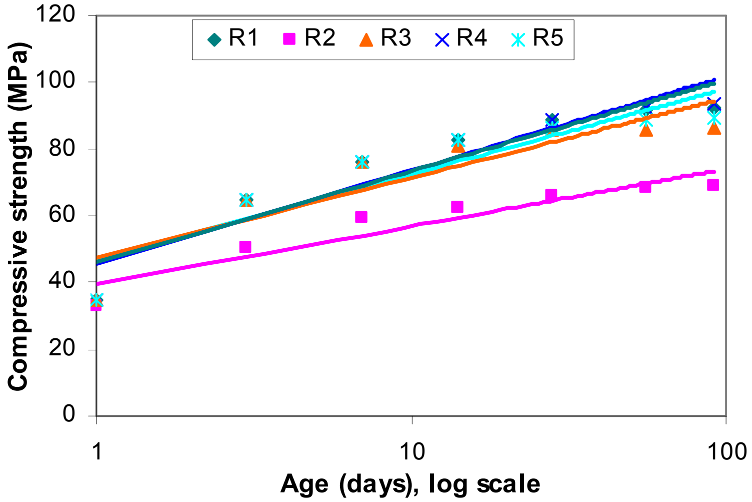
Fig. 4.13. Relative strength of mixes with respect to the corresponding control mix under R5 curing regime



(a) water/binder ratio: 0.45

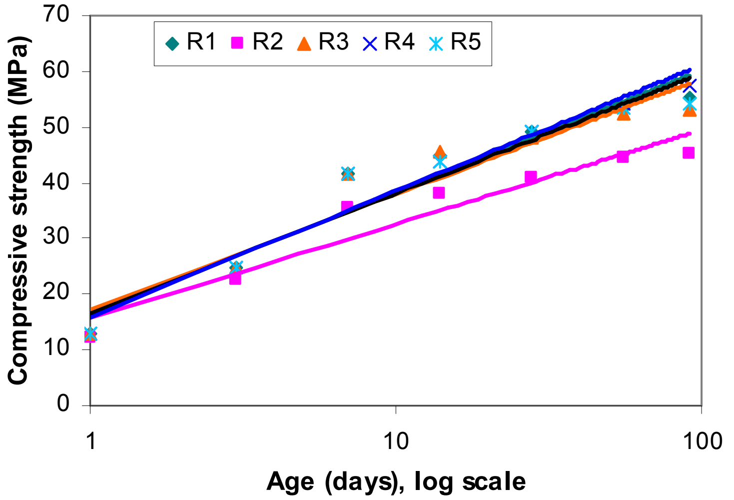


(b) water/binder ratio: 0.35

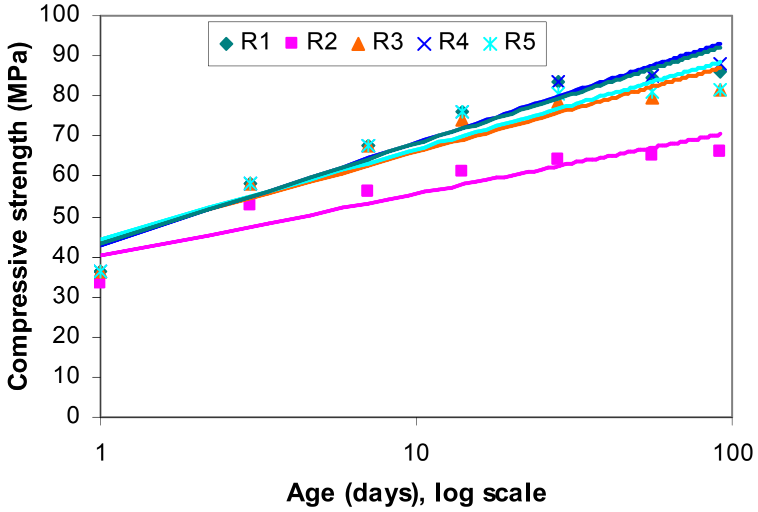


(c) water/binder ratio: 0.25

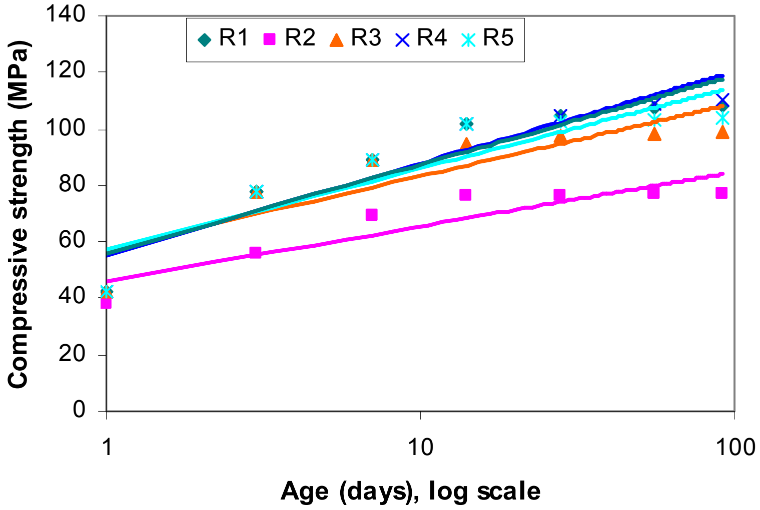
Fig. 4.14. Strength development plots of control mixes under various curing regimes



(a) water/binder ratio: 0.45

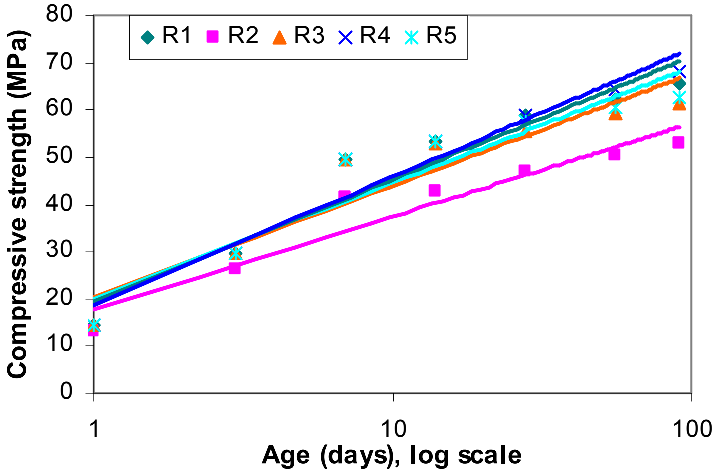


(b) water/binder ratio: 0.35

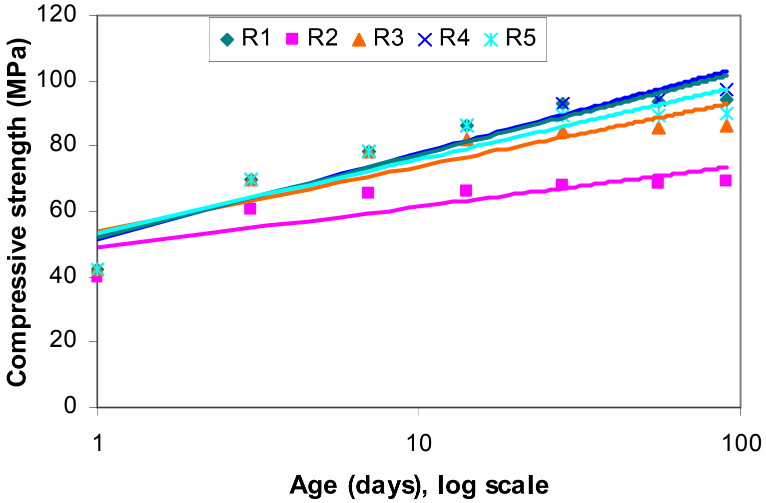


(c) water/binder ratio: 0.25

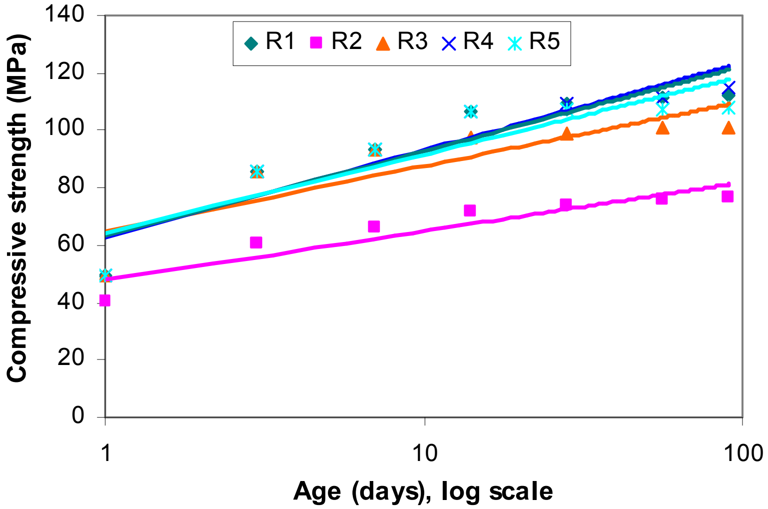
Fig. 4.15. Strength development plots of binary mixes with 5% silica fume under various curing regimes



(a) water/binder ratio: 0.45

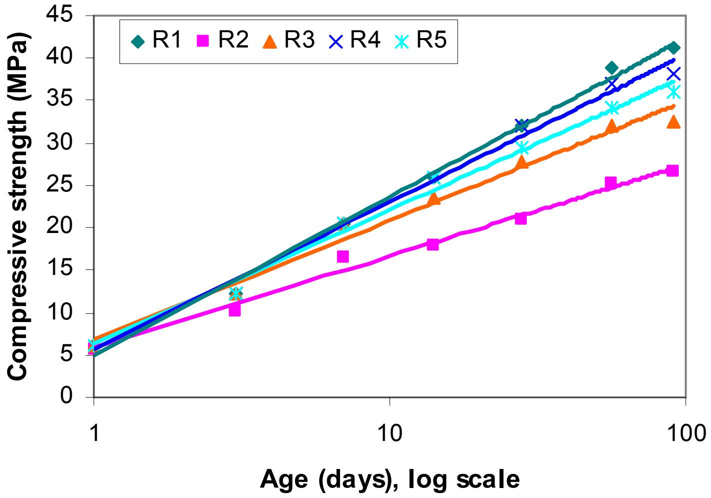


(b) water/binder ratio: 0.35

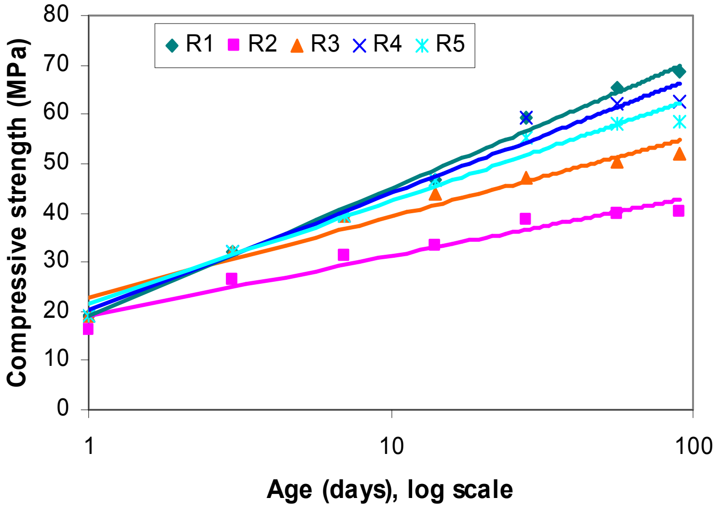


(c) water/binder ratio: 0.25

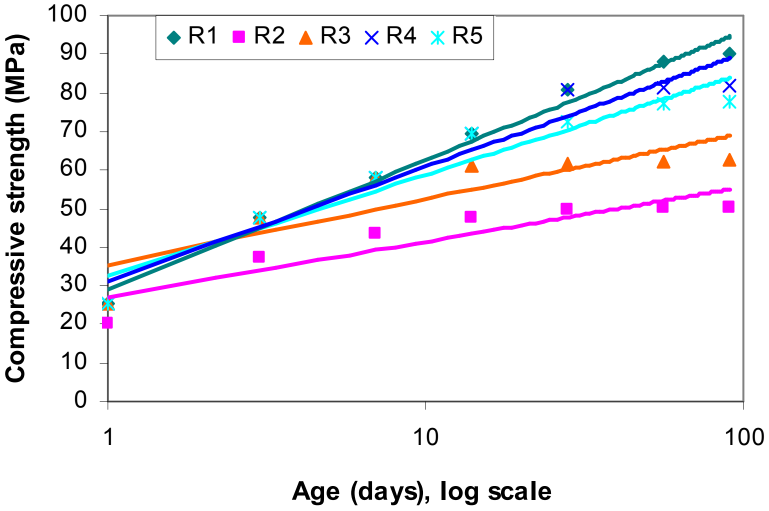
Fig. 4.16. Strength development plots of binary mixes with 10% silica fume under various curing regimes



(a) water/binder ratio: 0.45

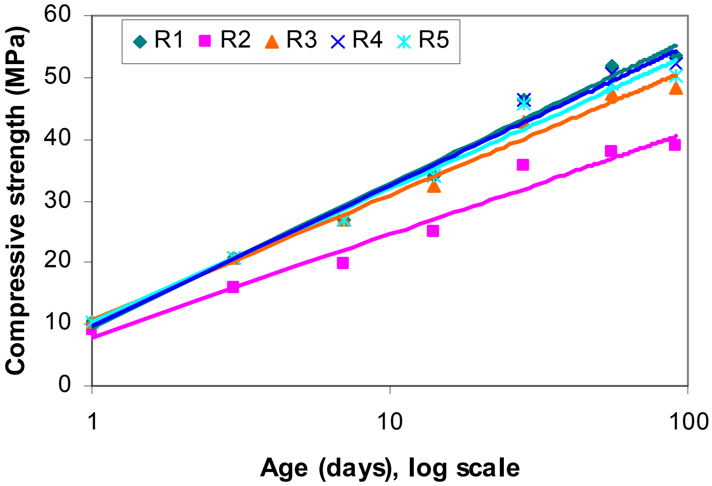


(b) water/binder ratio: 0.35

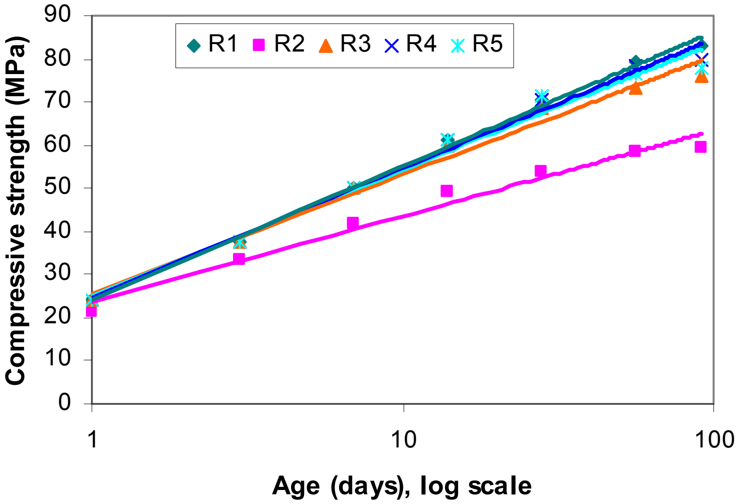


(c) water/binder ratio: 0.25

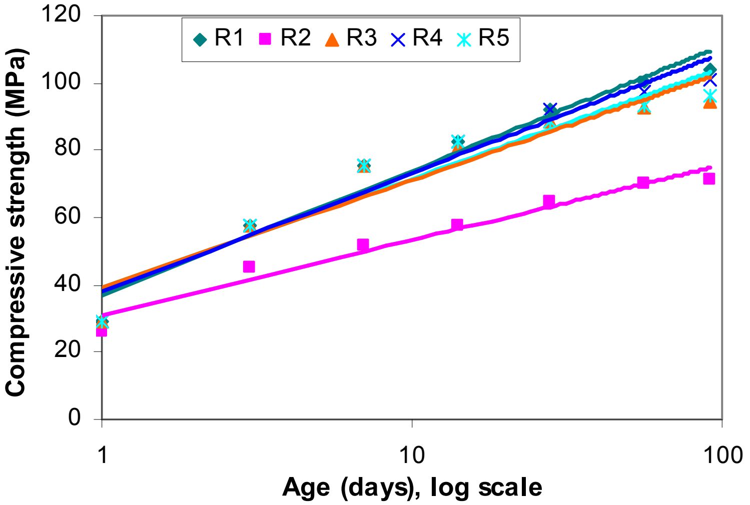
Fig. 4.17. Strength development plots of binary mixes with 30% fly ash under various curing regimes



(a) water/binder ratio: 0.45

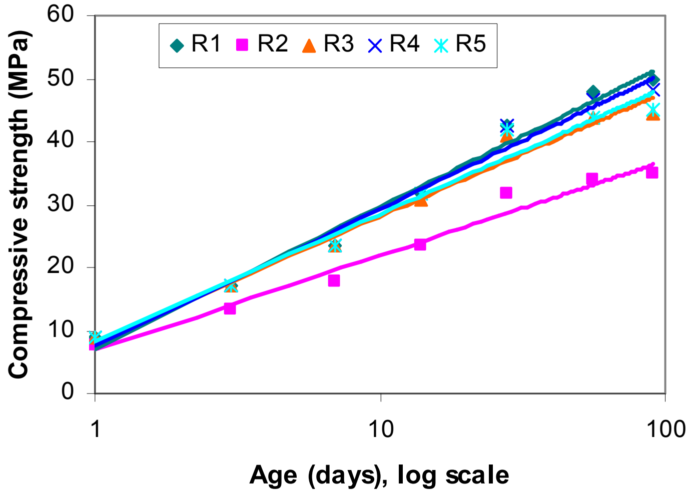


(b) water/binder ratio: 0.35

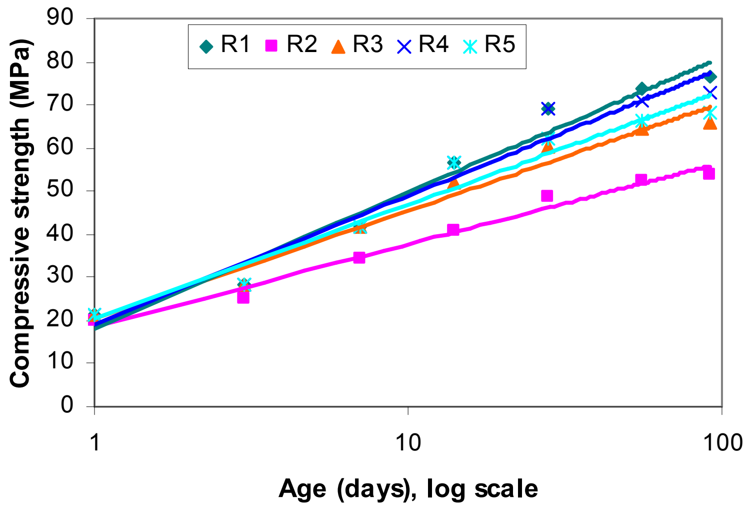


(c) water/binder ratio: 0.25

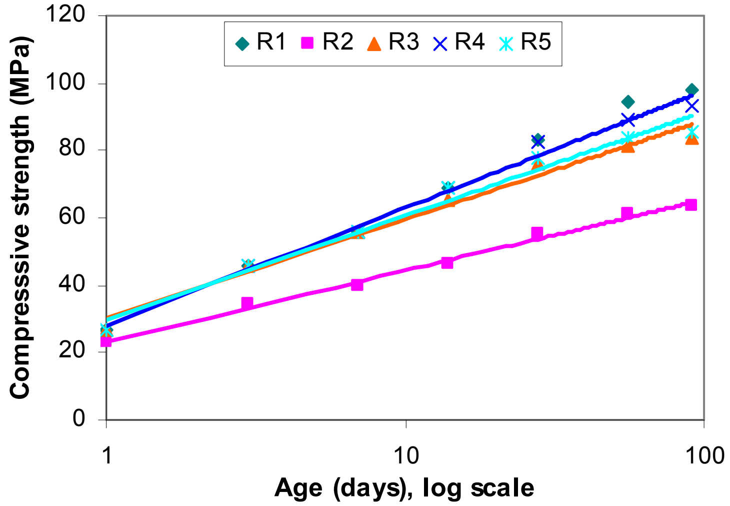
Fig. 4.18. Strength development plots of ternary mixes with 5% silica fume and 15% fly ash under various curing regimes



(a) water/binder ratio: 0.45

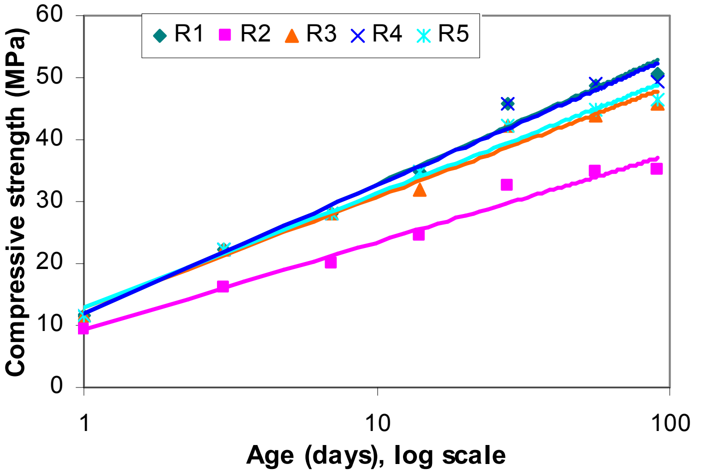


(b) water/binder ratio: 0.35

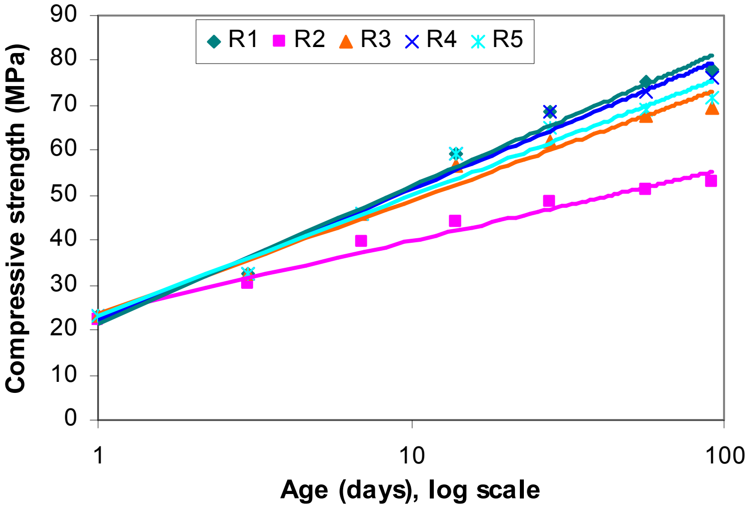


(c) water/binder ratio: 0.25

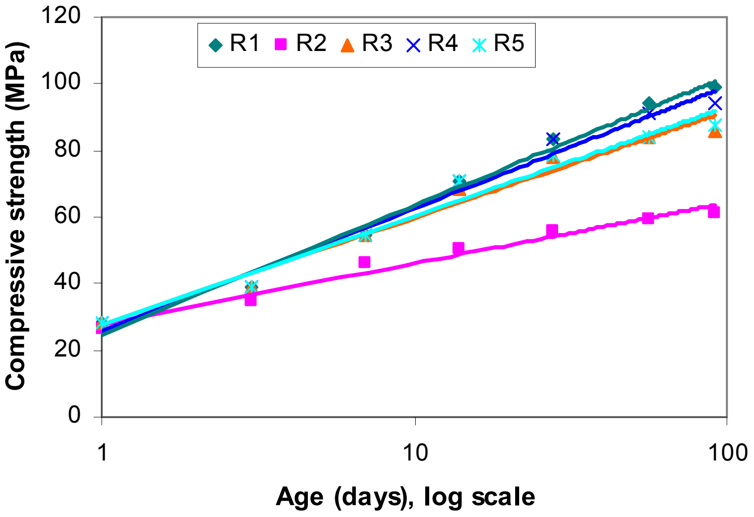
Fig. 4.19. Strength development plots of ternary mixes with 5% silica fume and 20% fly ash under various curing regimes



(a) water/binder ratio: 0.45

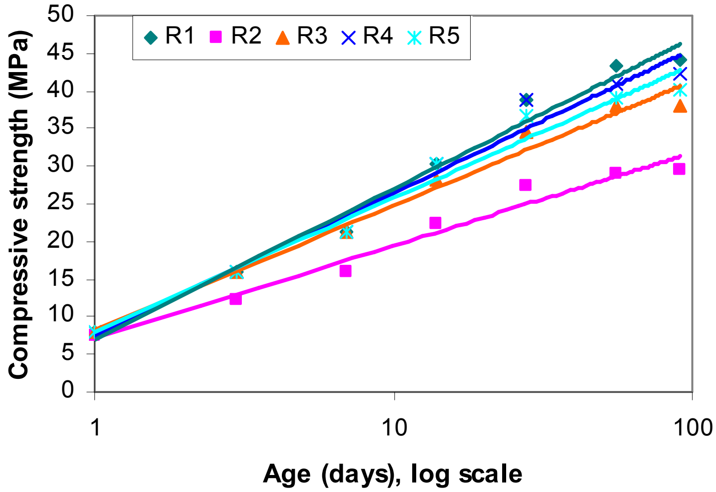


(b) water/binder ratio: 0.35

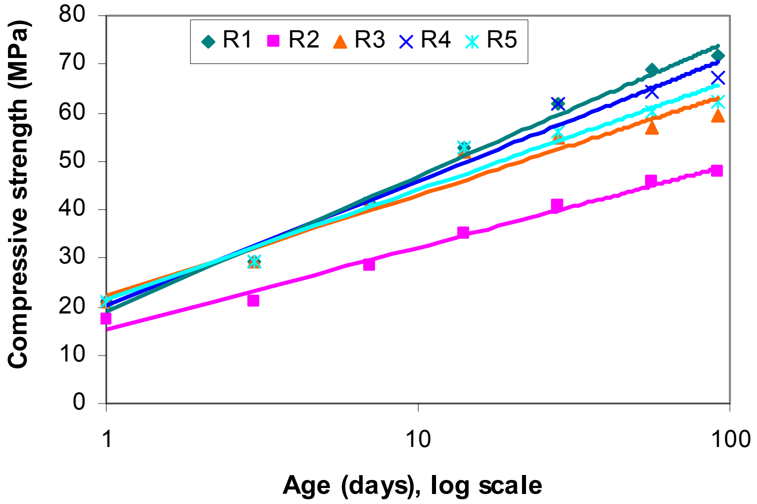


(c) water/binder ratio: 0.25

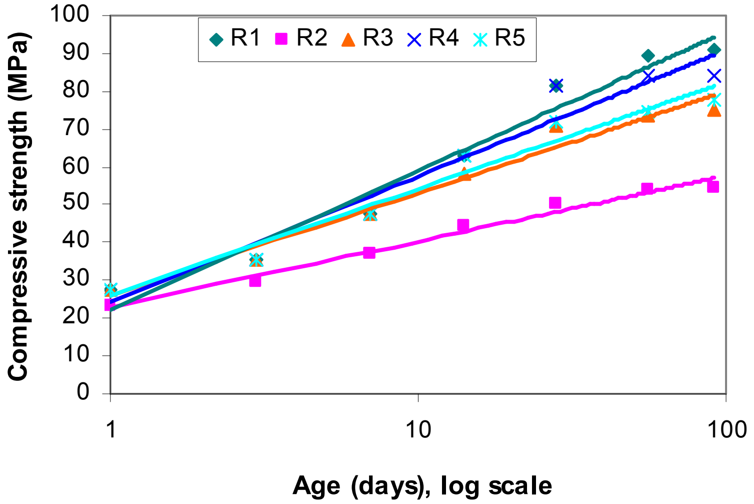
Fig. 4.20. Strength development plots of ternary mixes with 10% silica fume and 15% fly ash under various curing regimes



(a) water/binder ratio: 0.45



(b) water/binder ratio: 0.35



(c) water/binder ratio: 0.25

Fig. 4.21. Strength development plots of ternary mixes with 10% silica fume and 20% fly ash under various curing regimes

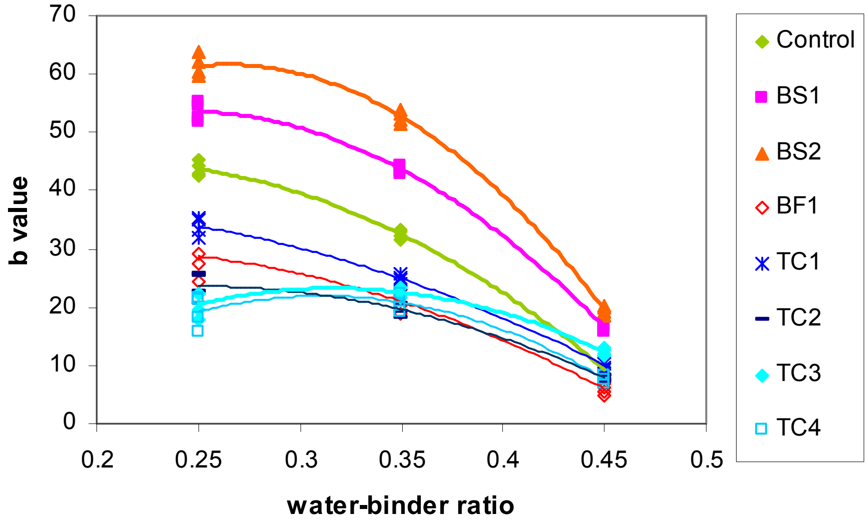
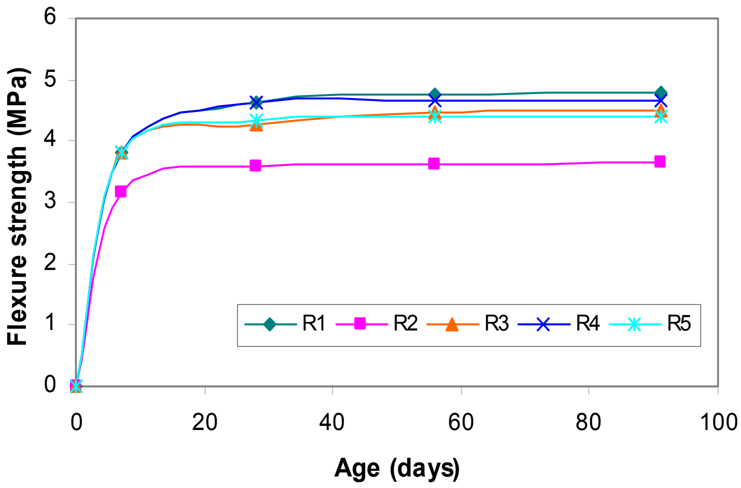
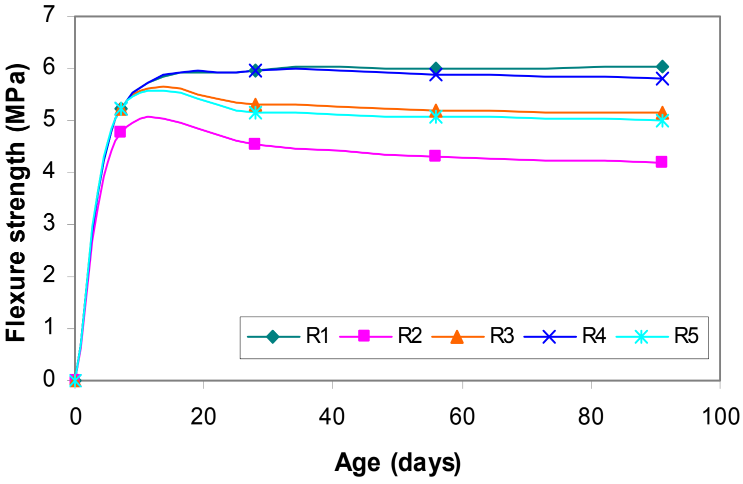


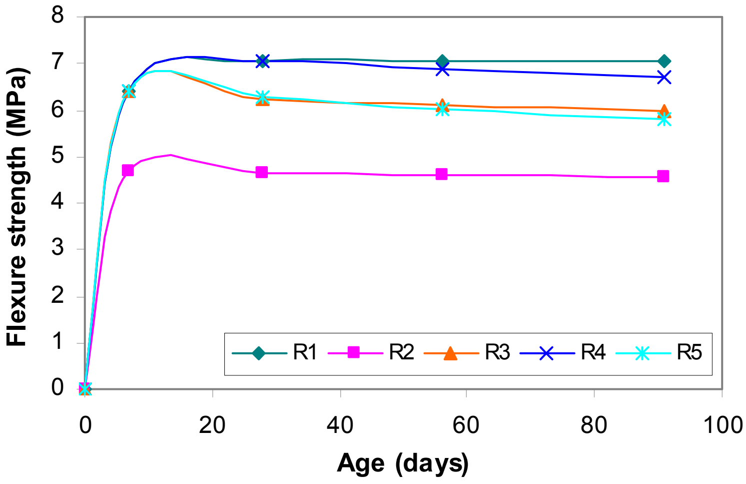
Fig. 4.22. Variation of b – value with water-to-binder ratio for all mixes



(a) water/binder ratio: 0.45

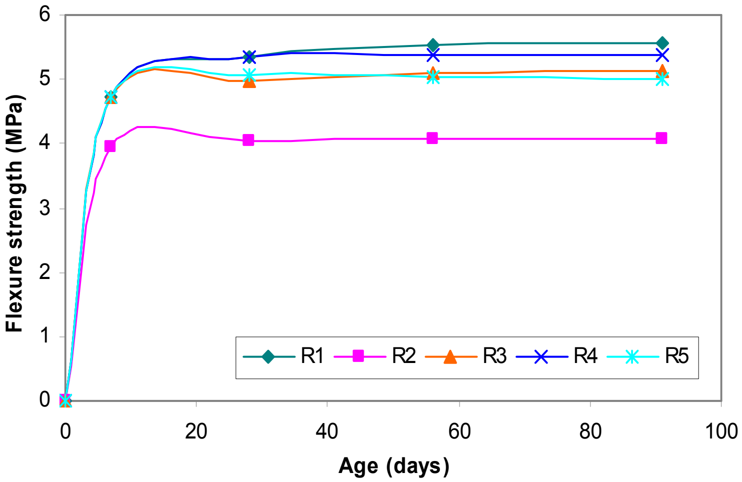


(b) water/binder ratio: 0.35

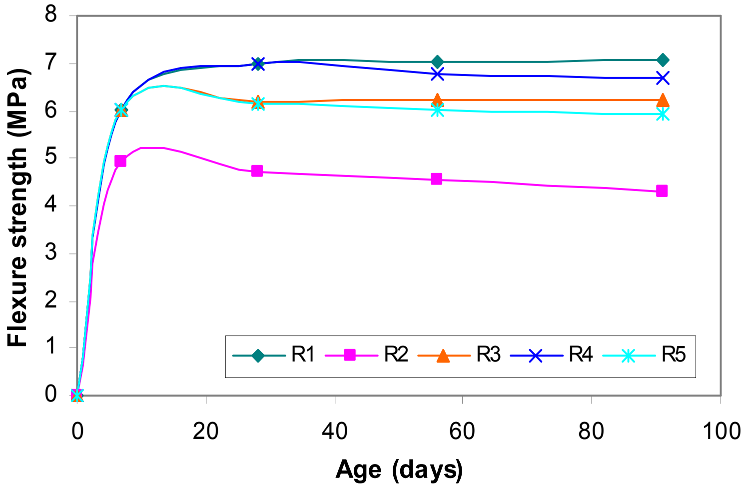


(c) water/binder ratio: 0.25

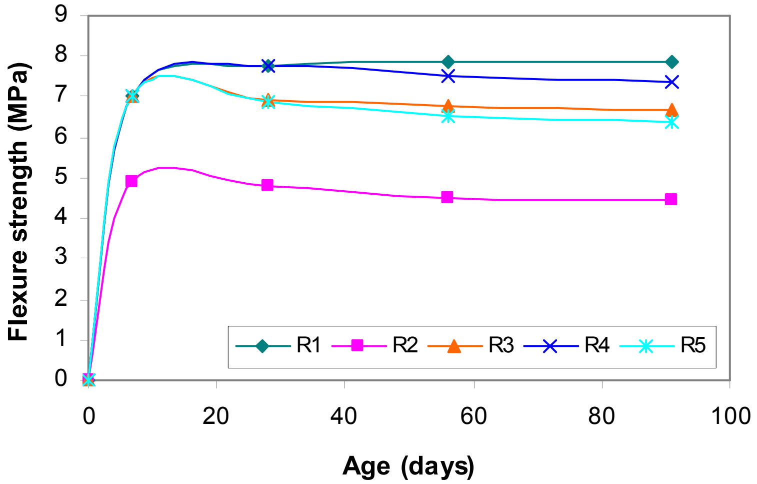
Fig. 4.23. Flexure strength development of control mixes under various curing regimes



(a) water/binder ratio: 0.45

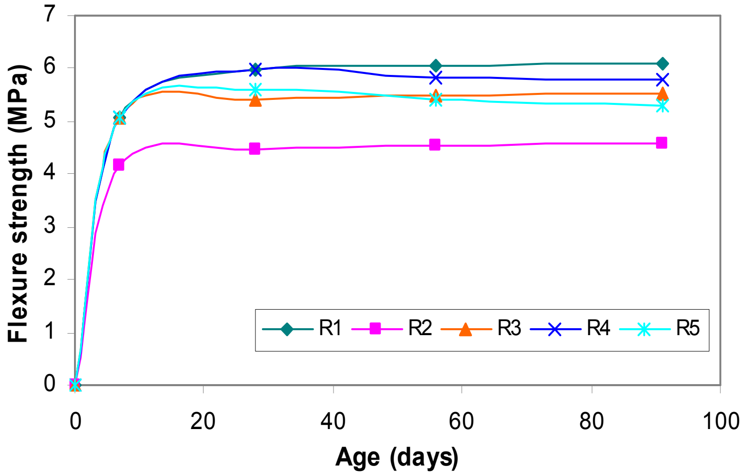


(b) water/binder ratio: 0.35

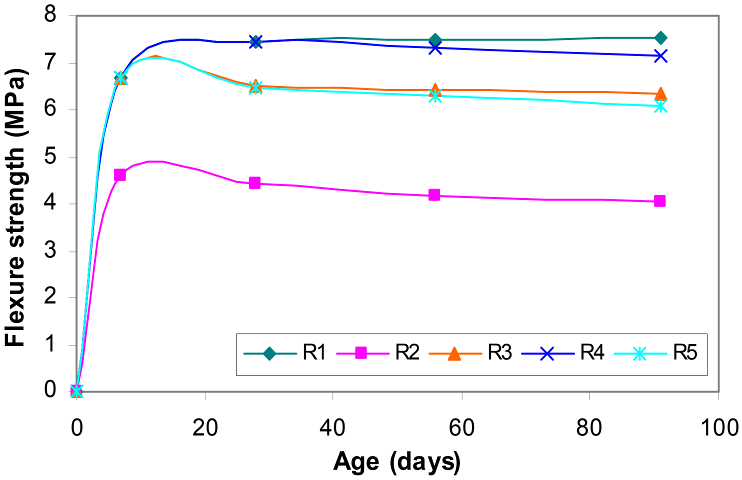


(c) water/binder ratio: 0.25

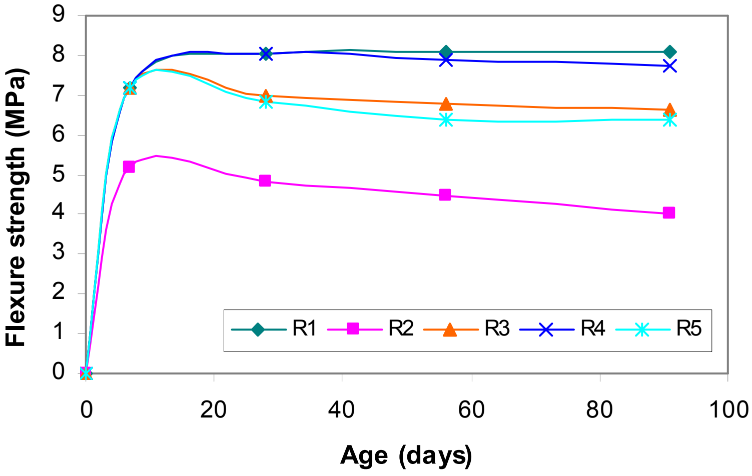
Fig. 4.24. Flexure strength development of binary mixes with 5% silica fume under various curing regimes



(a) water/binder ratio: 0.45

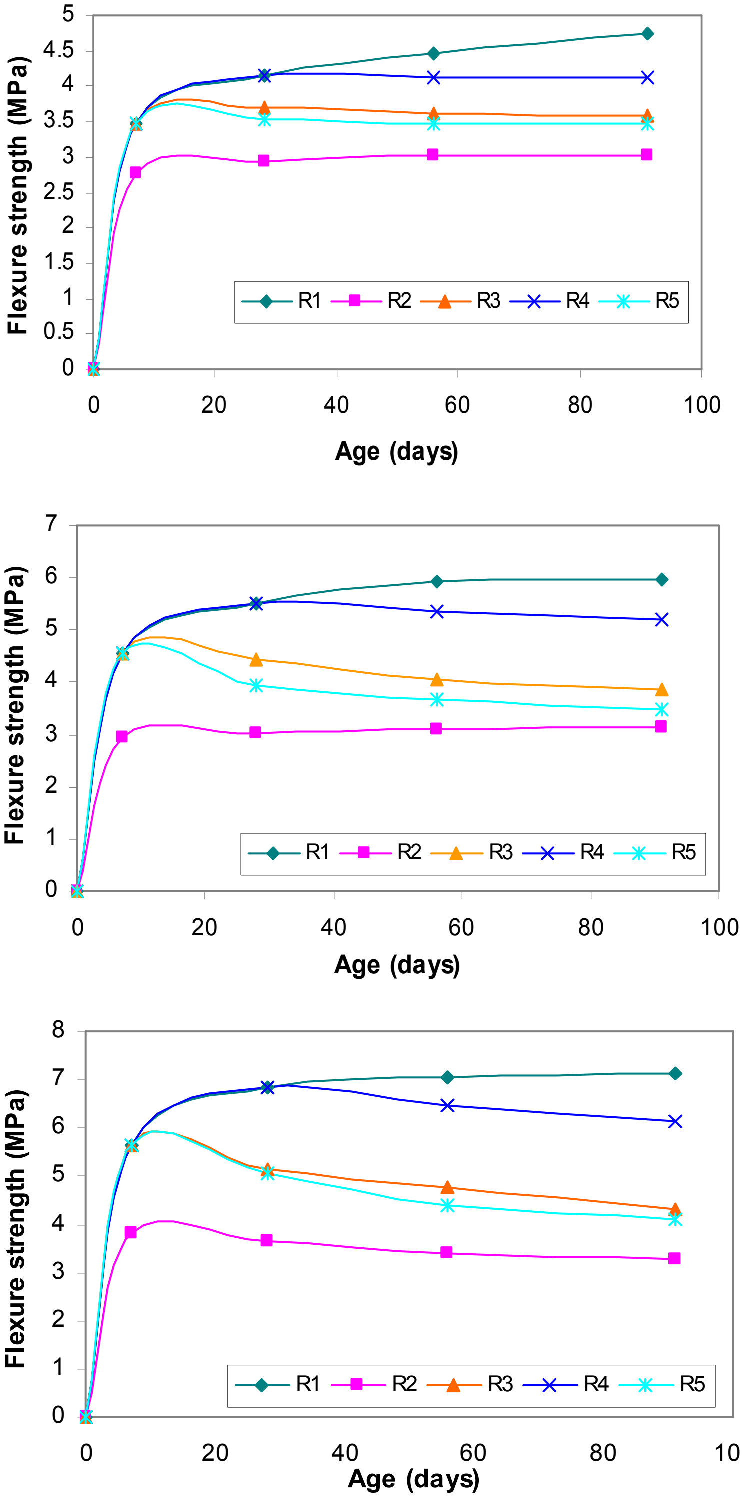


(b) water/binder ratio: 0.35



(c) water/binder ratio: 0.25

Fig. 4.25. Flexure strength development of binary mixes with 10% silica fume under various curing regimes

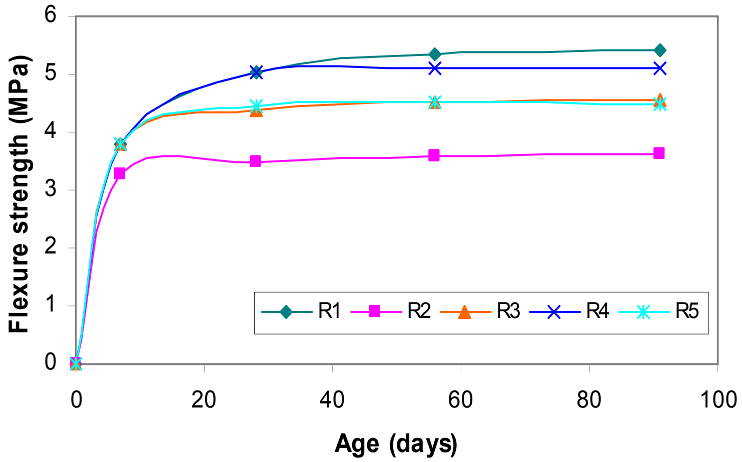


(a) water/binder ratio: 0.45

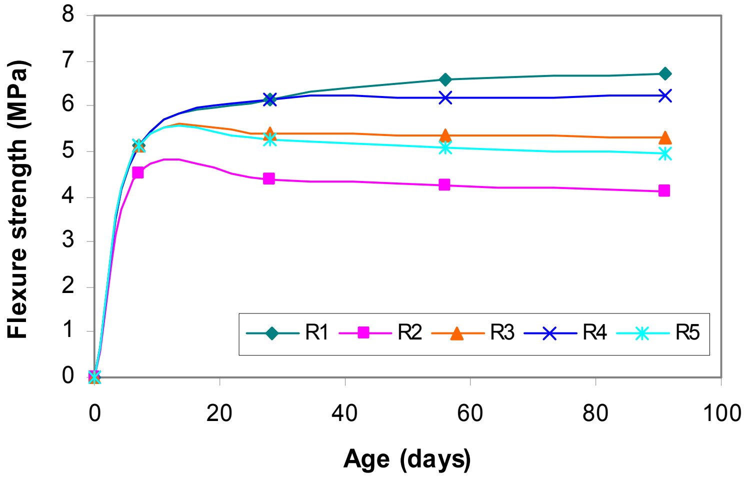
(b) water/binder ratio: 0.35

(c) water/binder ratio: 0.25

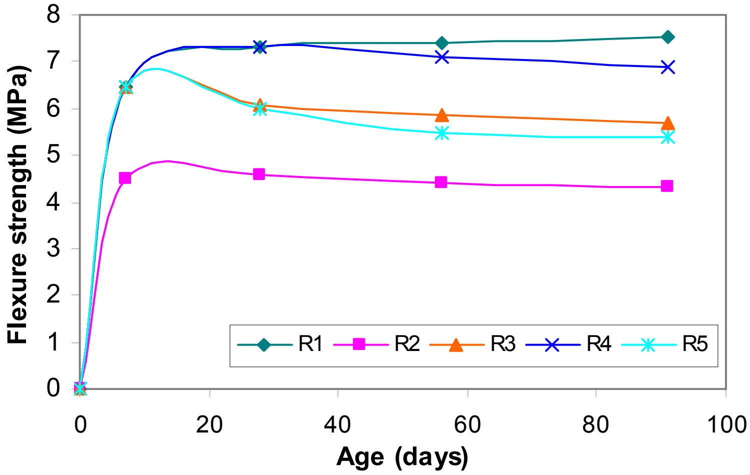
Fig. 4.26. Flexure strength development of binary mixes with 30% fly ash under various curing regimes



(a) water/binder ratio: 0.45

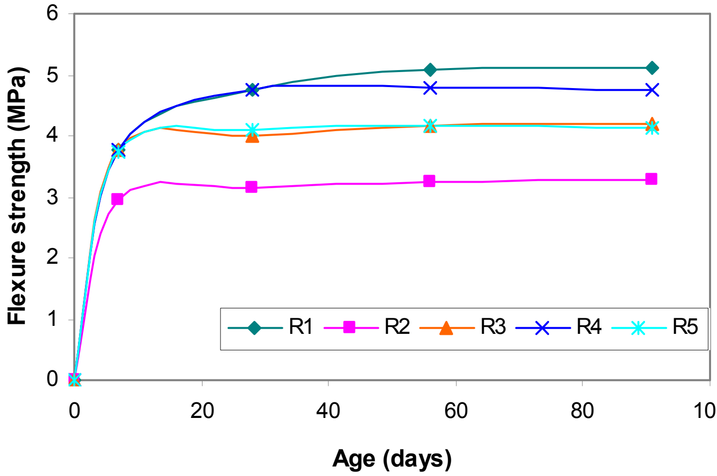


(b) water/binder ratio: 0.35

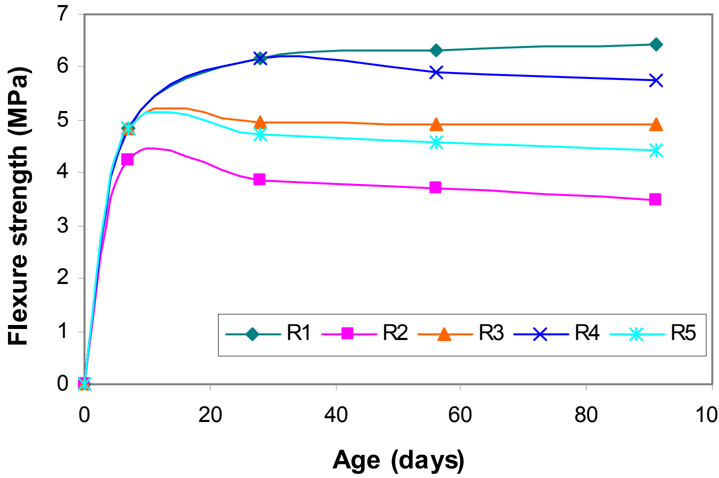


(c) water/binder ratio: 0.25

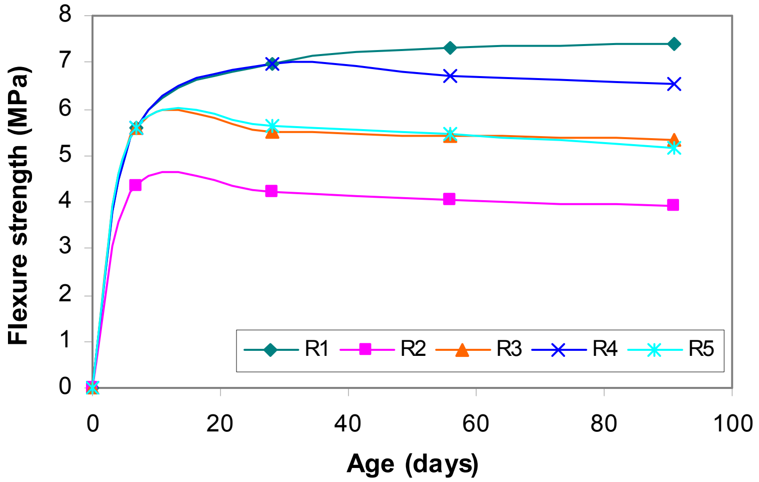
Fig. 4.27. Flexure strength development of ternary mixes with 5% silica fume and 15% fly ash under various curing regimes



(a) water/binder ratio: 0.45

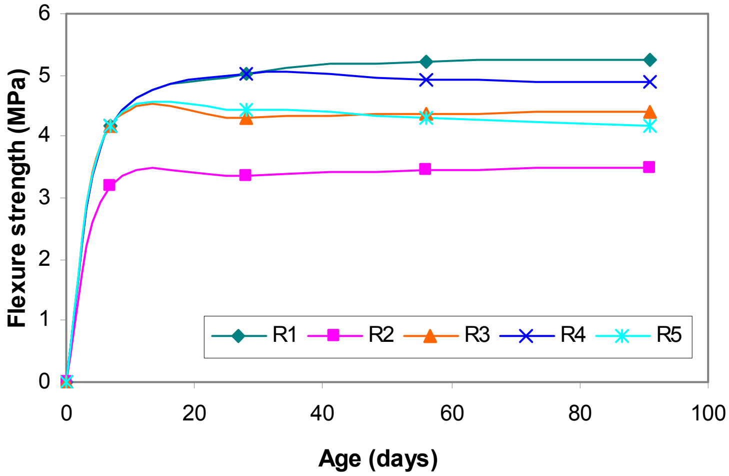


(b) water/binder ratio: 0.35

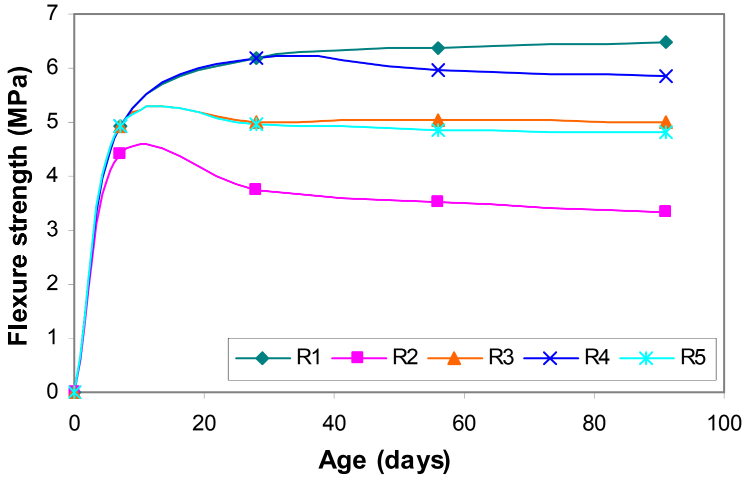


(c) water/binder ratio: 0.25

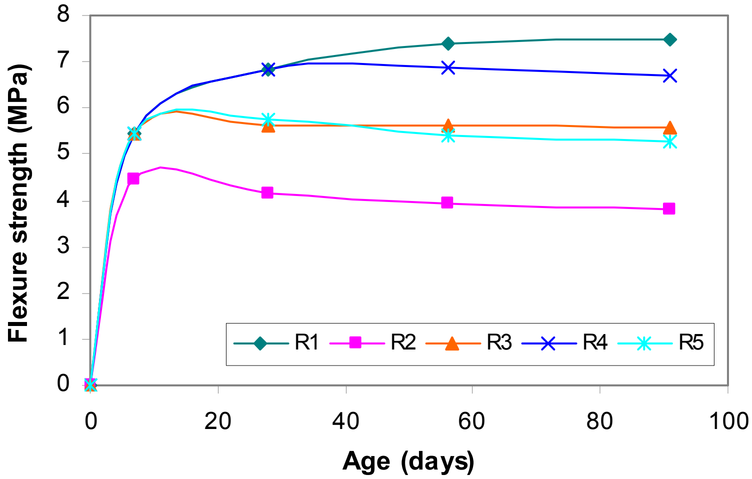
Fig. 4.28. Flexure strength development of ternary mixes with 5% silica fume and 20% fly ash under various curing regimes



(a) water/binder ratio: 0.45

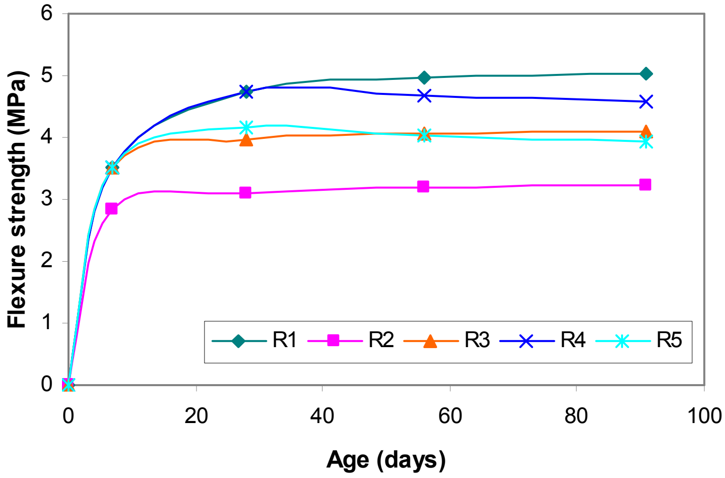


(b) water/binder ratio: 0.35

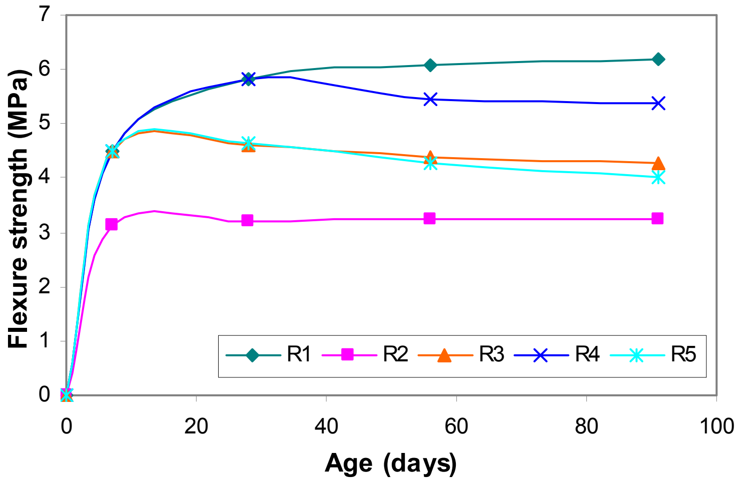


(c) water/binder ratio: 0.25

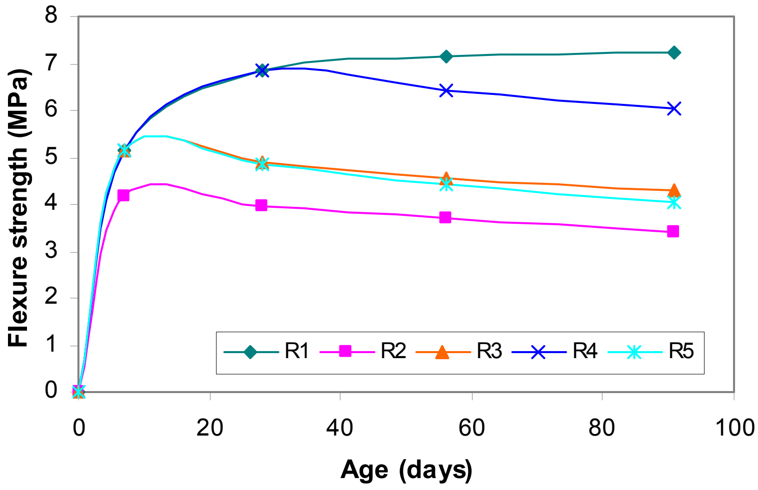
Fig. 4.29. Flexure strength development of ternary mixes with 10% silica fume and 15% fly ash under various curing regimes



(a) water/binder ratio: 0.45



(b) water/binder ratio: 0.35



(c) water/binder ratio: 0.25

Fig. 4.30. Flexure strength development of ternary mixes with 10% silica fume and 20% fly ash under various curing regimes

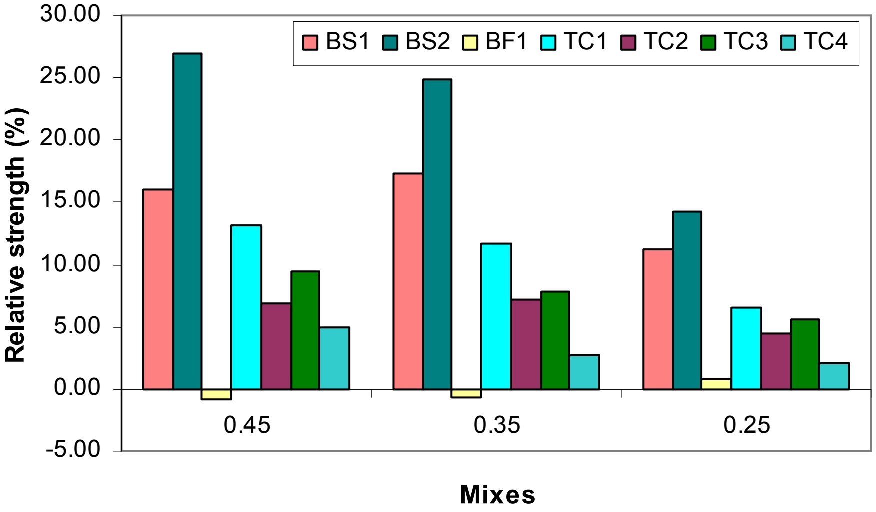


Fig. 4.31. Relative flexure strength of mixes with respect to the corresponding control mix under R1 curing regime (water-curing)

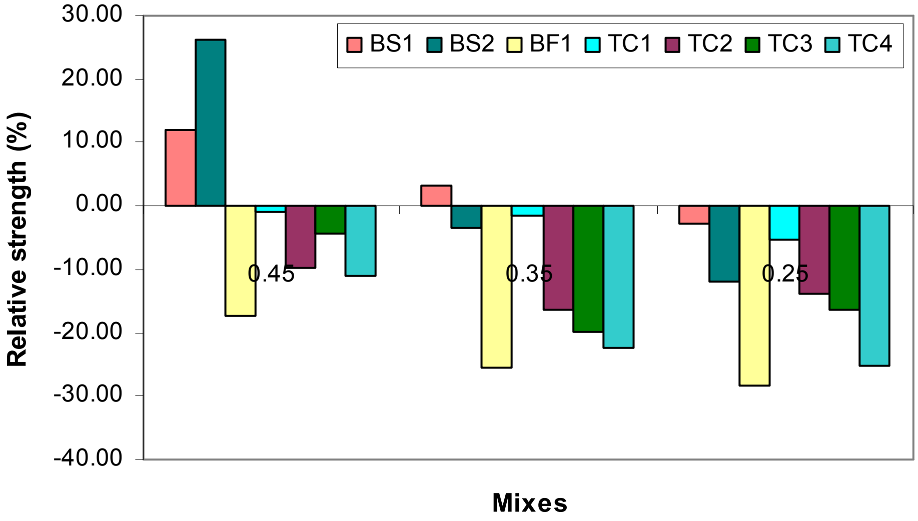


Fig. 4.32. Relative flexure strength of mixes with respect to the corresponding control mix under R2 curing regime (air-curing)

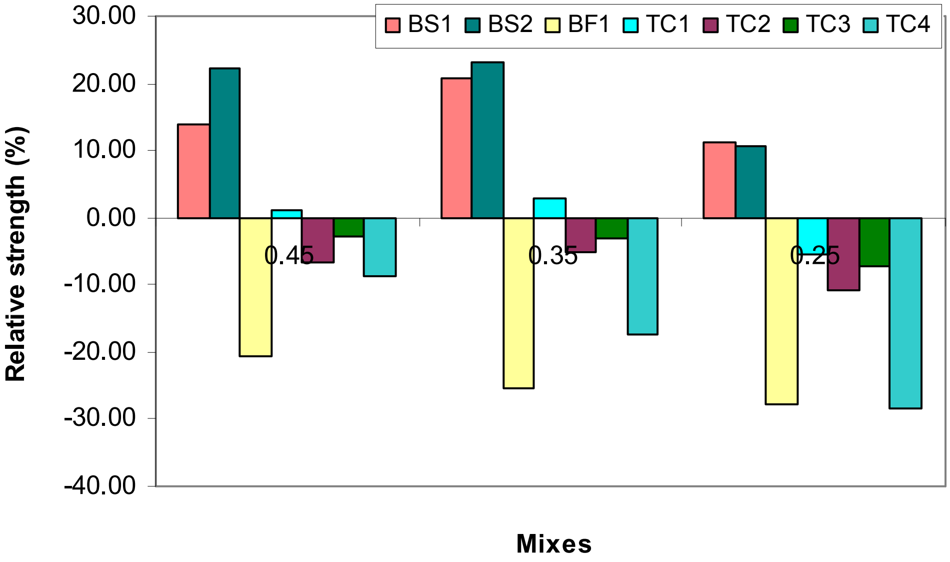


Fig. 4.33. Relative flexure strength of mixes with respect to the corresponding control mix under R3 curing regime

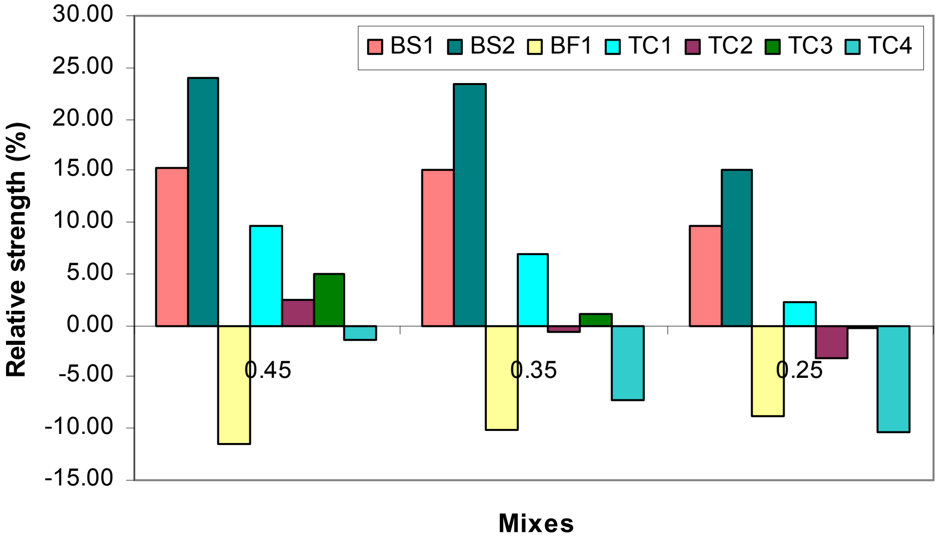


Fig. 4.34. Relative flexure strength of mixes with respect to the corresponding control mix under R4 curing regime

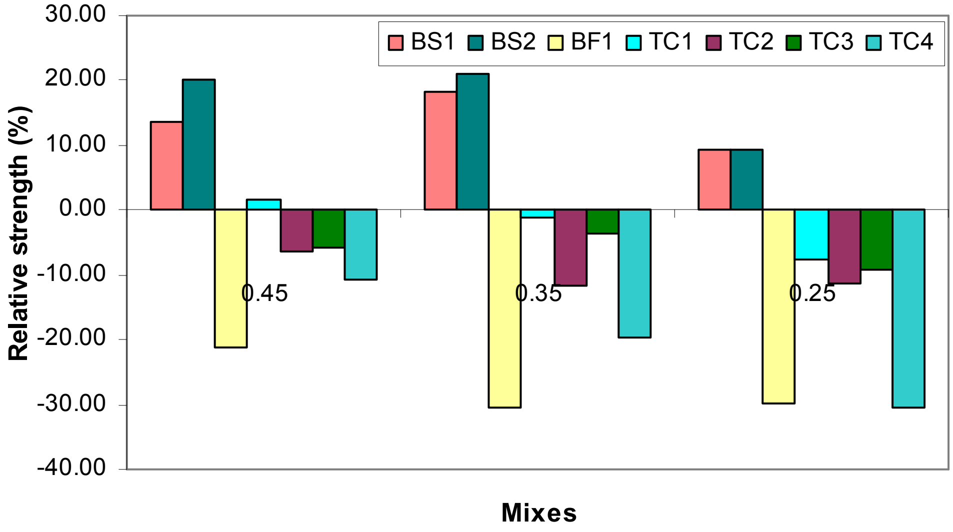


Fig. 4.35. Relative flexure strength of mixes with respect to the corresponding control mix under R5 curing regime

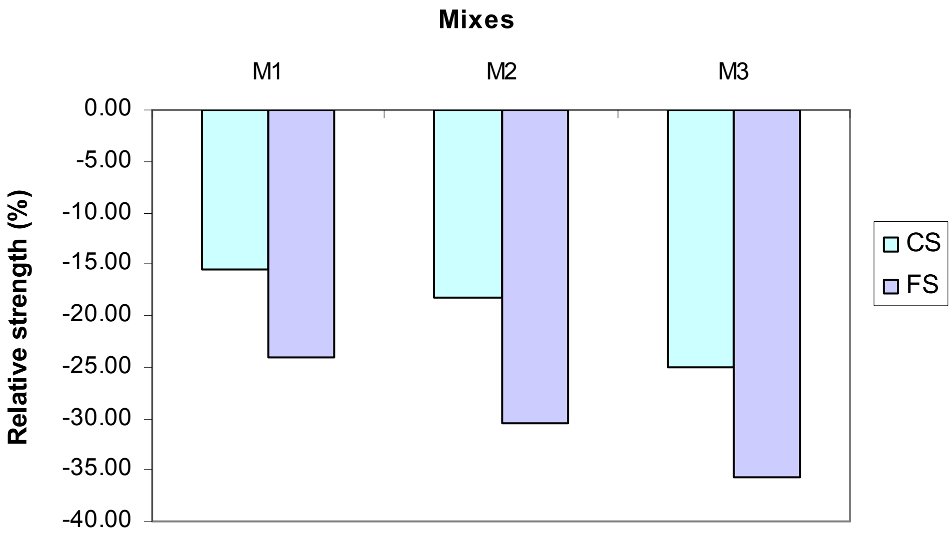


Fig. 4.36. Relative compressive strength and flexure strength of the control mixes under R2 curing regime (air-curing)

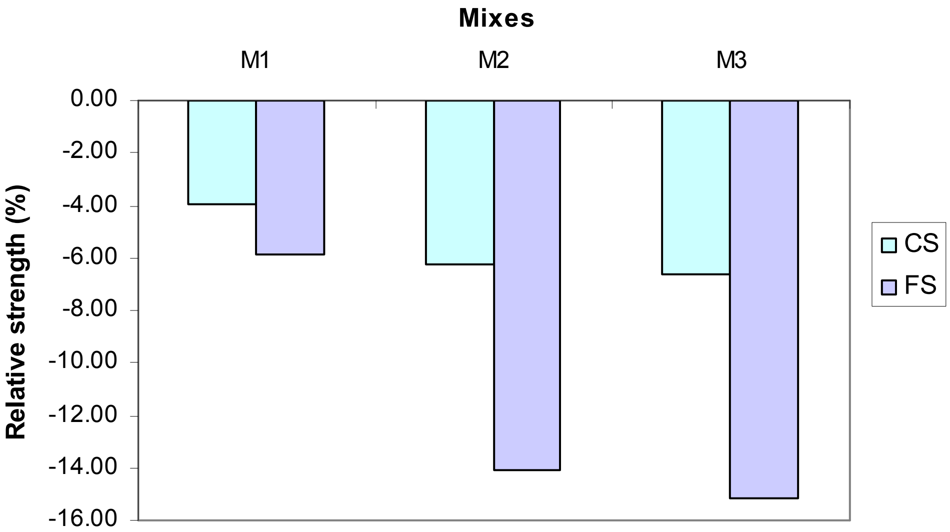


Fig. 4.37. Relative compressive strength and flexure strength of the control mixes under R3 curing regime

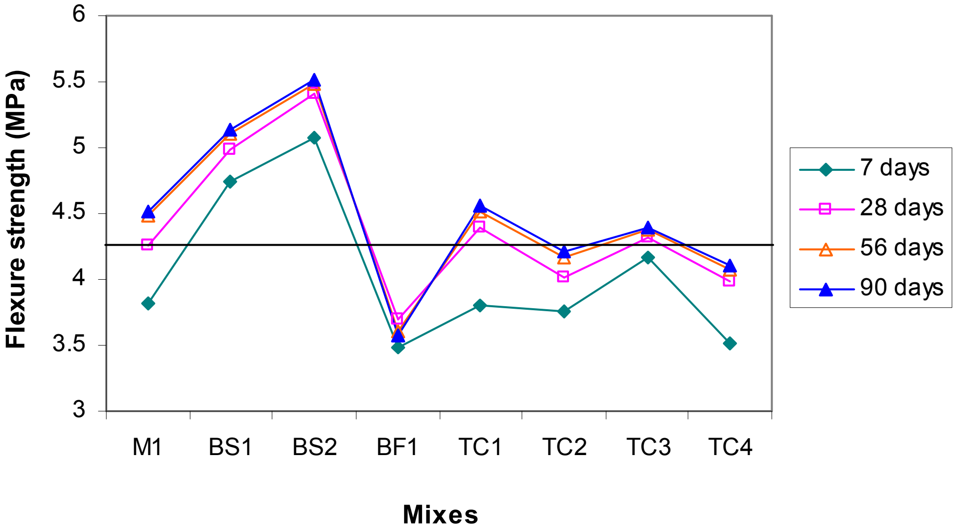


Fig. 4.38. Flexure strength development of all the mixes at water-to-binder ratio of 0.45 and under R3 curing regime

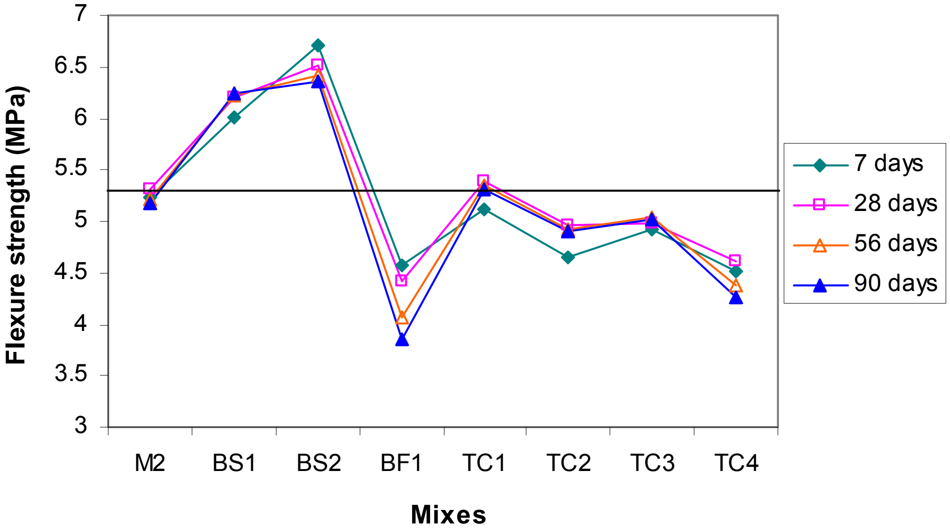


Fig. 4.39. Flexure strength development of all the mixes at water-to-binder ratio of 0.35 and under R3 curing regime

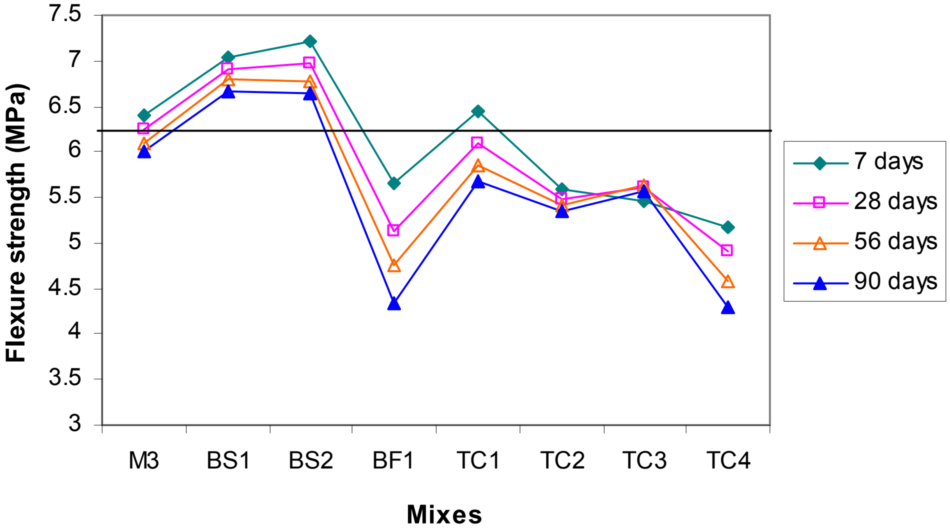
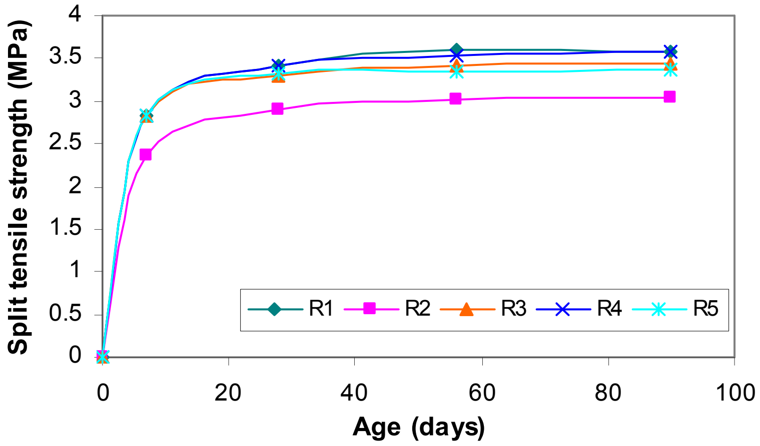
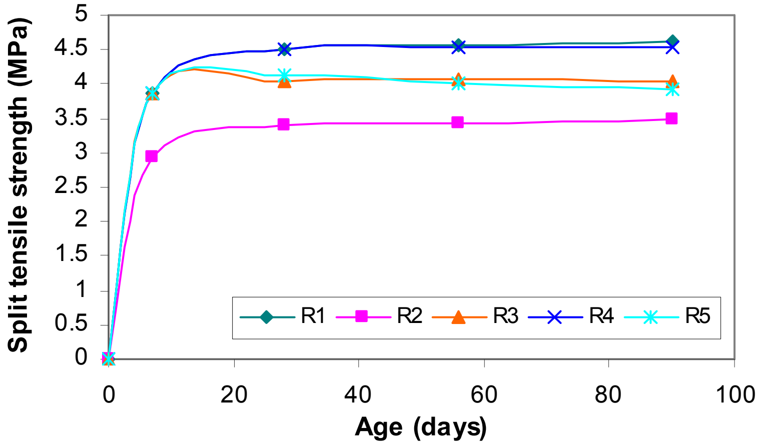


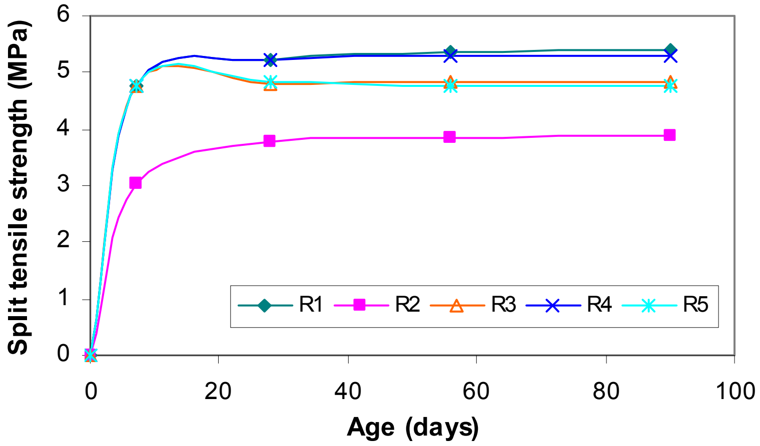
Fig. 4.40. Flexure strength development of all the mixes at water-to-binder ratio of 0.25 and under R3 curing regime



(a) water/binder ratio: 0.45

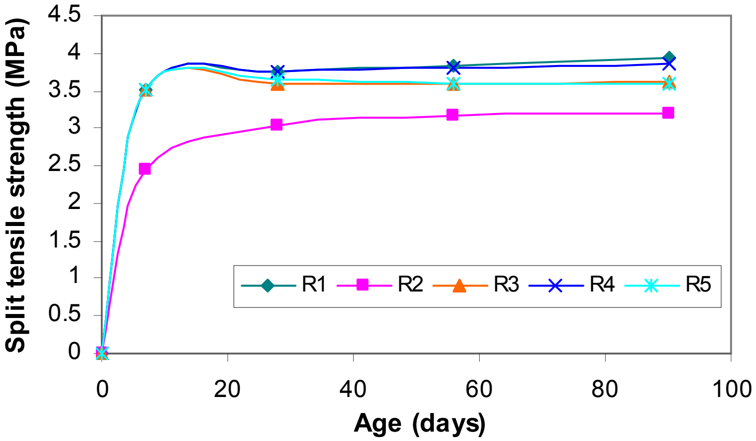


(b) water/binder ratio: 0.35

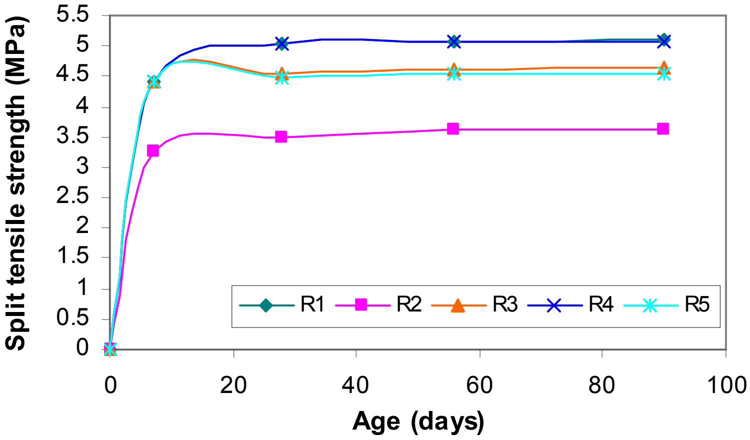


(c) water/binder ratio: 0.25

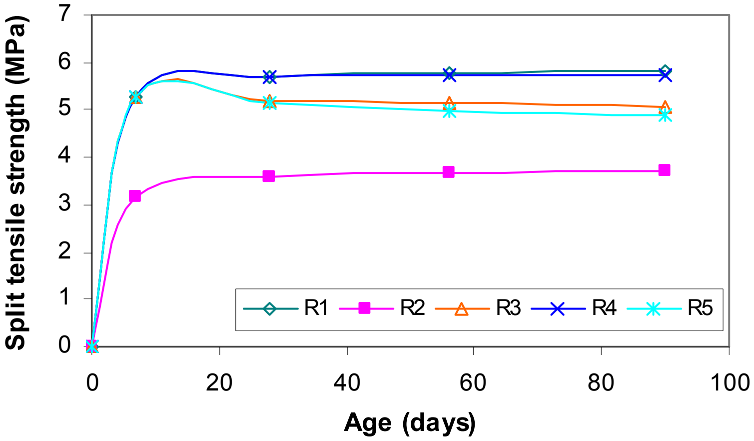
Fig. 4.41. Split tensile strength development of control mixes under various curing regimes



(a) water/binder ratio: 0.45

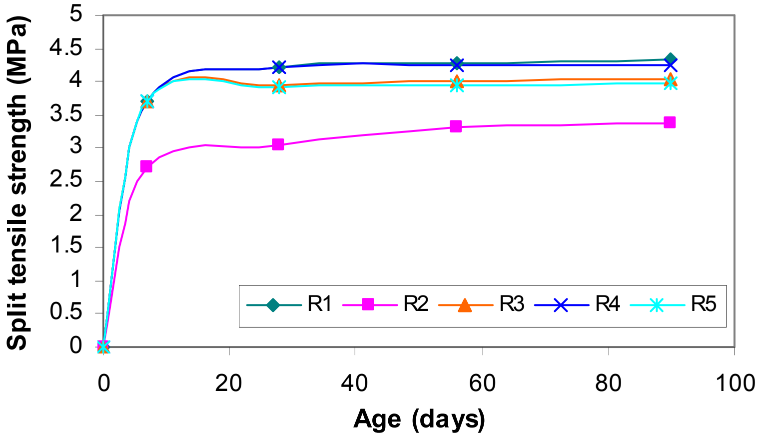


(b) water/binder ratio: 0.35

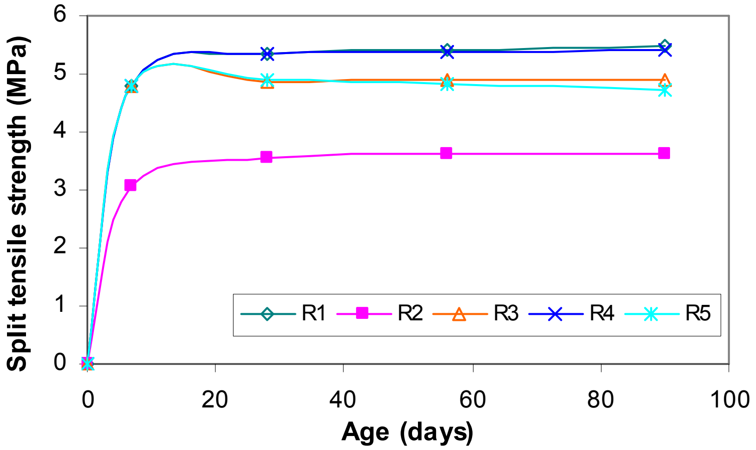


(c) water/binder ratio: 0.25

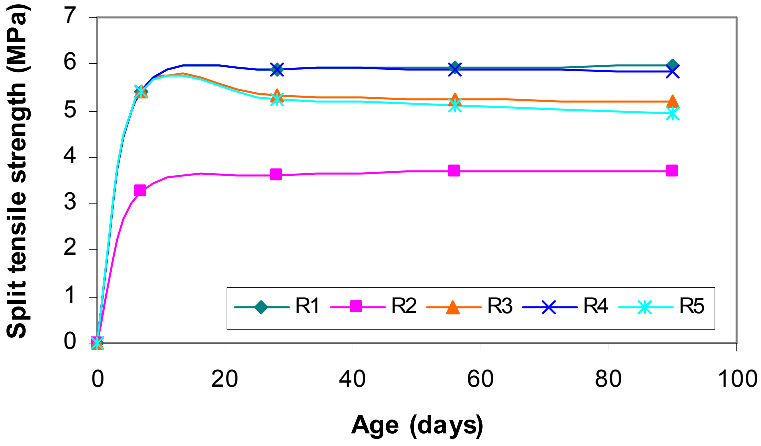
Fig. 4.42. Split tensile strength development of binary mixes with 5% silica fume under various curing regimes



(a) water/binder ratio: 0.45

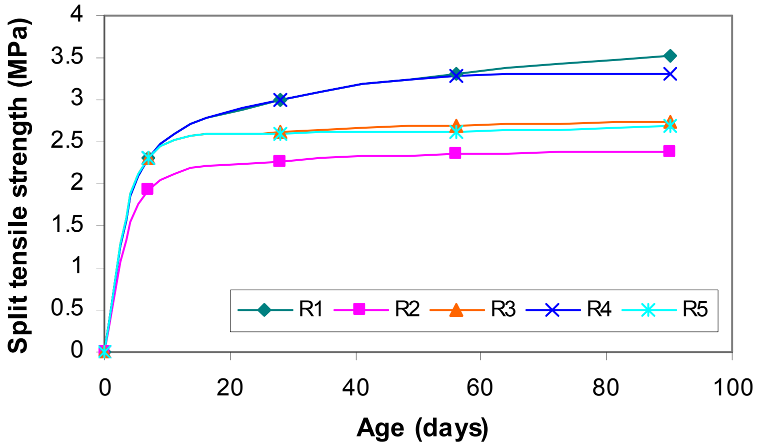


(b) water/binder ratio: 0.35

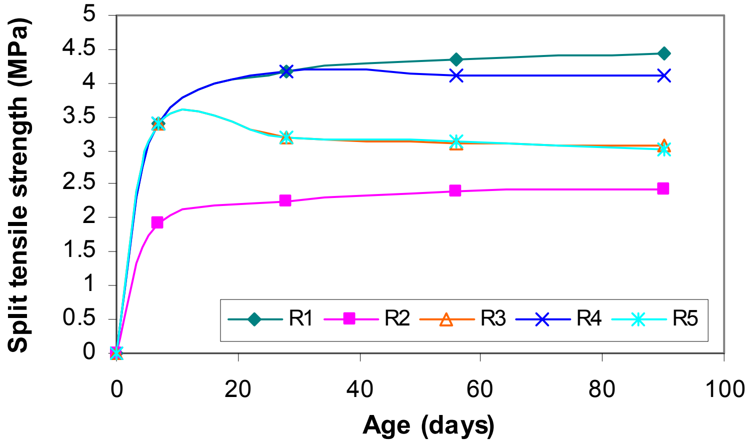


(c) water/binder ratio: 0.25

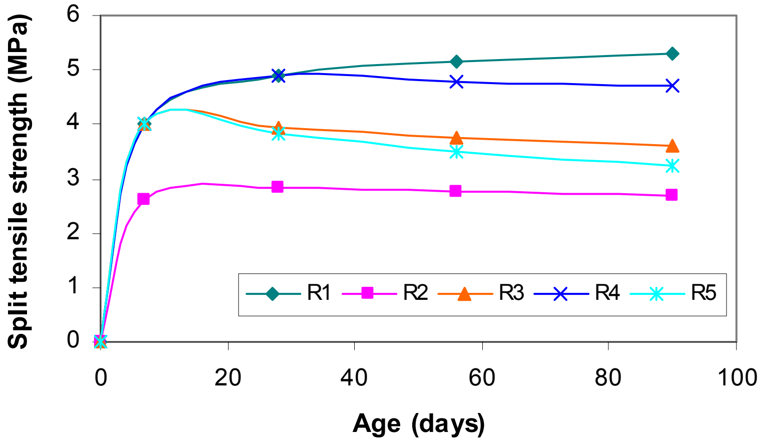
Fig. 4.43. Split tensile strength development of binary mixes with 10% silica fume under various curing regimes



(a) water/binder ratio: 0.45

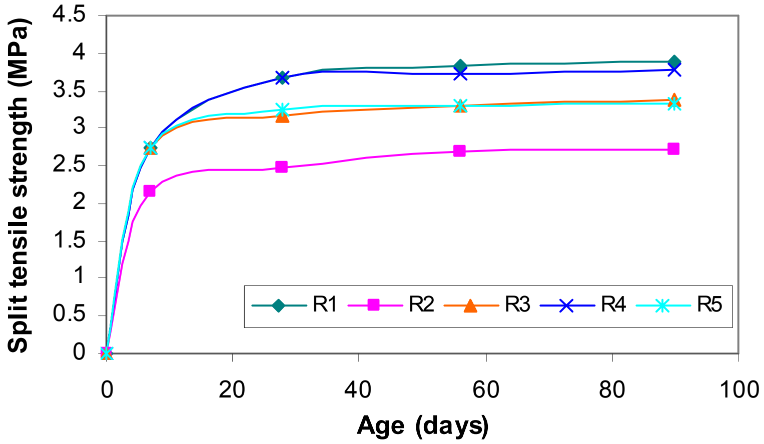


(b) water/binder ratio: 0.35

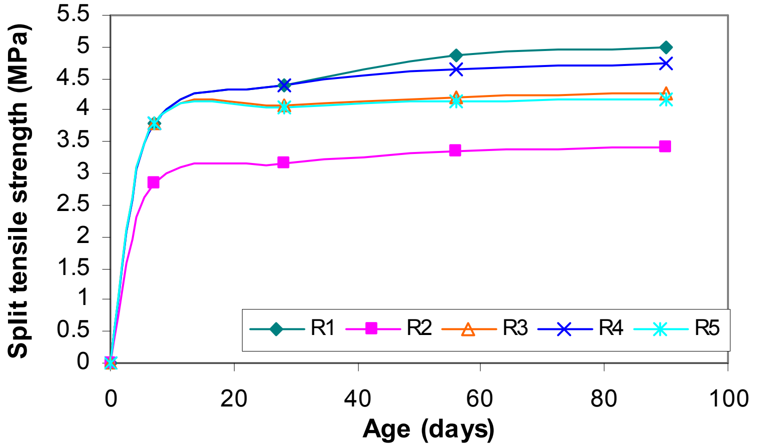


(c) water/binder ratio: 0.25

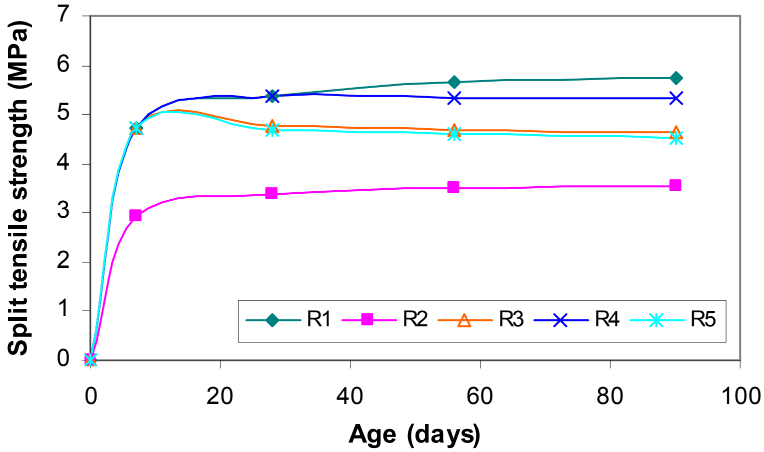
Fig. 4.44. Split tensile strength development of binary mixes with 30% fly ash under various curing regimes



(a) water/binder ratio: 0.45

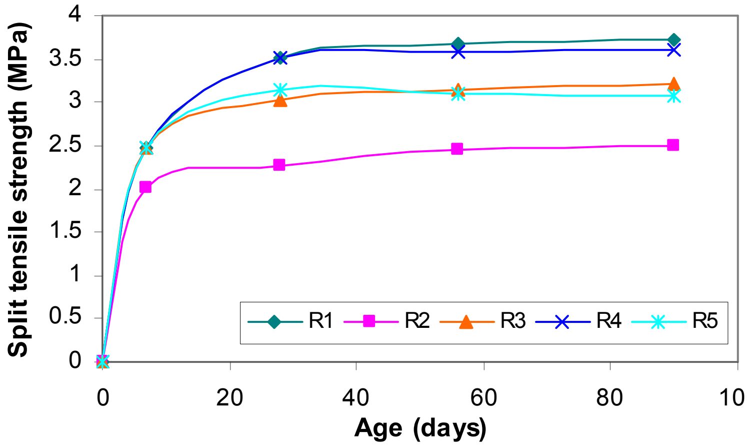


(b) water/binder ratio: 0.35

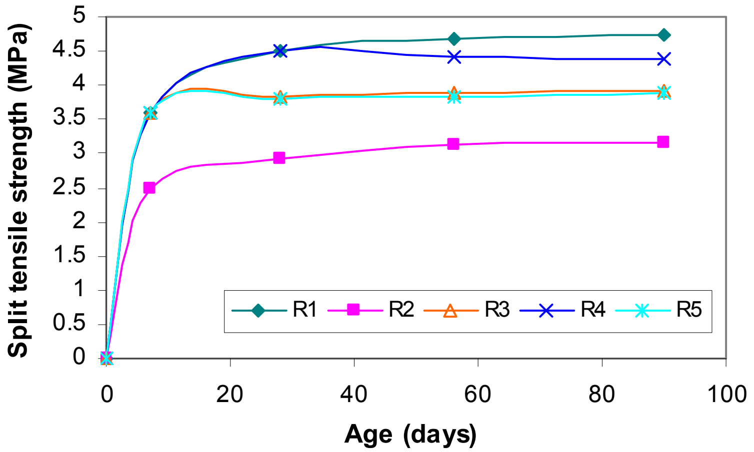


(c) water/binder ratio: 0.25

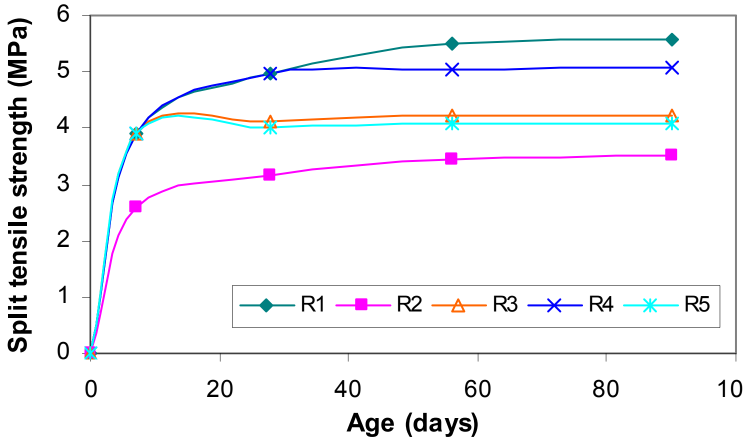
Fig. 4.45. Split tensile strength development of ternary mixes with 5% silica fume and 15% fly ash under various curing regimes



(a) water/binder ratio: 0.45

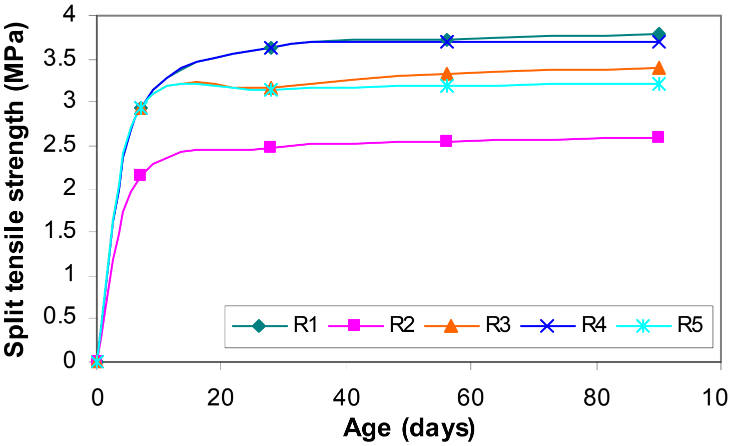


(b) water/binder ratio: 0.35

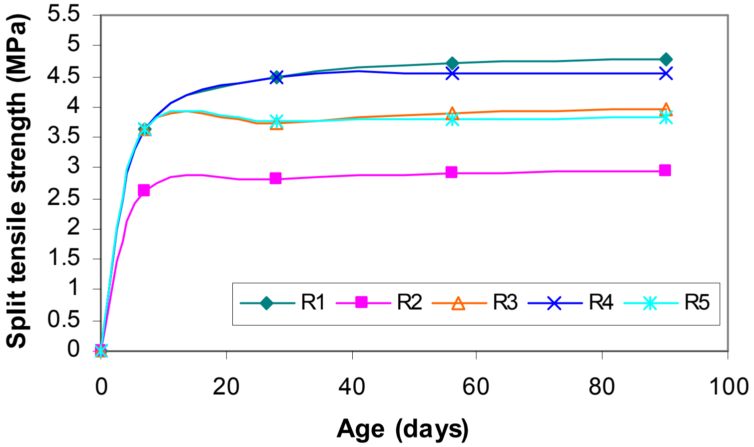


(c) water/binder ratio: 0.25

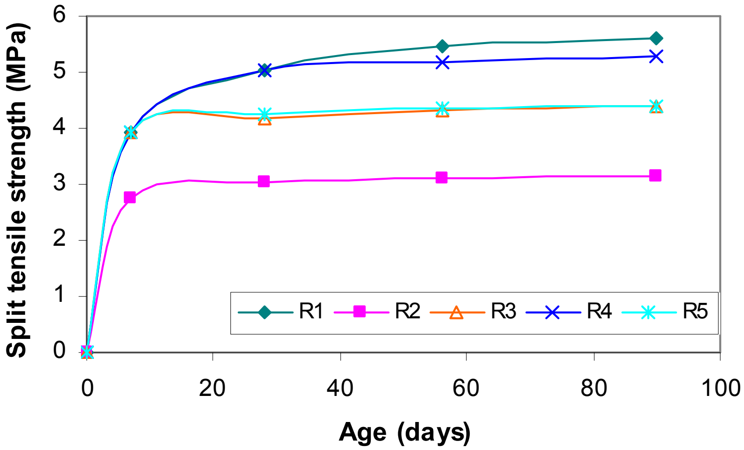
Fig. 4.46. Split tensile strength development of ternary mixes with 5% silica fume and 20% fly ash under various curing regimes



(a) water/binder ratio: 0.45

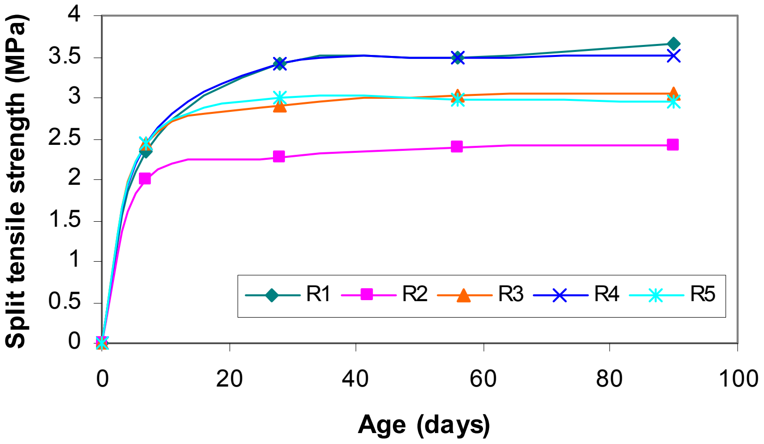


(b) water/binder ratio: 0.35

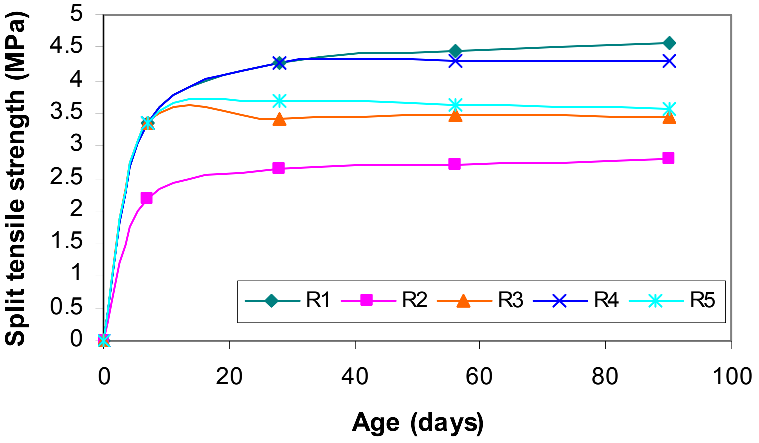


(c) water/binder ratio: 0.25

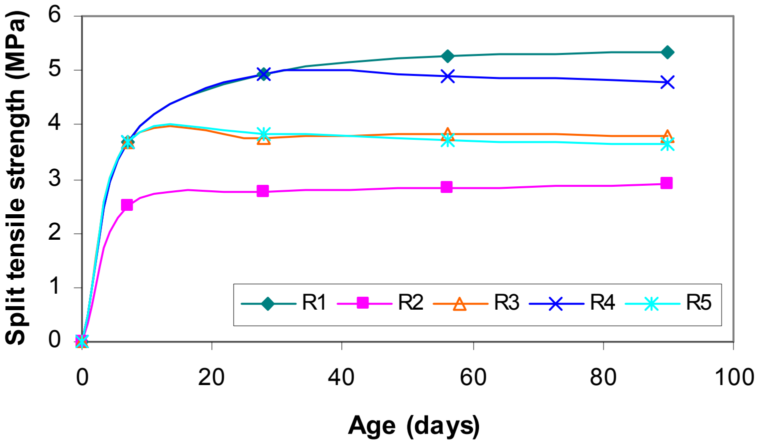
Fig. 4.47. Split tensile strength development of ternary mixes with 10% silica fume and 15% fly ash under various curing regimes



(a) water/binder ratio: 0.45



(b) water/binder ratio: 0.35



(c) water/binder ratio: 0.25

Fig. 4.48. Split tensile strength development of ternary mixes with 10% silica fume and 20% fly ash under various curing regimes

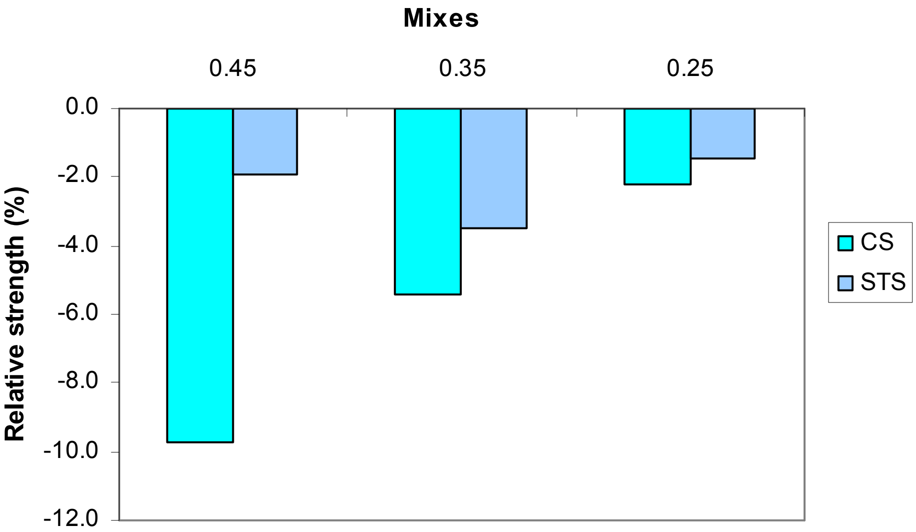


Fig. 4.49. Relative fall in compressive and split tensile strength with addition of 30% fly ash at different water-to-binder ratios

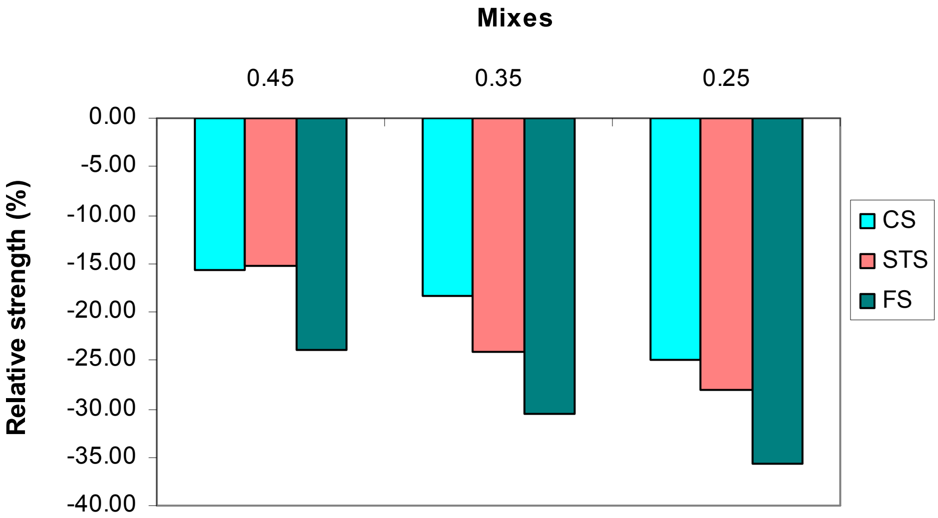


Fig. 4.50. Relative compressive, split tensile and flexure strength loss between air curing and water curing regimes for control mixes

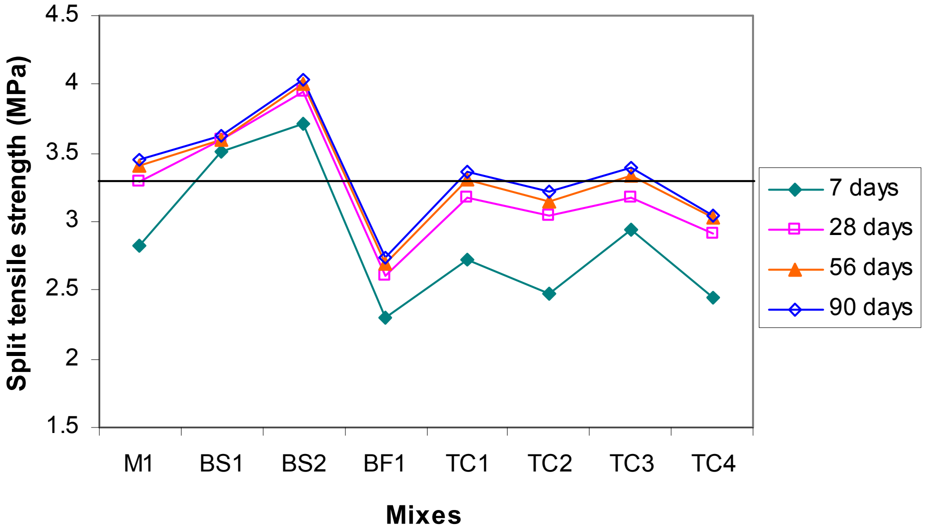


Fig. 4.51. Split tensile strength development of all the mixes at water-to-binder ratio of 0.45 and under R3 curing regime

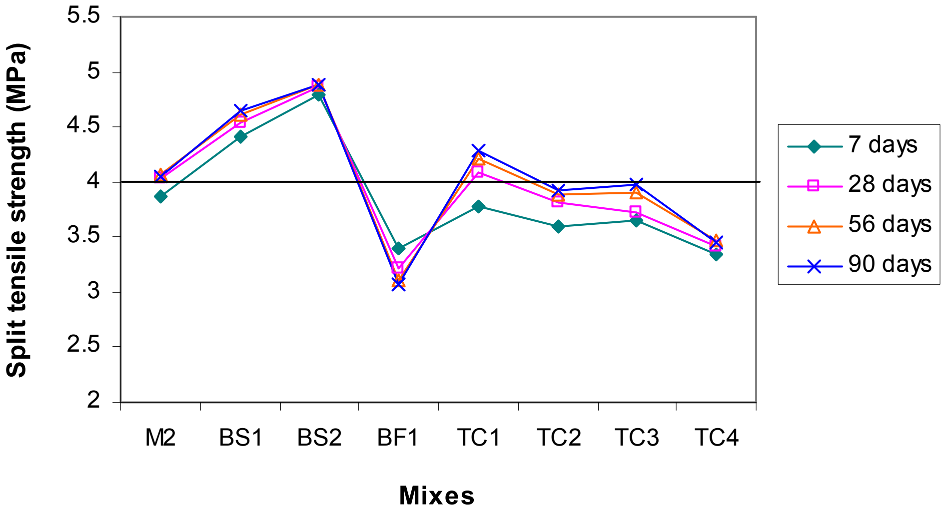


Fig. 4.52. Split tensile strength development of all the mixes at water-to-binder ratio of 0.35 and under R3 curing regime

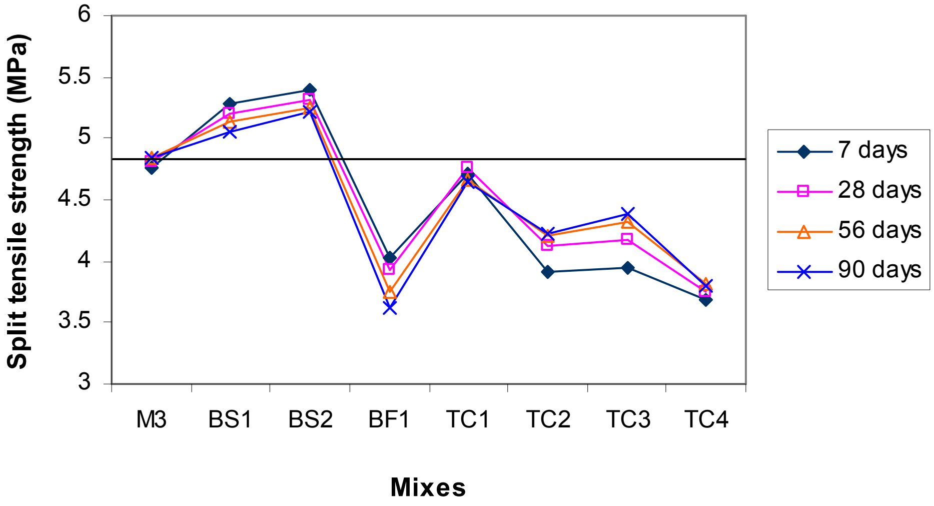


Fig. 4.53. Split tensile strength development of all the mixes at water-to-binder ratio of 0.25 and under R3 curing regime

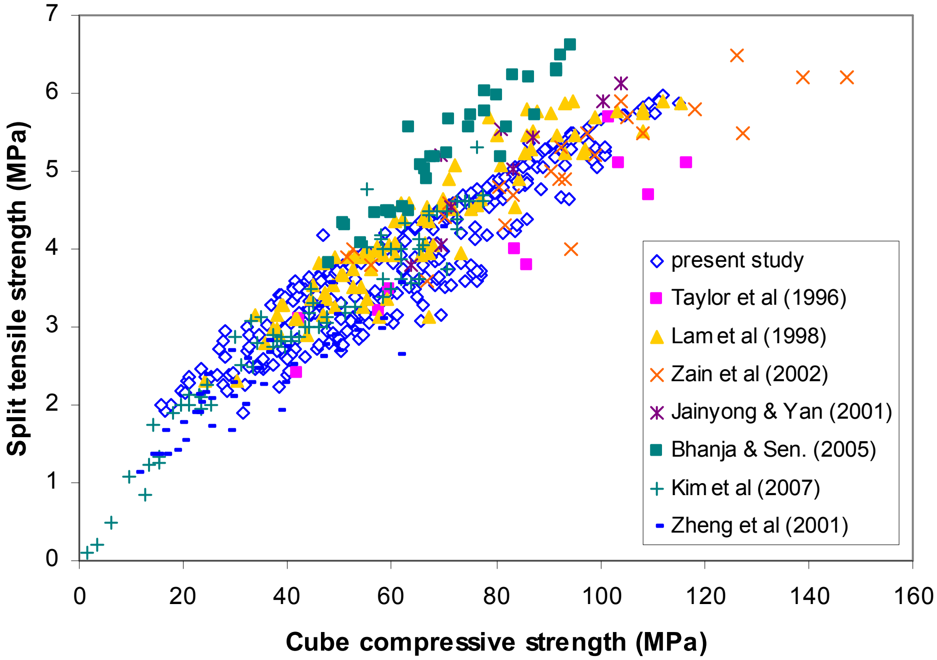


Fig. 4.54. Data points for validation of split tensile strength model

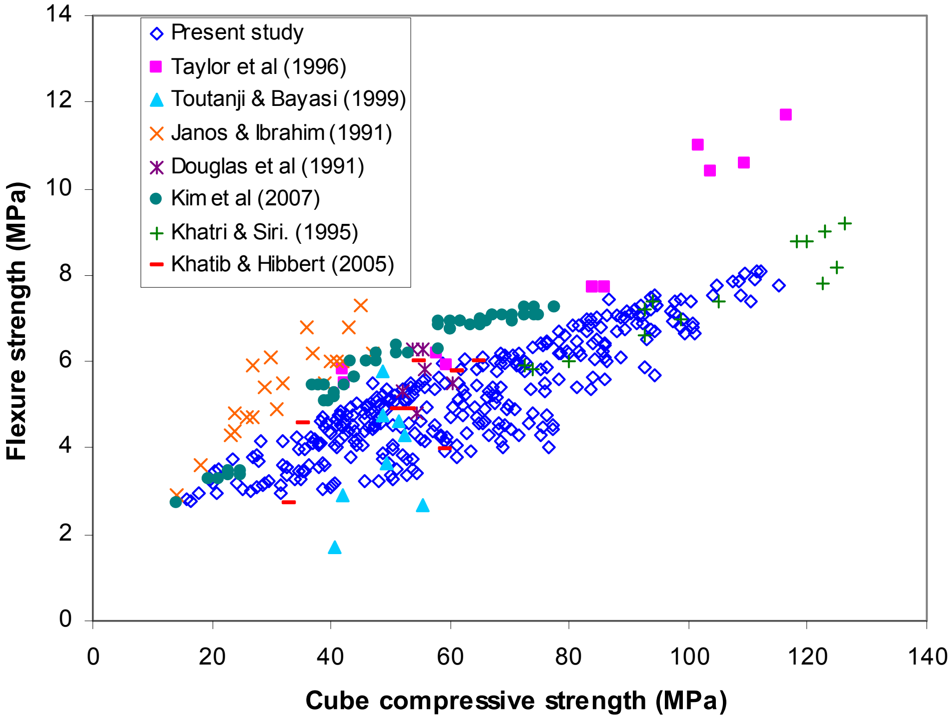
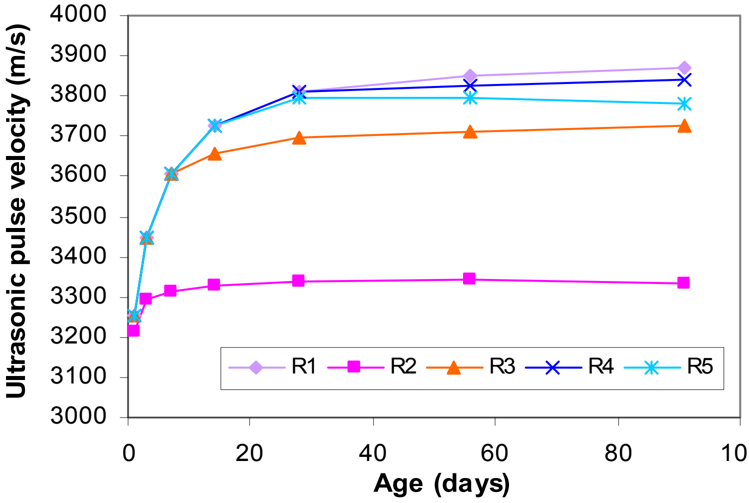
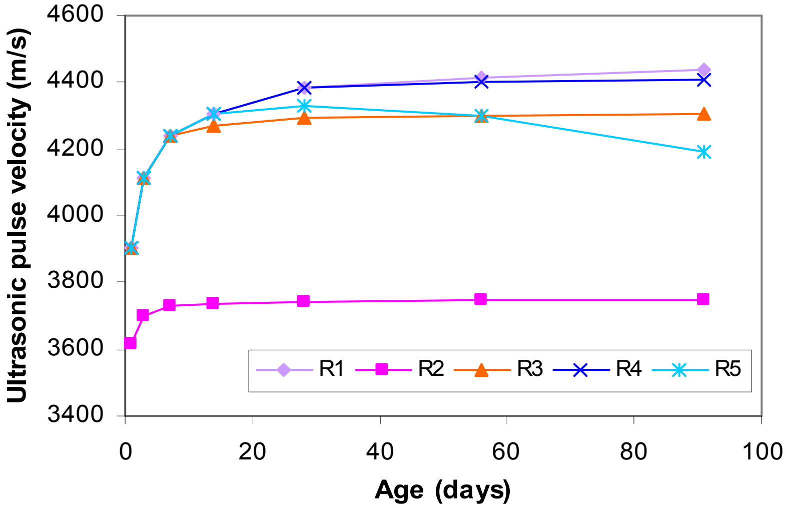


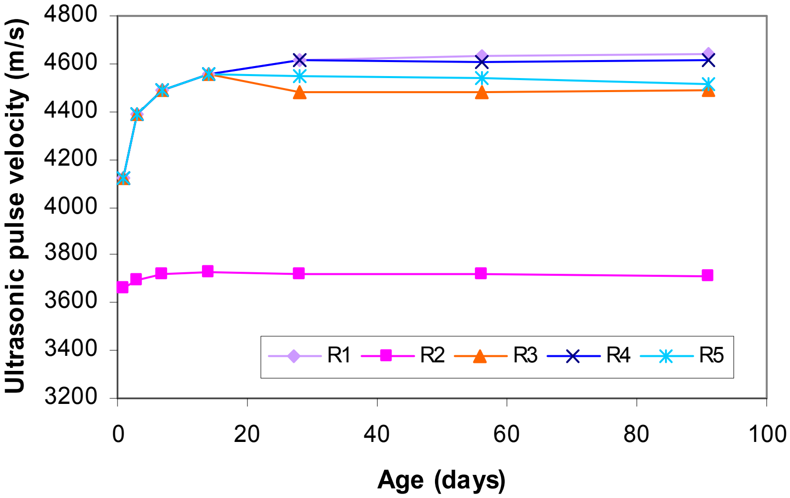
Fig. 4.55. Data points for validation of flexure strength model



(a) W/B ratio: 0.45

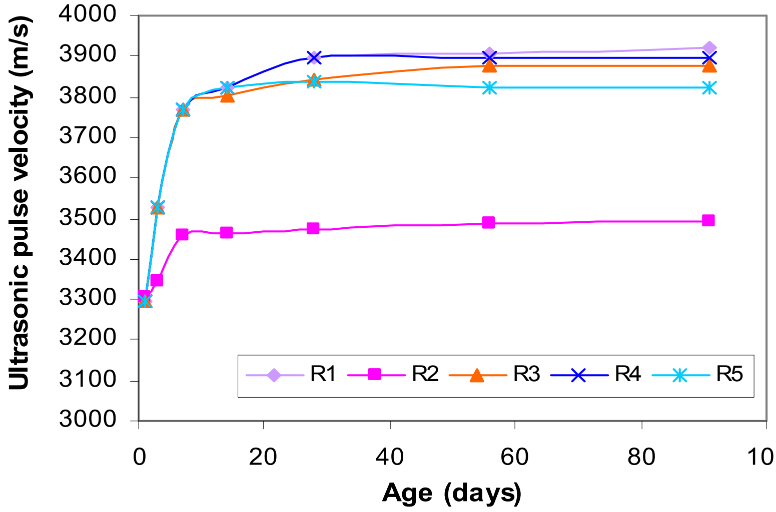


(b) W/B ratio: 0.35

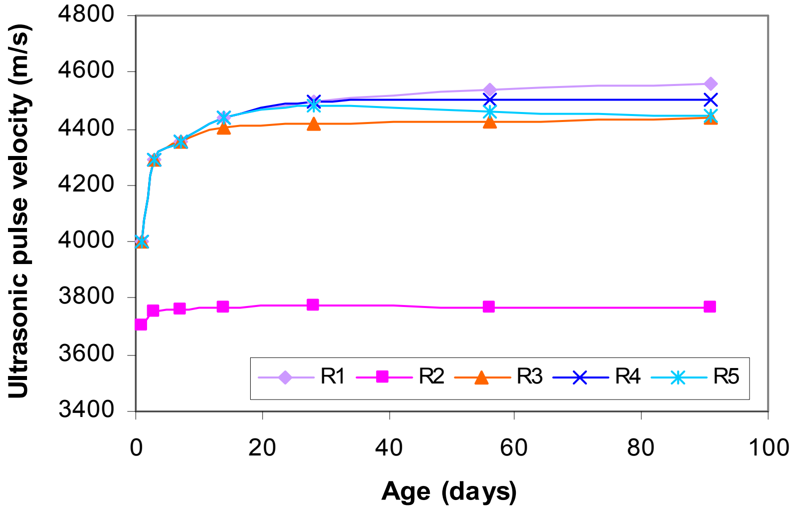


(c) W/B ratio: 0.25

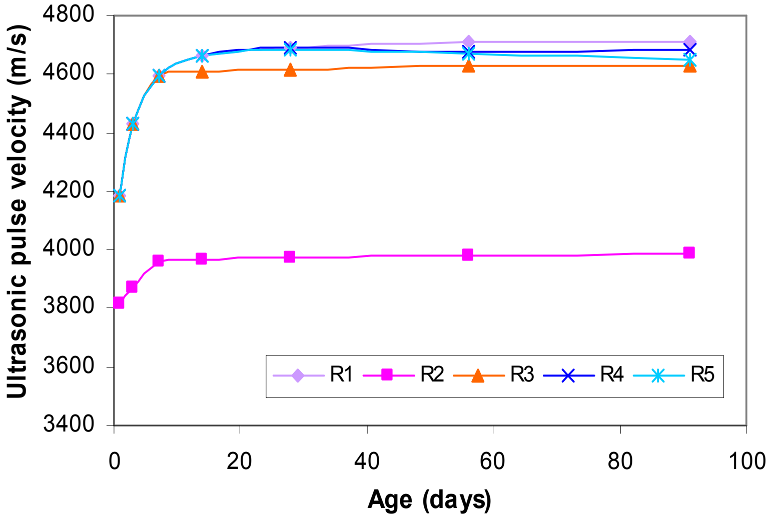
Fig. 4.56. Ultrasonic pulse velocity of control mixes under various curing regimes



(a) W/B ratio: 0.45

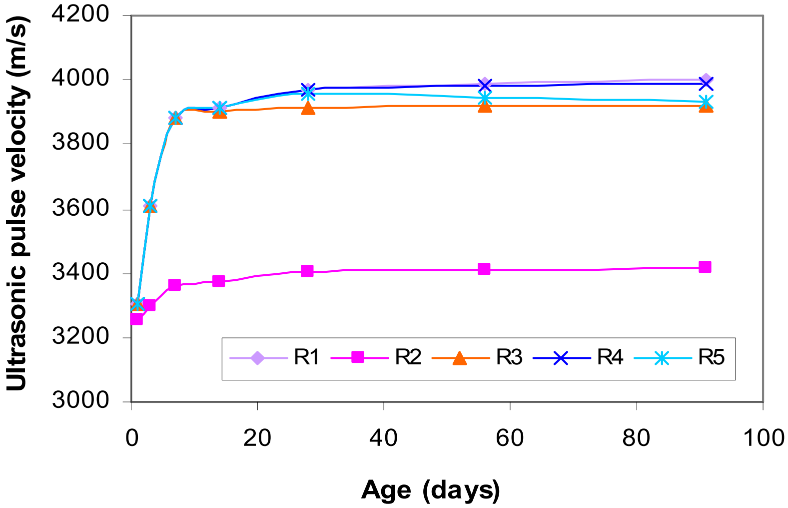


(b) W/B ratio: 0.35

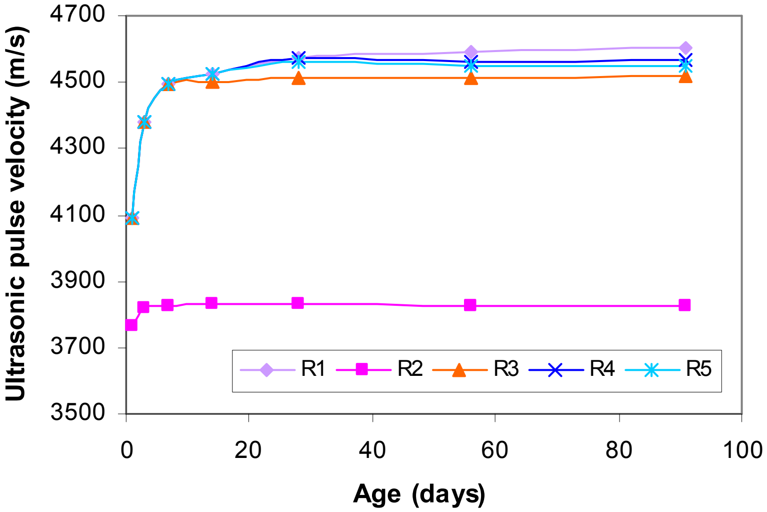


(c) W/B ratio: 0.25

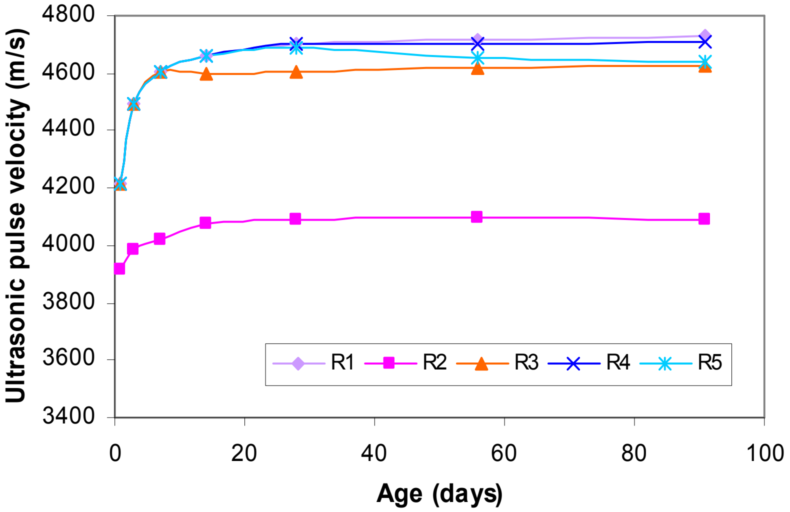
Fig. 4.57. Ultrasonic pulse velocity of BS1 mixes under various curing regimes



(a) W/B ratio: 0.45

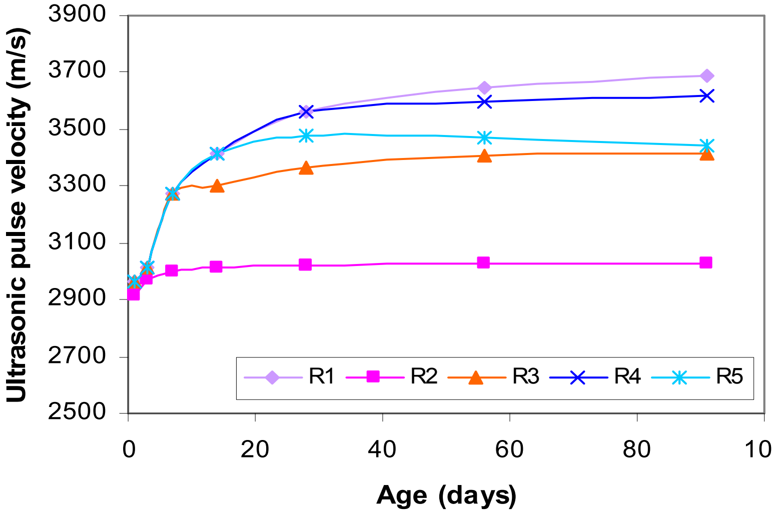


(b) W/B ratio: 0.35

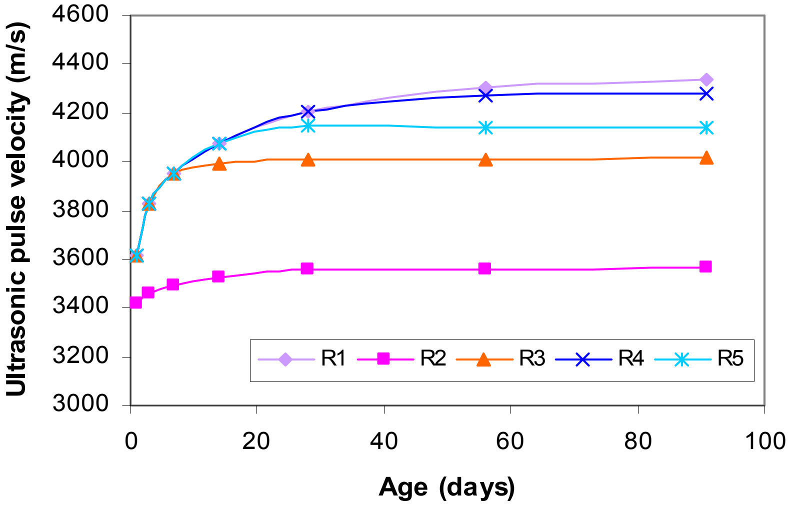


(c) W/B ratio: 0.25

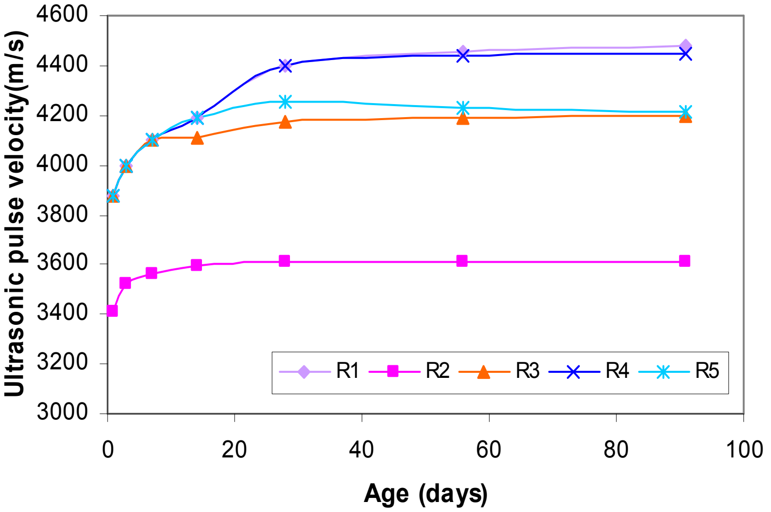
Fig. 4.58. Ultrasonic pulse velocity of BS2 mixes under various curing regimes



(a) W/B ratio: 0.45

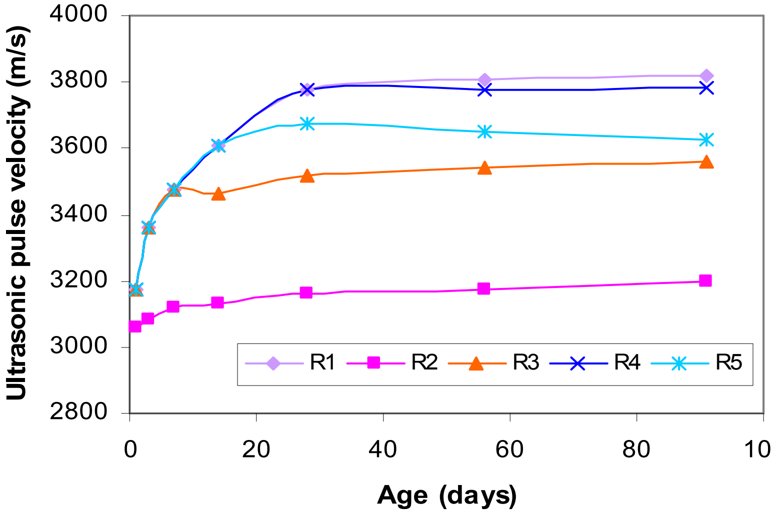


(b) W/B ratio: 0.35

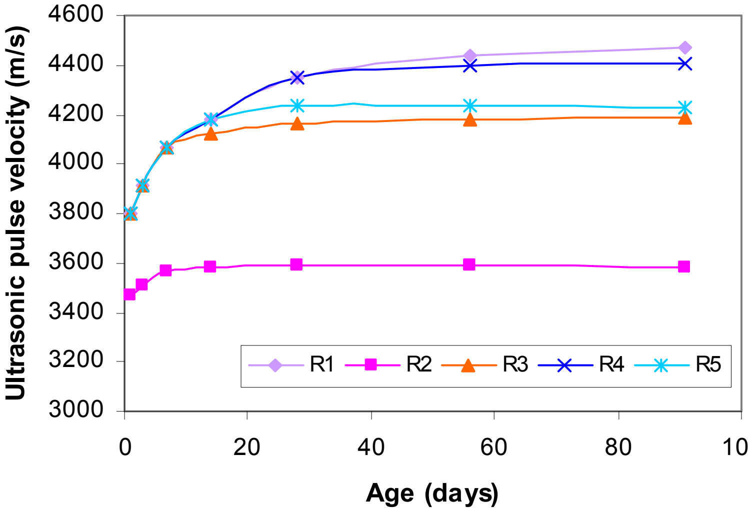


(c) W/B ratio: 0.25

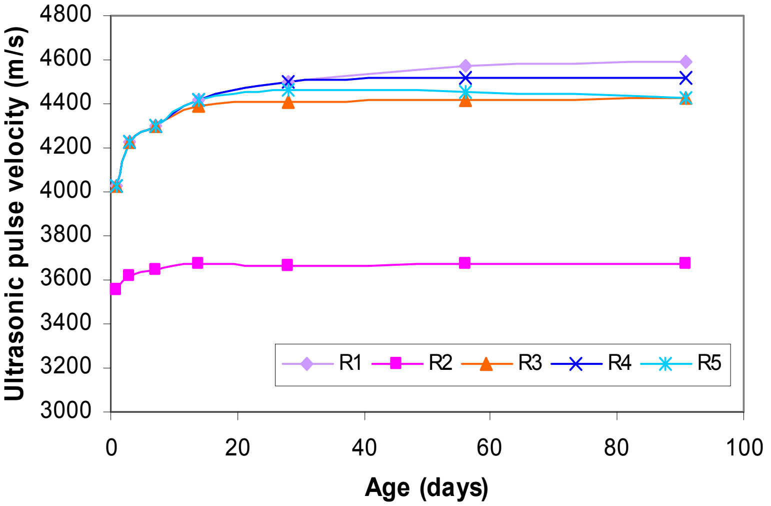
Fig. 4.59. Ultrasonic pulse velocity of BF1 mixes under various curing regimes



(a) W/B ratio: 0.45

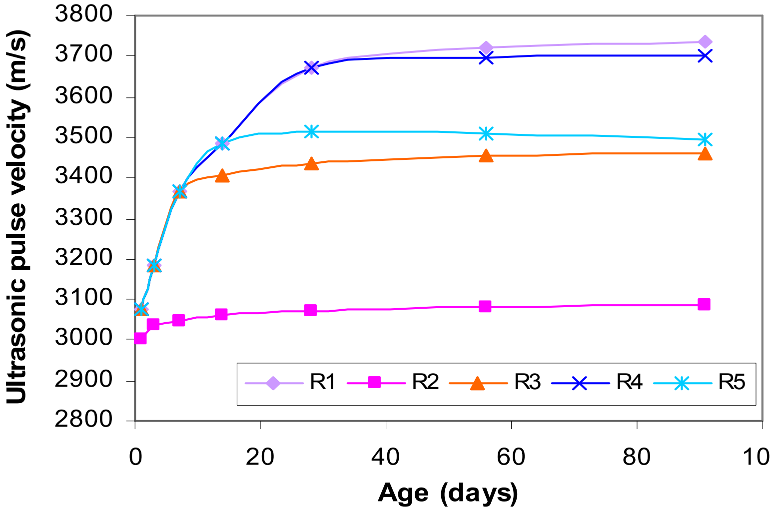


(b) W/B ratio: 0.35

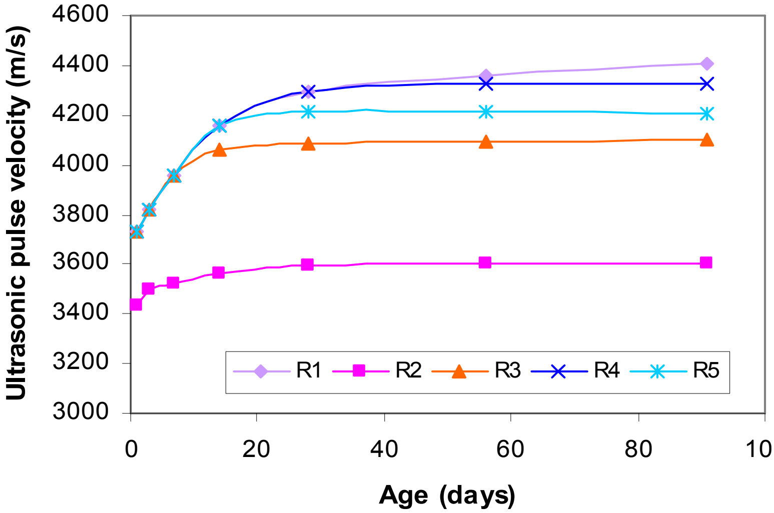


(c) W/B ratio: 0.25

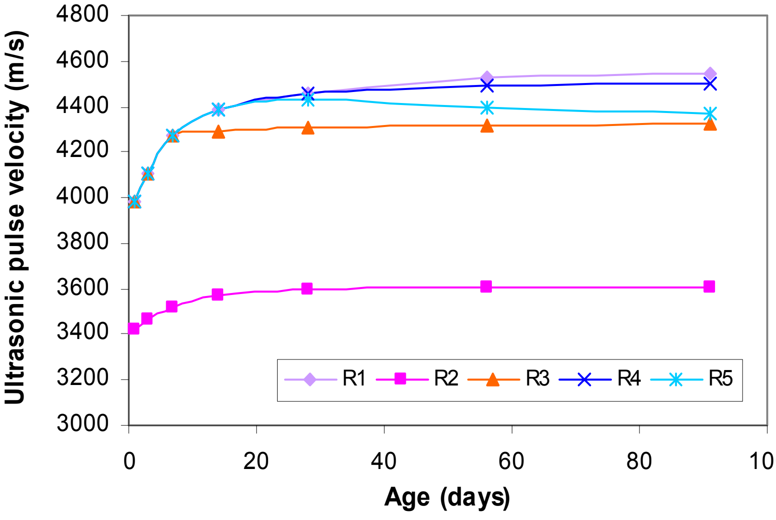
Fig. 4.60. Ultrasonic pulse velocity of TC1 mixes under various curing regimes



(a) W/B ratio: 0.45

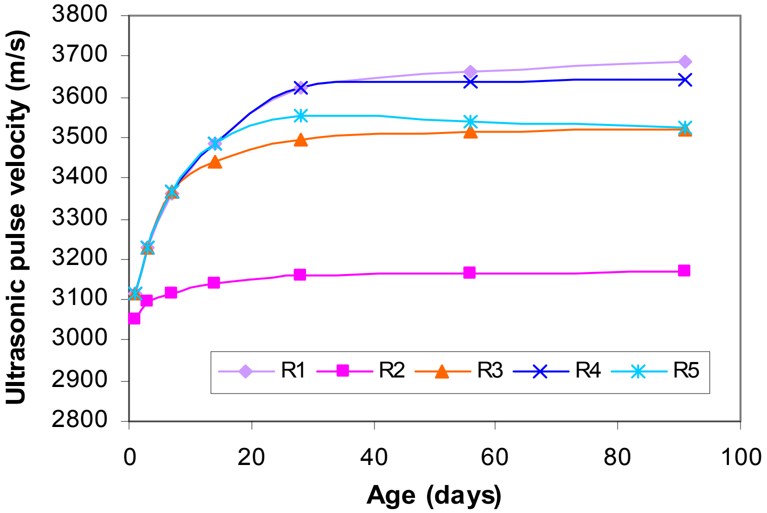


(b) W/B ratio: 0.35

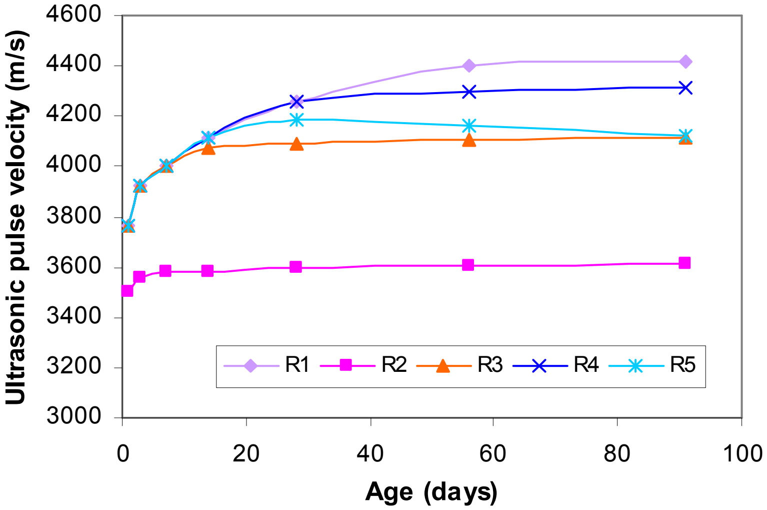


(c) W/B ratio: 0.25

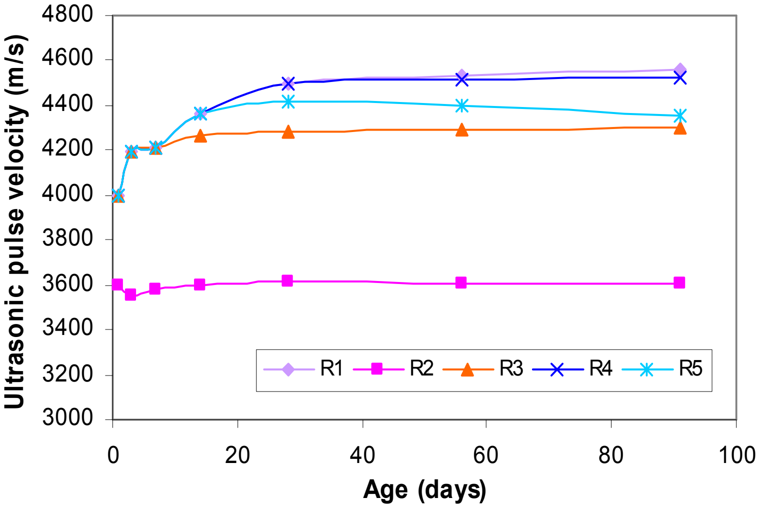
Fig. 4.61. Ultrasonic pulse velocity of TC2 mixes under various curing regimes



(a) W/B ratio: 0.45

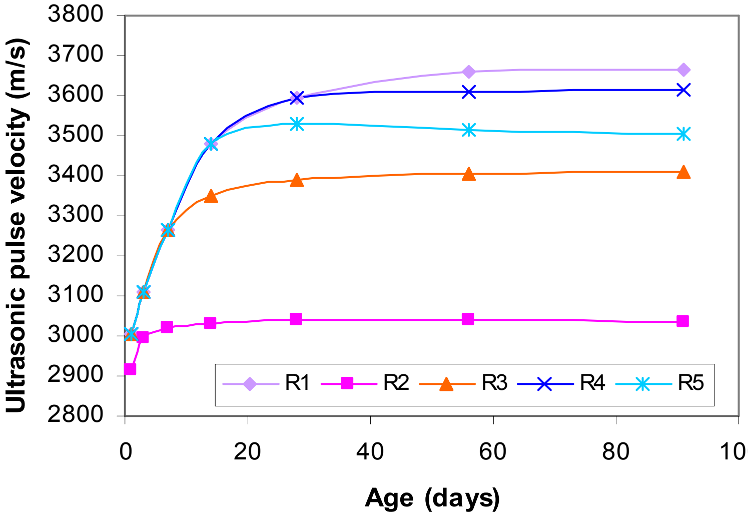


(b) W/B ratio: 0.35

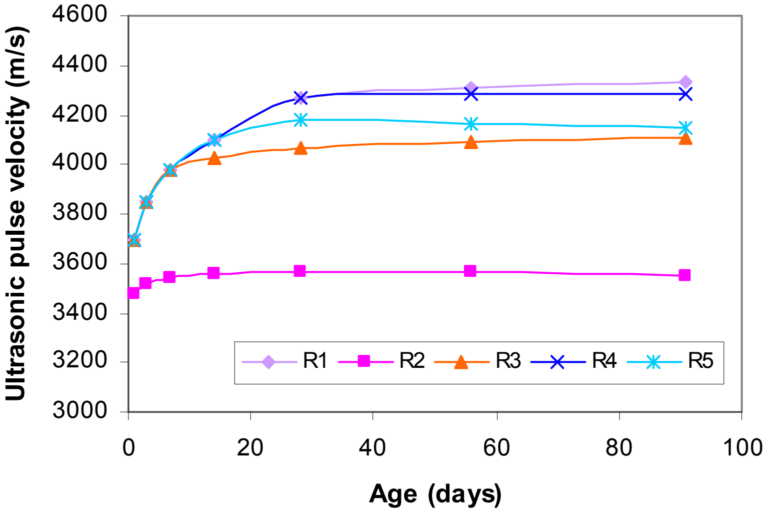


(c) W/B ratio: 0.25

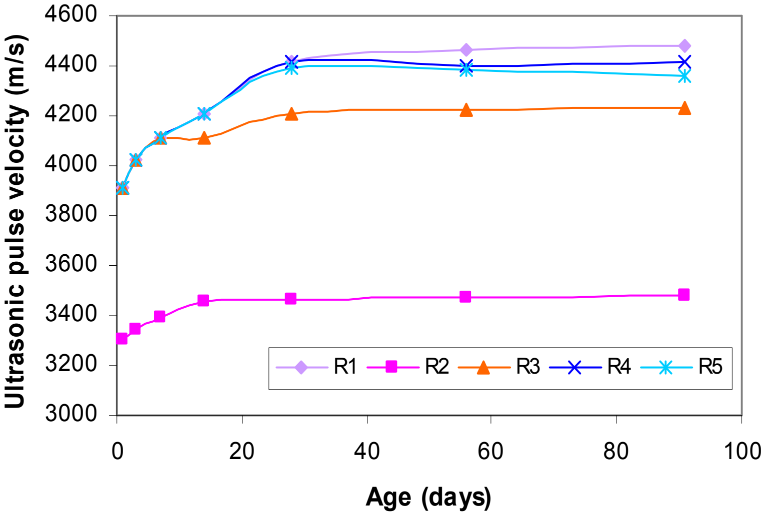
Fig. 4.62. Ultrasonic pulse velocity of TC3 mixes under various curing regimes



(a) W/B ratio: 0.45

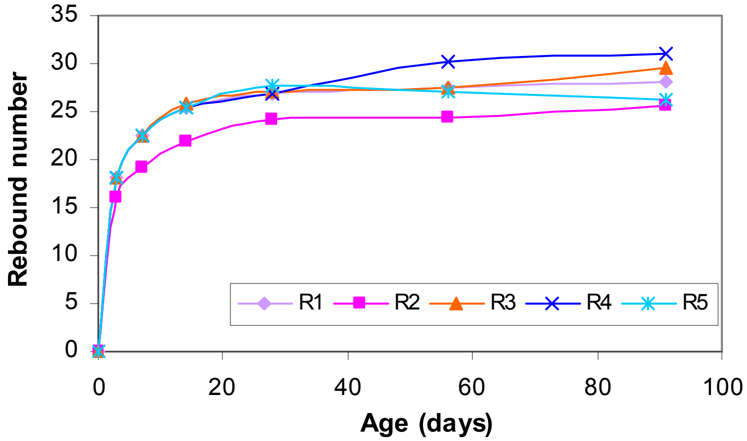


(b) W/B ratio: 0.35

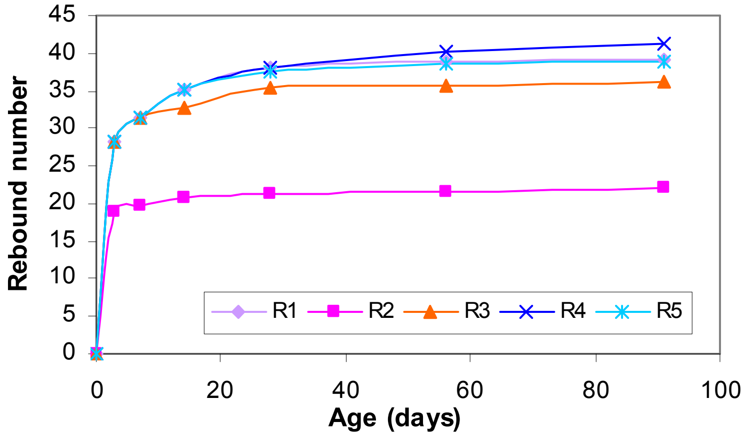


(c) W/B ratio: 0.25

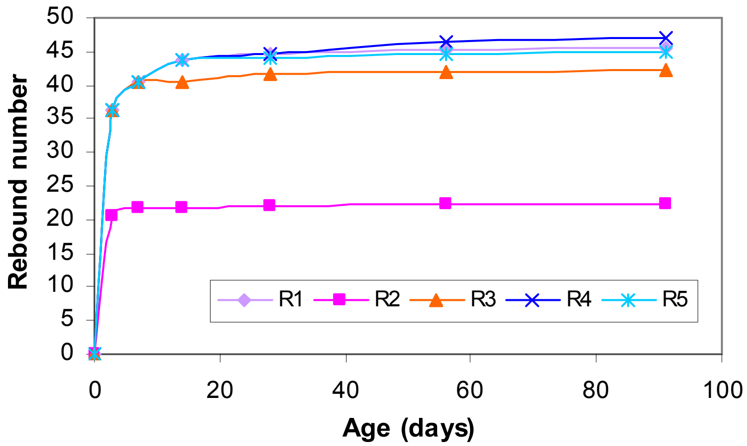
Fig. 4.63. Ultrasonic pulse velocity of TC4 mixes under various curing regimes



(a) water/binder ratio: 0.45

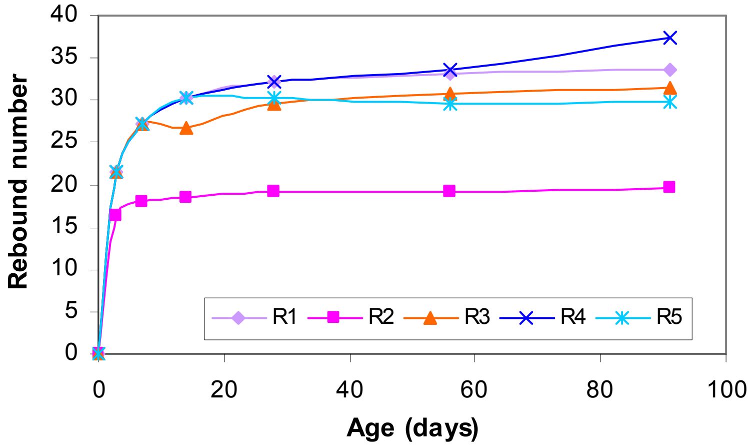


(b) water/binder ratio: 0.35

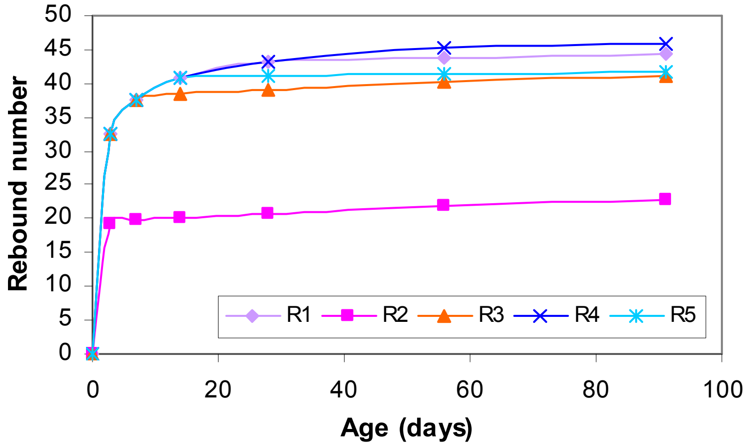


(c) water/binder ratio: 0.25

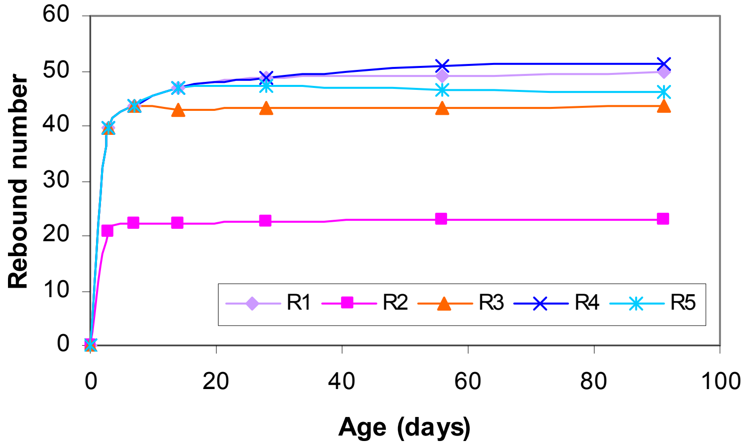
Fig. 4.64. Rebound number of control mixes under various curing regimes



(a) water/binder ratio: 0.45

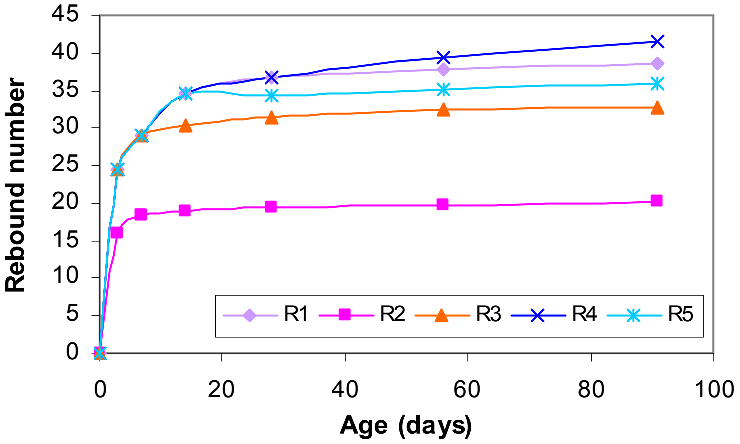


(b) water/binder ratio: 0.35

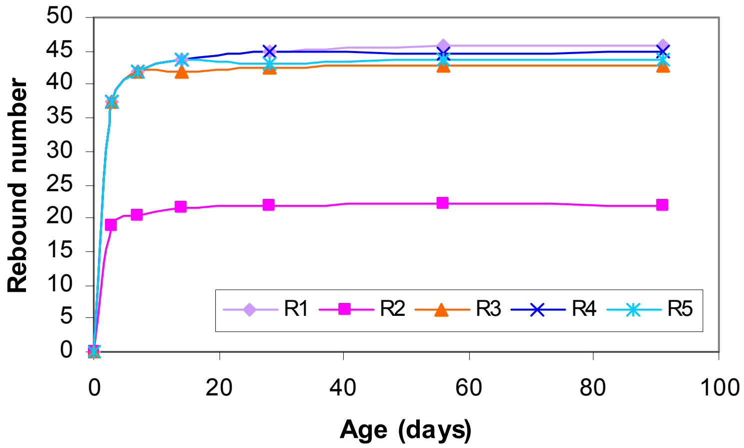


(c) water/binder ratio: 0.25

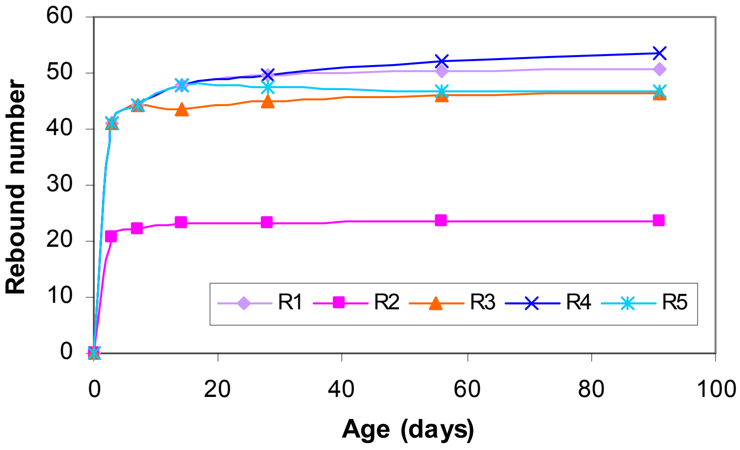
Fig. 4.65. Rebound number of binary mixes with 5% silica fume under various curing regimes



(a) water/binder ratio: 0.45

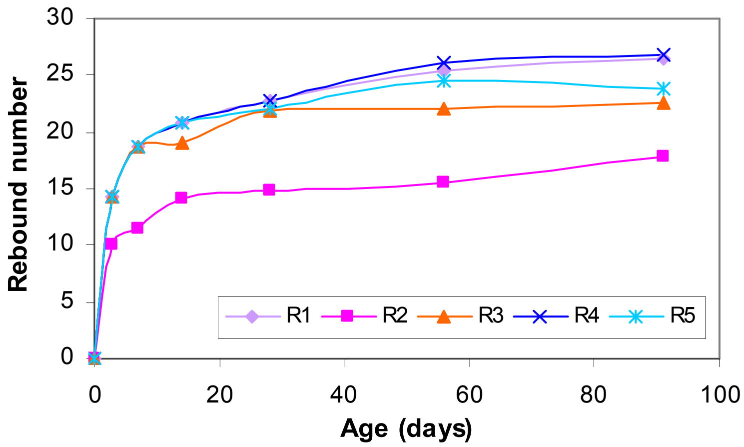


(b) water/binder ratio: 0.35

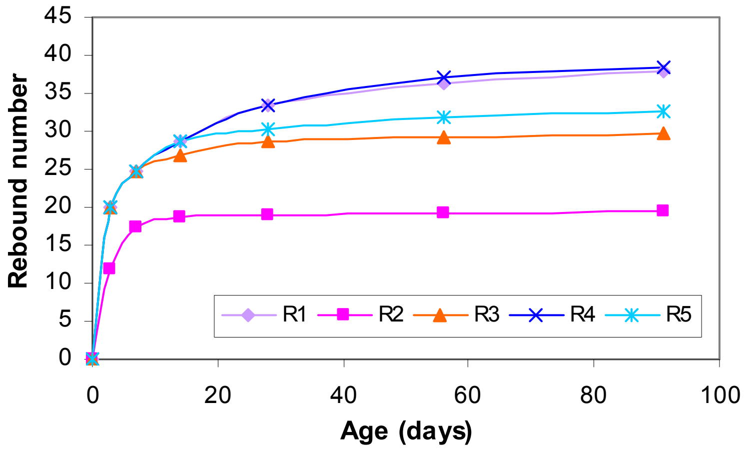


(c) water/binder ratio: 0.25

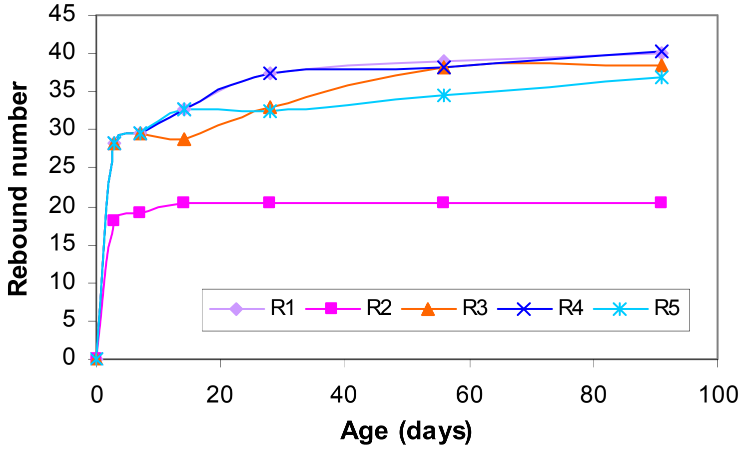
Fig. 4.66. Rebound number of binary mixes with 10% silica fume under various curing regimes



(a) water/binder ratio: 0.45

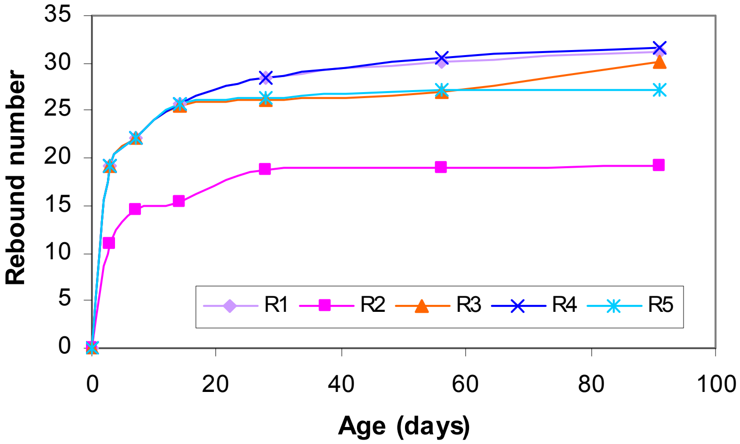


(b) water/binder ratio: 0.35

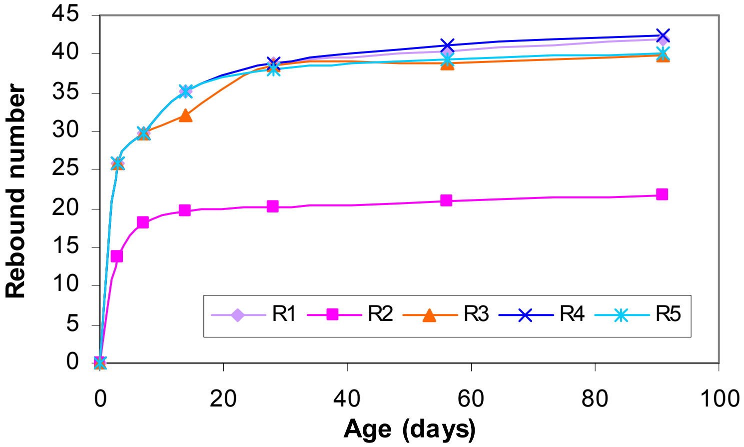


(c) water/binder ratio: 0.25

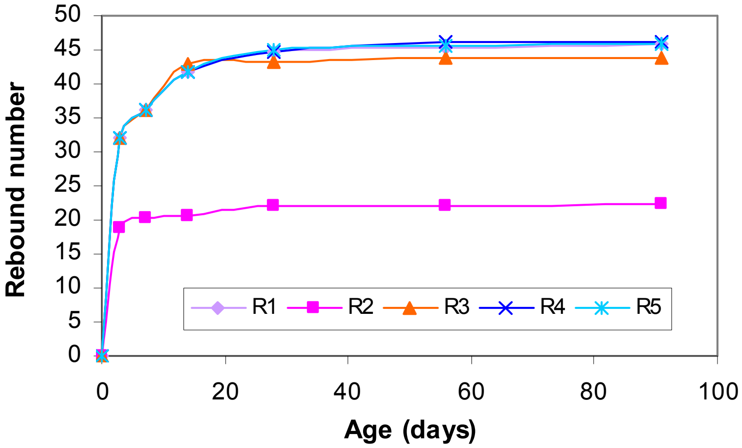
Fig. 4.67. Rebound number of binary mixes with 30% fly ash under various curing regimes



(a) water/binder ratio: 0.45

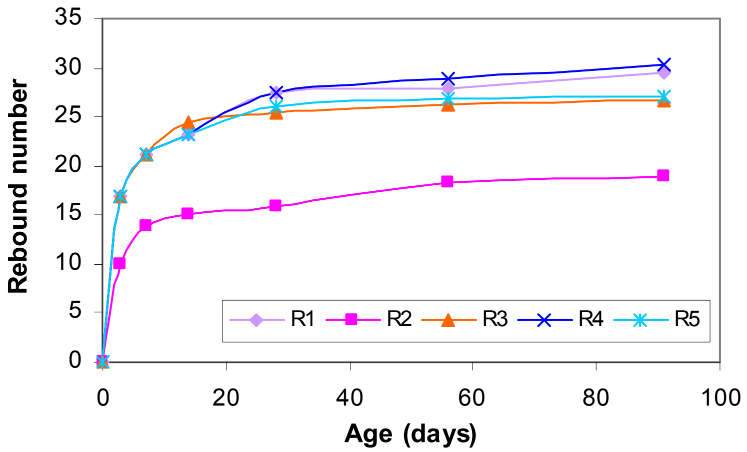


(b) water/binder ratio: 0.35

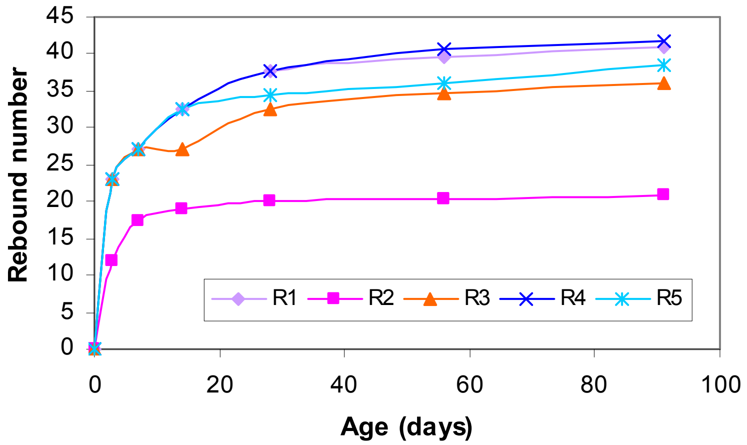


(c) water/binder ratio: 0.25

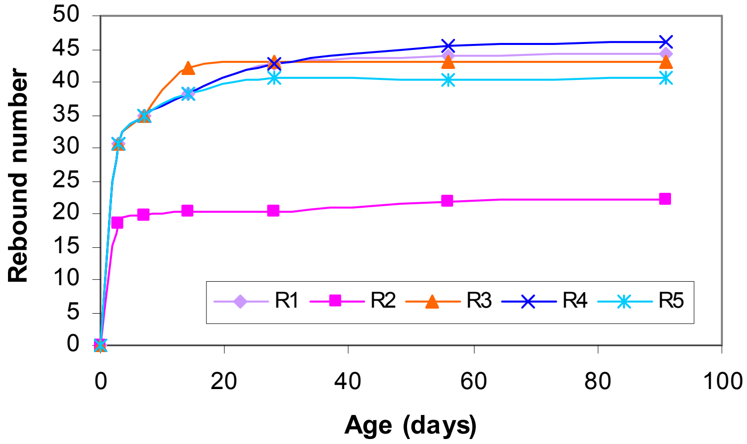
Fig. 4.68. Rebound number of ternary mixes with 5% silica fume and 15% fly ash under various curing regimes



(a) water/binder ratio: 0.45

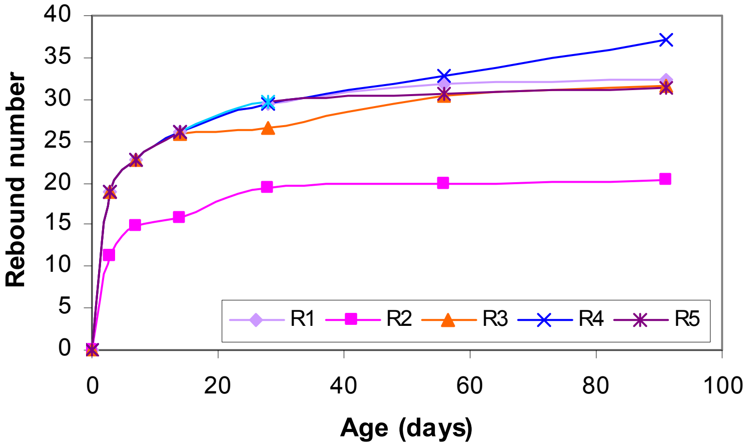


(b) water/binder ratio: 0.35

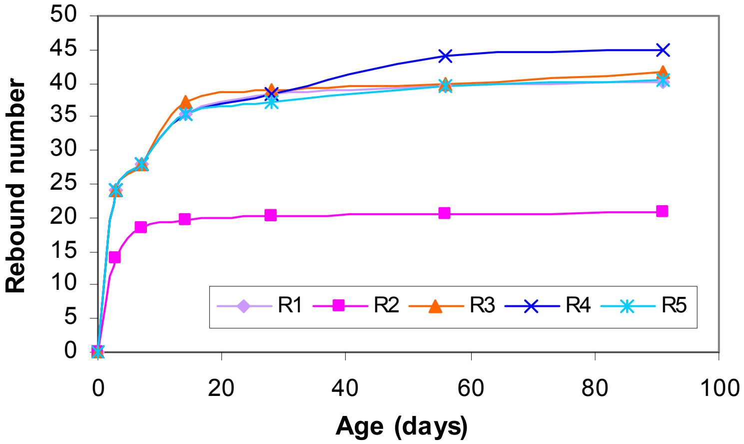


(c) water/binder ratio: 0.25

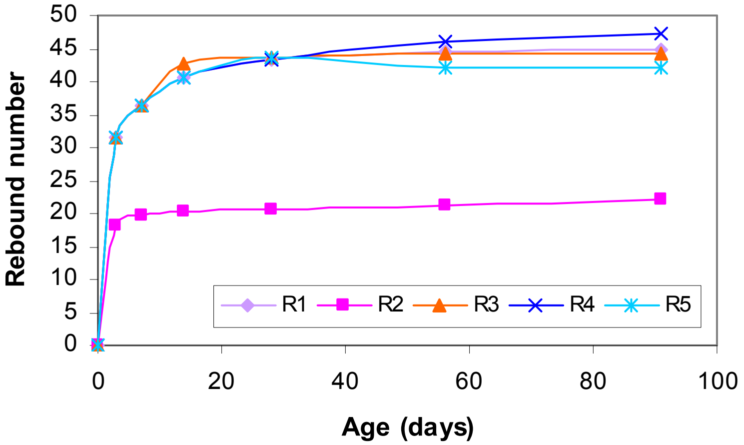
Fig. 4.69. Rebound number of ternary mixes with 5% silica fume and 20% fly ash under various curing regimes



(a) water/binder ratio: 0.45

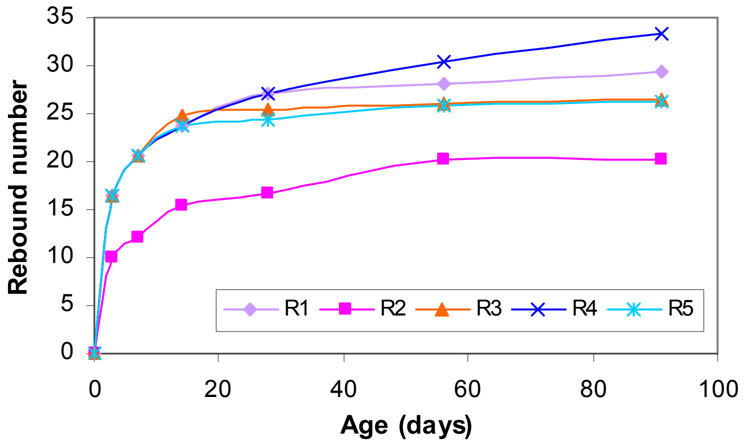


(b) water/binder ratio: 0.35

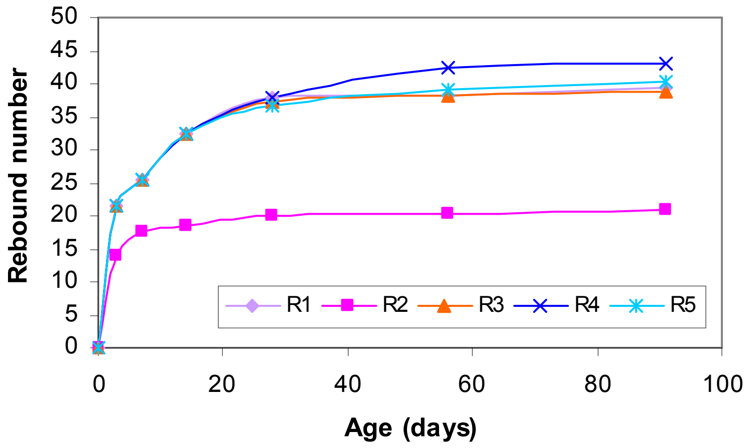


(c) water/binder ratio: 0.25

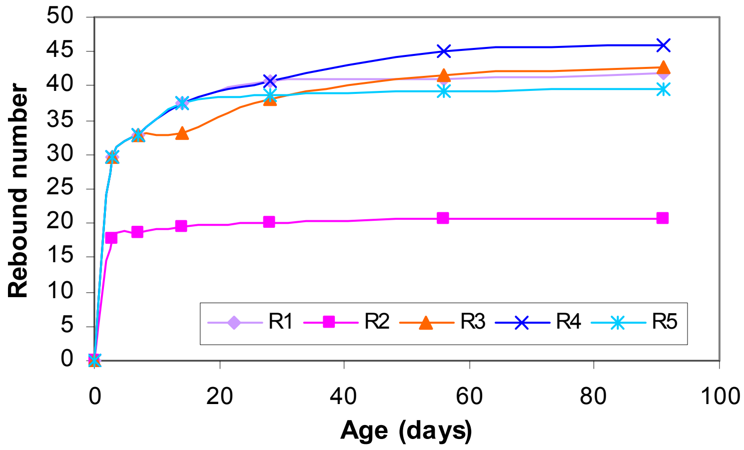
Fig. 4.70. Rebound number of ternary mixes with 10% silica fume and 15% fly ash under various curing regimes



(a) water/binder ratio: 0.45



(b) water/binder ratio: 0.35



(c) water/binder ratio: 0.25

Fig. 4.71. Rebound number of ternary mixes with 10% silica fume and 20% fly ash under various curing regimes

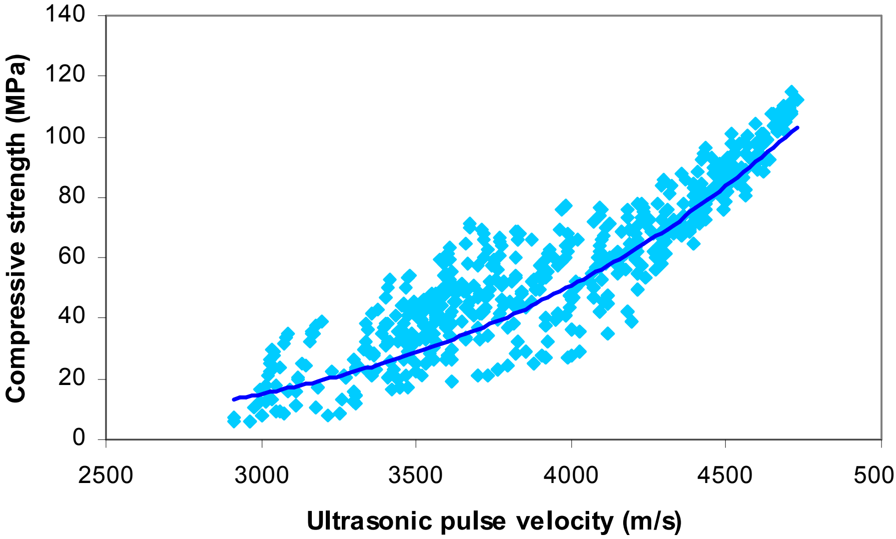


Fig. 4.72. Relationship between ultrasonic pulse velocity and compressive strength

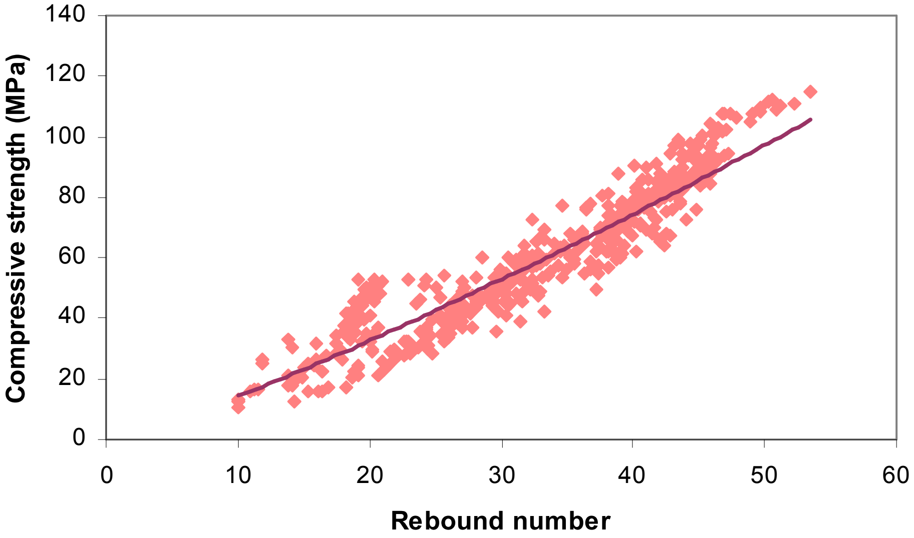


Fig. 4.73. Relationship between rebound number and compressive strength

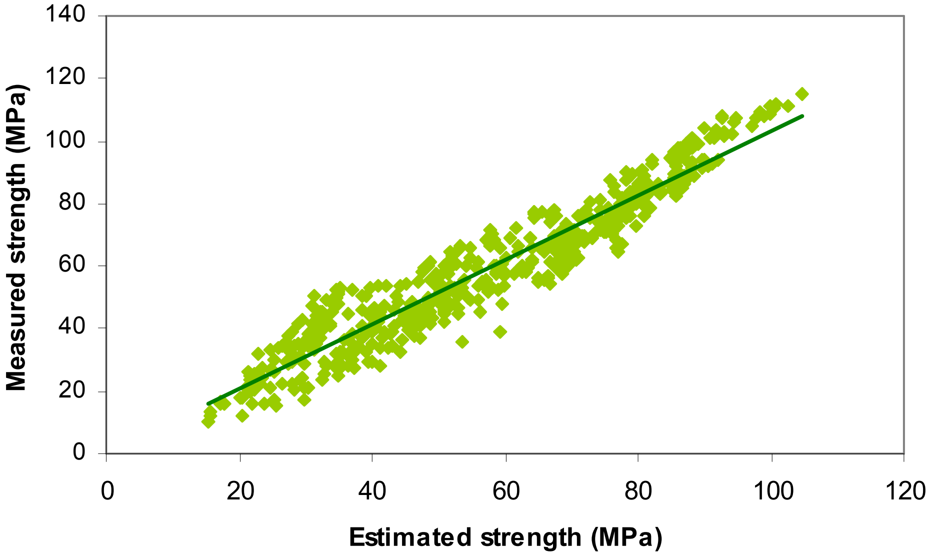


Fig. 4.74. Relation between estimated strength by using combined method and measured strength

CHAPTER 5

DURABILITY ASPECTS OF TESTED CONCRETE

5.1. GENERAL

A significant engineering property of concrete is its durability and resistance to chemical attacks. The deterioration of concrete due to aggressive environment is an issue of major concern throughout the world. If the concrete that is economical while considering strength aspects does not have good chemical resistance against aggressive solutions, it causes enormous damage in the long term, thus increasing the repair cost of the structure. Therefore, chemical resistance of concrete decides the overall economy of the system. It determines the service life of concrete structures very significantly. For this reason, the present study gives an equal importance to strength and durability aspects of concrete. In the first part, the emphasis has been laid on deciding the combination of silica fume and fly ash that gives best performance in strength development and also on the number of curing days that are necessary and sufficient to reach at a particular strength level. In the second part of the study, the emphasis is on the number of curing days required for the mixes to reach a desired water impermeability level and the behaviour of the selected mixes in aggressive environmental conditions. For studying the durability of concrete, the mixes that are found to be best in strength and water impermeability studies are chosen and are subjected to aggressive chemical of different concentrations, as described in Chapter 3. The change in properties after exposure to chemicals is investigated and discussed in the ensuing chapter.

Initially discussions on water impermeability characteristics of different mixes under five curing conditions are presented based on which the best curing regime is selected. Then the effect of various aggressive chemicals on the performance of mixes is discussed in detail. The first part deals with the acid attack, which includes the discussion on the effect of sulfuric acid, hydrochloric acid and nitric acid on the strength loss and weight loss of concrete. The second part deals with the effect of sulfates, which includes sodium sulfate and magnesium sulfate, on the performance of concrete. The performance is judged by studying the weight loss and strength loss; and also by visual investigation of the changes on the surface of concrete. The last part of the chapter is about the effect of chlorides, sodium chloride and calcium chloride, on the properties of concrete. The chloride ingress is studied by drawing the chloride profiles for different mixes and also by judging the relation between free chlorides and total chlorides for different mixes. Finally, a brief discussion about the best mix from the durability aspect is presented at the end of the chapter.

5.2. WATER IMPERMEABILITY TEST

The depth of water penetration of all mixes when subjected to variable curing regimes is shown in Figs. 5.1 to 5.3 for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively**.** The effect of various parameters on water penetration, and hence permeability, is discussed in the following sections.

5.2.1. Effect of Mineral Admixtures

From Figs. 5.1 to 5.3, it can be seen that at all water-to-binder ratios, addition of silica fume in the binary system invariably leads to reduction in water penetration depth and permeability. Among the ternary mixes, water penetration depth is least in the case of TC1 mix. Permeability of TC1 mix (having a combination of 5% silica fume and 15% fly ash) is even lesser that BS1 and BS2 mix, in which silica fume is used as a binary system. It indicates that the better pore refinement can be achieved by using a proper combination of silica fume and fly ash as mineral admixtures, rater than using only silica fume. The impermeability test links directly with the durability of concrete. It is due to the fact that the segmentation of the capillary pores governs the durability aspect of concrete. This observation further emphasis the importance of suitable ternary mixes, containing both silica fume and fly ash, to get better concrete in terms of both strength and durability.

5.2.2. Effect of Curing Regimes

The effect of curing regimes on water penetration depth of various mixes follows the trend similar to the effect on strength development. The water penetration depth is maximum in the air cured regime (R2) for all the mixes, confirming that air curing is the worst curing regime and should not be followed as a construction practice. Some days of initial water curing is necessary in order to obtain strong and durable mix.

It has already been pointed out that the segmentation of capillary pores govern the durability aspects of concrete. It is well known that 7 days of curing period is generally required at water-to-binder ratio of 0.45 for segmentation of capillary pores *(Neville 2004 a).* From Fig. 5.1, it can be seen that 7 days of water curing followed by air drying (R3 curing regime) leads to the water penetration depth of 76.7 mm at 90 days at the water-to-binder ratio of 0.45. The corresponding values of the penetration depth for all mixes, except the one with only fly ash as a binary system, is lesser than the value for OPC concrete, indicating the performance of silica fume concrete and silica fume- fly ash concrete is even better that OPC concrete when the initial water curing of only 7 days is provided. Same trend is observed for all other water-to-binder ratios although below the water-to-binder ratio of 0.45, the segmentation of capillary pores will take place much before 7 days. All these facts establish that 7 days of water curing is necessary and sufficient for the proper strength and durability of concrete when the mix has silica fume in the system, used as a binary or ternary system.

5.2.3. Relationship between Permeability, Compressive Strength and Tensile Strength

In order to judge which strength (compressive or tensile) gives the better idea of permeability characteristics (and hence durability aspects) of concrete, water penetration depth is plotted against compressive strength, flexure strength and split tensile strength, as shown in Figs. 5.4 to 5.6 respectively. It can be seen from the figures that tensile strength of concrete is better correlated to the penetration depth than the compressive strength. The correlation coefficients are 0.6, 0.81 and 0.84 for compressive strength, split tensile strength and flexure strength respectively. Similar conclusions were drawn by *Kumar and Bhattacharjee (2002)* while relating initial surface absorption rate and in situ strength of concrete specimens.

5.3. ACID ATTACK ON CONCRETE

5.3.1. General

Acidic attack represents a worrying topic of increasing significance, owing to the spread of damage of concrete structures all over the world. To study the acid attack on concrete, three mixes are chosen for each water-to-binder ratio. The mixes for each water-to-binder ratio are: control mix, binary mix containing 5% of silica fume as replacement of cement, and ternary mix containing a combination of 5% silica fume and 15% fly ash as cement replacement. Both these mixes are selected because from the strength studies, it has been established that the performance of binary mix with 5% silica fume and the ternary mix with 5% silica fume and 15% fly ash is almost similar and the ternary mix is further found out to be more economical than the binary mix. The purpose of studying these mixes together is to observe whether the ternary mix performs better than the binary mix when subjected to aggressive chemicals. These mixes are given the initial water curing of 7 days, followed by air drying till 90 days so that the strength of concrete reaches a stable level before exposure to aggressive chemicals. This curing condition is found to be sufficient to explore the pozzolanic activity of these mixes.

In order to evaluate acid corrosion resistance of the mixes, the specimens are tested in three aggressive chemical environmental conditions that are simulated by using the following chemicals: 1% sulfuric acid (H_2SO_4), 1% hydrochloric acid (HCl), and 1% nitric acid (HNO_3). The value of pH obtained by using above mentioned concentration of acids comes under the category of strong chemical attack as per DIN EN 206 Standard *(Beddoe and Doner 2005).* The maximum exposure duration is kept as 48 weeks, as mentioned in Chapter 3 and the deterioration process is analyzed by progressive strength loss and weight loss in the specimens. The following sections deal with the results and discussion on the change in various parameter after subjecting the samples to the above mentioned chemicals.

5.3.2. Behaviour under Sulfuric Acid Exposure

Fig. 5.7 to 5.9 presents the weight change data of specimens as a function of time at water-to-binder ratios of 0.45, 0.35 and 0.25 respectively when exposed to a solution of 1% sulfuric acid. Similarly, Figs. 5.10 to 5.12 present relative strength loss with respect to time for all the three water-to-binder ratios.

Looking at Figs. 5.7 to 5.9 for weight loss, it is observed that irrespective of water-to-binder ratio and type of mix, the weight of specimens increases until around 4 to 5 weeks, thereafter, the weight starts decreasing gradually. The initial weight gain cannot be attributed to saturation of specimens because in the test program, they are dried for 24 hours before weighing. Actually, when sulfuric acid comes in contact with concrete, it reacts with portlandite and calcium aluminate hydrate to form gypsum and ettringite as expressed in the following reactions *(Monteny et al 2000):*

$$H_2SO_4 + \underset{portlandite}{Ca(OH)_2} \rightarrow \underset{gypsum}{CaSO_4.2H_2O} \qquad \ldots(5.1)$$

$$3(CaSO_4.2H_2O) + \underbrace{3CaO.Al_2O_3.12H_2O}_{calcium\ alumnate\ hydrate} + 14H_2O \rightarrow \underset{ettringite}{3CaO.Al_2O_3.3CaSo_4.32H_2O} \qquad \ldots(5.2)$$

The solubility of calcium sulfate, so formed is low (0.22 gm/100 gm of water at 0°C) *(Pavlik et al 1994, Zivica and Bajza 2001),* therefore, its dissolution does not take place. On the other hand, these reaction products have very low structural stability in comparison to the reactants they replace. They involve an increase in volume and therefore occupy the space available as voids in concrete that leads to increase in initial weight. However, after some time, the continued expansion causes cracking that ultimately leads to peeling off of the surface layer of concrete that is indicated by mass loss of concrete that starts after around 1 month of exposure to sulfuric acid solution.

5.3.2.1. Effect of Water-to-Binder Ratio

While comparing the effect of water-to-binder ratio on the deterioration caused by sulfuric acid solution, it is observed that the weight loss and strength loss gives contradictory outcomes. If the ultimate weight loss and compressive strength loss of all the three mixes prepared at three water-to-binder ratios at the end of 48 weeks is compared, (Fig. 5.13 and Fig. 5.14), it can be noticed that for all the mixes, while weight loss increases with the decrease in water-to binder ratio, the compressive strength loss decreases with the decrease in water-to-binder ratio. In fact, with the decrease in water-to-binder ratio, a combination of opposite effects takes place. On one hand, due to lower water-to-binder ratio, porosity decreases that implicate lower corrosion, while on the other hand, the relative amount of cement increases, that implicates higher corrosion *(Monteny et al 2000).* Mass loss is a surface phenomenon and therefore, reflects only one effect of lowering water-binder-ratio, i.e. relative increase in cement content which leads to greater formation of gypsum on the surface layer that causes expansion and ultimately disruption of surface layer. Also, due to brushing of the specimens, the loose debris is removed that leads to more reduction in weight with the decrease in water-to-binder ratio. On the other hand, strength measurement takes into consideration the properties of whole of the concrete matrix. Lower strength loss indicates that although the mass loss is high, the deterioration has taken place only on the surface and the inner matrix is still unaffected by the acid attack. It shows that lowering of water-to-binder ratio is beneficial in acidic attack. A contradictory view is presented in some research works that conclude that the rate of corrosion is increased with decrease in water cement ratio *(Pavlik and Uncik 1997; Hewayde et al 2007; Fattuhi and Hughes 1988 a).* In these works, only mass loss is taken as the parameter for judging corrosion. It leads to the conclusion that mass loss is not the reliable index in measuring the efficiency against acidic media and can lead to misleading conclusions.

5.3.2.2. Effect of Mineral Admixtures

From Figs. 5.7 to 5.12, it can be seen that for entire water-to-binder ratio range, the use of supplementary cementitious materials help in arresting both weight loss and compressive strength loss. The reduction of deterioration process with the addition of mineral admixtures can be explained from the fact that with the addition of supplementary cementitious materials, due to pozzolanic reaction, both permeability and amunt of calcium hydroxide required for sulfuric acid attack are reduced that helps in reducing the detrimental effect of sulfuric acid solution.

At each water-to-binder ratio, the weight loss and compressive strength loss of ternary mixes with a combination of silica fume and fly ash is lesser than the corresponding binary mixes with only silica fume as the mineral admixture. It shows that ternary mixes perform better than binary mixes in sulfuric acid exposure.

5.3.3. Behaviour under Hydrochloric Acid Exposure

Fig. 5.15 to 5.17 presents the weight change data of specimens as a function of time at water-to-binder ratios of 0.45, 0.35 and 0.25 respectively when exposed to 1% hydrochloric acid, while Figs. 5.18 to 5.20 present relative strength loss with respect to time for all three water-to-binder ratios.

One particular observation that is unique to hydrochloric acid attack is the identification of brownish belts on the surface of specimens, as can be seen in Plate 5.1. It is probably due to the presence of ferric hydroxide. The similar observation was made by other researchers also *(Chandra 1988, De Ceukelaire 1992)*. Further, with the passage of time, the surface layer, in the case of hydrochloric acid attack, is completely peeled off (Plate 5.2). Due to the peeling off of the surface, the specimens undergo higher amount of weight loss as compared to what is experienced in sulfuric acid attack.

5.3.3.1. Effect of Water-to-Binder Ratio

The ultimate weight loss and compressive strength loss of all the three mixes prepared at three water-to-binder ratios at the end of 48 weeks is compared in Figs. 5.21 and 5.22 respectively. It is observed from the figures that with the decrease in water-to-binder ratio, there is an increase in weight loss and decrease in compressive strength loss. This observation is similar to sulfuric acid attack. However, the difference in the values is not as high as the ones observed in sulfuric acid attack that indicates that hydrochloric acid attack does not depend much on water-to-binder ratio. The phenomenon of sulfuric acid and hydrochloric acid attack are different. In fact, the mechanism of concrete deterioration by acidic attack can be schematically represented as shown in Fig. 5.23. As can be seen from the figure, there are two courses of action in acidic attack. First course of action is the one in which the salt formed is soluble and hence can be leached out, leading to major effect on mass loss without introducing any internal stresses that can cause micro cracking and hence major loss of strength. This course of action is adopted during hydrochloric acid attack, in which when calcium hydroxide dissolves in acid, the reaction product that is formed is calcium chloride which is highly soluble in water (279.3g/100g of water at 0°C) and therefore, is leached out of the mortar without forming micro cracks that can effect the internal structure and hence strength characteristics of concrete. This type of action has more effect on the weight loss, as has been observed from the peeling off of the surface of specimens in hydrochloric acid attack. On the other hand, the second course of action is the one in which reaction products are not soluble but are expansive in nature, therefore can cause micro cracking and high loss of strength and lesser mass loss. This course of action is adopted by sulfuric acid attack, as has already been explained. Therefore, while the weight loss is more in hydrochloric acid attack due to continuous leaching of the reaction products, the strength loss is very small as compared to the loss observed in sulfuric acid attack.

5.3.3.2. Effect of Mineral Admixtures

Similar to the observation made in sulfuric acid attack, it is found from Figs. 5.15 to 5.20 that for the entire water-to-binder ratio range, the use of supplementary cementitious materials helps in arresting both weight loss and compressive strength loss. At each water-to-binder ratio, the weight loss and compressive strength loss of ternary mixes with a combination of silica fume and fly ash is lesser than the corresponding binary mixes with only silica fume as the mineral admixture. It shows that ternary mixes perform better than binary mixes in hydrochloric acid exposure also.

5.3.4. Behaviour under Nitric Acid Exposure

Fig. 5.24 to 5.26 presents the weight change data of specimens as a function of time at water-to-binder ratios of 0.45, 0.35 and 0.25 respectively when exposed to 1% nitric acid, while Figs. 5.27 to 5.29 present relative strength loss with respect to time for all three water-to-binder ratios.

5.3.4.1. Effect of Water-to-Binder Ratio and Mineral Admixtures

The ultimate weight loss and compressive strength loss of all the three mixes prepared at three water-to-binder ratios at the end of 48 weeks is compared in Figs. 5.30 and 5.31 respectively. From the figures, it is clear that the effect of nitric acid is similar to the effect of hydrochloric acid attack with the only difference that the strength losses are comparatively lesser in nitric acid attack. This may be due to higher solubility of calcium chloride (279.3g/100g of water at 0°C) as compared to calcium nitrate (266g/100g of water at 0°C) *(Pavlik 1994)*. However, the difference in solubility is very small and therefore, the presence of some other factor cannot be over ruled. A detailed investigation by considering other parameters that involves micro structural studies is required to have a clear understanding of nitric acid attack.

5.4. SULFATE ATTACK ON CONCRETE

5.4.1. General

Deterioration of concrete due to sulfate attack is the second major durability problem, only after reinforcement corrosion. Sulfate attack on concrete is a complex process that is governed by many parameters related to material selection and mixture proportioning like cement type, water-to-binder ratio, use and proportions of supplementary cementitious materials, characteristics of aggregates etc. Along with the properties of concrete, sulfate ion concentration and the cation associated with sulfate ions have a significant impact on the nature and magnitude of concrete deterioration.

In the present investigation, in order to study the sulfate attack on concrete, four mixes are chosen for each water-to-binder ratio. These include control mix for each water-to-binder ratio, binary mixes containing 5% and 10% of silica fume as partial replacement of cement, and ternary mix containing a combination of 5% silica fume and 15% fly ash as cement replacement. The binary mixes are taken in order to analyze the effect of silica fume on the chemical resistance of concrete and the ternary mix (TC1) is chosen because from the strength studies, this mix is found to perform best in terms of strength development and impermeability characteristics of concrete. After the common initial curing regime of 7 days water curing followed by air drying till 90 days, the specimens are stored in two different solutions containing 5% of sodium sulfate and 5% of magnesium sulfate respectively. The above exposure conditions represent very severe sulfate exposure conditions as per ACI 318-99. The maximum exposure duration is kept as 12 monthly cycles of wetting and drying, as mentioned in Chapter 3 and the deterioration process is analyzed by progressive strength loss and weight loss in the specimens. Prior to compressive strength tests, the cubical specimens are visually examined thoroughly for any signs of deterioration in the form of cracking, spalling, disintegration etc. Along with this, ultrasonic pulse velocity of the specimens is also measured for each sample. The following sections deal with the results and discussion on the change in various parameters after subjecting the samples to the above mentioned chemicals.

5.4.2. Compressive Strength Loss

Figs. 5.32 to 5.34 show the compressive strength loss of specimens when exposed to 5% sodium sulfate solution prepared at water-to-binder ratio of 0.45, 0.35 and 0.25 respectively. The negative values of all specimens at early stages of exposure indicate the initial increase in strength of specimens exposed to sodium sulfate solution. It can be attributed to the filling up of the pore space by the expansive products, thus densifying the matrix in the early period of immersion and prior to the deterioration due to high tensile strain *(Al Amoudi 1998; Al Amoudi et al 1994; Lee et al 2005; Moon et al 2003; Brown 1981).* After the initial strength gain, the loss of strength is experienced by all mixes prepared at three water-to-binder ratios. For all water-to-binder ratios, the loss of strength is restricted with the partial replacement of cement by mineral admixtures. Among the mineral admixtures, the use of silica fume alone in binary mixes does not significantly affect compressive strength loss, while the use of a combination of silica fume and fly ash restrict the CSL to barest minimum value. For investigating the influence of water-to-binder ratio on sulfate attack, Fig. 5.35 is prepared using the data presented in Figs. 5.32 to 5.34. It can be observed from the figure that lowering the water-to-binder ratio tends to improve the performance in sodium sulfate exposure. For instance, the compressive strength loss of the control mix is reduced from 39% to 19.4% and further to 16% when the water-to-binder ratio is reduced from 0.45 to 0.35 and then to 0.25.

Figs. 5.36 to 5.38 show the compressive strength loss with increasing cycles of exposure to magnesium sulfate solution for concretes at water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. The figures indicate that the deterioration mechanism in magnesium sulfate solution is not similar to sodium sulfate solution. In magnesium sulfate immersion, the strength deterioration of specimens containing mineral admixtures is more pronounced than the corresponding specimens without mineral admixtures. Also, all the specimens do not register initial strength gain. For all water-to-binder ratios, OPC concrete show strength gain up to 2 cycles of exposure and thereafter loss of strength is observed during whole of the testing procedures. For mineral admixture concrete, the strength loss starts immediately after exposure to magnesium sulfate solutions. For investigating the influence of water-to-binder ratio on magnesium sulfate attack, Fig. 5.39 is prepared using the data presented in Figs. 5.36 to 5.38. Figure 5.39 shows that in the case of magnesium sulfate attack also, the reduction of water-to-binder ratio tends to mitigate the sulfate attack. However, the effect of lowering of water-to-binder ratio is not as effective as the corresponding influence seen in the case of sodium sulfate solution.

5.4.3. Visual Observations

A thorough visual examination has been carried out on the specimens before doing the destructive compressive strength tests to evaluate visual signs of softening, cracking or spalling of concrete specimens. The level of visual deterioration is evaluated based on the work by *Irassar et al (2003)* which is summarized in Table 5.1 and are presented in Tables 5.2 and 5.3 for specimens exposed to sodium sulfate and magnesium sulfate solutions respectively. From the periodic observations, it is clear that initial deterioration invariably starts at the corner of the specimens. It may be due to the fact that near the corners, the intrusion takes place from two adjacent faces *(Al-Amoudi 1995).* The results of Table 5.2 indicate that in sodium sulfate attack, at higher water-to-binder ratio, OPC concrete start showing visual deterioration after around 6 months of exposure when small cracks appear at corners. After the appearance of cracks, the specimens expand rapidly and at the end of one year, extensive cracking is noticed with widening of all cracks, but the cracks are still restricted to edges. On the contrary, for the same water-to-binder ratio, mineral admixture concrete requires around 10 months of exposure to show first visual signs of deterioration. Even at the end of one year, the cracks are small and thin, that are restricted to the corners. The similar observation is made at all water-to-binder ratios with one general trend that with the decrease of water to binder ratio, the signs of deterioration starts appearing at the early stages, and the final level of visual disintegration is a bit higher at lower water-to-binder ratios. From the visual observation, it is clear that the incorporation of mineral admixtures in OPC concrete helps in providing the excellent sulfate resistance, when the associated cation type is sodium.

On the other hand, in the case of immersion in magnesium sulfate solution, the different tendency is exhibited by all the specimens. The first observation is that in all the specimens white substance start depositing on all the faces of specimens as shown in Plate 5.3. Also, the visual deterioration is higher as compared to sodium sulfate attack. The deterioration also increases with the decrease in water-to-binder ratio. The visual examination indicates that the intensity of damage is greater with inclusion of mineral admixtures and the level of damage increases with the increase in replacement percentage of cement by mineral admixtures. Some cases (TC1 mixes prepared at water-to-binder ratio of 0.25) have shown complete disintegration at surface at the end of 1 year. It can, therefore, be concluded from visual examination that contrary to sodium sulfate attack, increasing the percentage replacement of cement by mineral admixtures negatively affect the resistance of concrete against magnesium sulfate attack.

5.4.4. Concrete Weight Loss

The weight loss of concrete specimens prepared at water-to-binder ratios of 0.45, 0.35 and 0.25; and exposed to sodium sulfate solutions are shown respectively in Figs. 5.40 to 5.42. The figures exhibit that initially there is marginal weight gain in almost all the specimens, especially in OPC concrete, which is followed by the decrease in weight. The initial weight gain can be attributed to the filling up of pores by the expansive reaction products, thereby densifying the concrete matrix leading to an increase in weight *(Montemor et al 2000).* When the pores are all filled up by the expansive reaction products, with further formation of expansive products, the disruption of the cementitious matrix takes place resulting in the decrease in weight of the specimens *(Hossain and Lachemi 2006).*

For the control concrete at water-to-binder ratio of 0.45, the weight in specimens increase up to 4 months and then the specimens start registering decrease in weight. For control mixes at water-to-binder ratios of 0.35 and 0.25, the trend is same; however, the initial increase in weight is lesser as the water-to-binder ratio is reduced. Fig. 5.43 shows the ultimate weight loss after 12 monthly cycles of exposure that is achieved by all the mixes at different water-to-binder ratios. From the figure, it can be observed that with the decrease in water-to-binder ratio, the final weight loss is higher for all the mixes. This drift is in pattern with the observation made during the visual examination carried out on the specimens. However, it is contrary to the trend obtained from compressive strength loss studies. Actually, the phenomenon of sulfate attack is not a simple function of water permeability *(Al-Amoudi 1995; Hughes 1985)* due to the fact that sulfate attack is not purely physical in nature. Infact, it is a combination of physical and chemical attacks. At higher water-to-binder ratios, the number of pores present are more and the amount of calcium hydroxide is less due to the lesser amount of cement used. Therefore, the amount of expansive reaction products formed is less and these are accommodated in the large pore space available. However, due to high porosity, the attacking solution travels deep into the matrix, thus making it more susceptible to attack. On the other hand, at lower water-to-binder ratios, amount of calcium hydroxide in the matrix is high and secondly the concrete specimen is not capable of accommodating the expansive reaction products, which is very much clear from the amount of weight gain in the specimens. Due to higher amount of expansive reaction products formed and lesser space available for its accommodation, disruptive cracks start appearing at the surface at early ages leading to more amount of weight loss. Along with this, the lesser porosity helps in restricting the attack to the surface only and the inner matrix remains intact, which is clear from compressive strength loss plots.

While comparing the effect of mineral admixtures on weight loss, it is found that with the addition of mineral admixtures in concrete, the weight loss decreases at all water-to-binder ratios with the maximum effect shown while using a combination of 5% silica fume and 15% fly ash for all water-to-binder ratios. Actually, when pozollans are added to OPC concrete, they react with calcium hydroxide produced during the primary hydration reaction and produces secondary C-S-H. The consumption of calcium hydroxide reduces the formation of gypsum which is the expansive reaction product and leads to disruption of the matrix. Along with this, secondary C-S-H results in densification of the matrix, thus making the matrix impermeable for sulfate ions to penetrate *(Al-Amoudi 2002).*

The weight loss of concrete specimens under magnesium sulfate attack is shown in Fig. 5.44 to 5.46 for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. The pattern of weight change with the immersion period is similar to one obtained under sodium sulfate attack in which specimens exhibited initial weight gain followed by the loss of weight. The initial weight gain can be due to the formation of expansive reaction products. The other reason of weight gain can be the white deposits that appeared on the surface of the specimens under magnesium sulfate attack as shown in Plate 5.3. The ultimate mass loss is higher than the corresponding sodium sulfate solution indicating more amount of surface degradation in magnesium sulfate attack.

In order to observe the effect of water to binder ratio on weight loss, bar chart has been plotted using the data from the Figs. 5.44 to 5.46. Fig. 5.47 represents the ultimate weight loss of all the mixes under magnesium sulfate exposure prepared at different water-to-binder ratios. It can be seen that in magnesium sulfate attack also, with the decrease in water-to-binder ratio, the amount of weight loss increases. The addition of mineral admixtures in concrete at any water-to-binder ratio exhibits negative effect in terms of weight loss, although the variation of weight is found to be negligible in most of the cases.

The effect of water-to-binder ratio on the compressive strength loss and weight loss is opposite in both sodium sulfate and magnesium sulfate solutions. It can be due to the fact that the weight loss is the surface phenomenon and is the indicator of surface deterioration of the specimen, while the compressive strength loss is the indicator of the behaviour of entire depth of the specimen. Therefore, it can be said that observing weight loss is not a suitable measure to indicate the sulfate attack.

5.4.5. Ultrasonic Pulse Velocity Results

Ultrasonic pulse velocity tests are used to find the extent of deterioration caused by fire, mechanical or chemical attack *(Shannag and Shaia 2003).* In the present investigations, the ultrasonic pulse velocity is measured prior to the destructive compressive strength tests. The results in terms of relative ultrasonic pulse velocity with respect to the reference pulse velocity are presented in Figs. 5.48 to 5.53 for all three water-to-binder ratios when exposed to sodium sulfate and magnesium sulfate solutions respectively. For all the mixes, the trend of ultrasonic pulse velocity change is consistent with the compressive strength loss pattern, yet even at the end of 12 exposure cycles, the quality of concrete judged by ultrasonic pulse velocity still remains under ‘good grading condition’ as per IS 13311: Part I: 1992. The reason behind it is that the damage due to sulfate exposure is restricted to the concrete surface layers while the interior matrix still remains intact.

5.4.6. Mechanism of Sulfate Attack

Results presented in this investigation indicate that the sulfate attack is a progressive phenomenon starting from the surface and moving inwards, and involves several stages. These stages depend both upon the rate of ingress of solution into the specimen and the chemical nature of the specimen. The different behaviour of samples subjected to sodium sulfate and magnesium sulfate environments indicate that the mechanism of deterioration into these environments is different from each other. Based on the results reported in the present study and from the thorough review of the literature, the sequence and mechanism of both sodium sulfate attack (NS) and magnesium sulfate (MS) attack can be summarized as under. In the equations representing the mechanism of attack, various symbols are used which indicate

$$C = CaO, \quad N = Na_2O, \quad M = MgO, \quad S = SO_3, \quad Si = SiO_2, \quad H = H_2O$$

5.4.6.1. Mechanism of Sodium Sulfate Attack

The sequence of attack is schematically illustrated in Fig. 5.54 and it has following stages:

Stage I: Two counter ion flow

At early ages, concrete and solution system involves the flow of SO_4^{2-} from the solution to the specimen and diffusion of Ca^{2+} from inside the specimen to the solution *(Gallop and Taylor 1995; Bonen and Cohen 1992)*

Stage 2: Gypsum and ettringite formation

The sulfate ions coming in concrete has a greater affinity to react with calcium hydroxide (portlandite or CH) that is a product formed during cement hydration. This results in the formation of gypsum

$$CH + NS + 2H \rightarrow \underset{(gypsum)}{CSH_2} + NH \qquad \ldots (5.3)$$

The formation of gypsum causes softening of external layer of mortar while the interior of the matrix still remains cohesive *(Mehta 1983, Rasheeduzzafar 1992, Mangat and Khatib 1993).* Gypsum thus liberated will react with tricalcium aluminate (C_3A) phase of cement

$$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32}\,(ettringite) \qquad \ldots (5.4)$$

It is often called ‘secondary’ ettringite to differentiate from ‘primary’ ettringite that is formed during the setting of Portland cement when the concrete is in the plastic stage. Secondary ettringite is expansive in nature due to its low density of (1.73 g/cm^3) as compared to the density for the other products of hydration (2.5 g/cm^3) *(Al-Amoudi 2002).* The mechanism by which expansion is caused is still a subject of controversy. Exertion of pressure by forming ettringite crystals and swelling due to absorption of water in the alkaline environment by poorly crystalline ettringite are two of the several hypotheses that are supported by most researchers. This expansion leads to deterioration of the surface zone, which makes the way for further ingress of solution into the specimen. Therefore, at advanced stages, there are three distant zones within the specimen:

1. the disintegrated surface,
2. zone of deposition of attack products
3. interior uncracked zone that is chemically unaltered *(Santhanam et al 2003 a)*

The attack thus progresses at the steady state until a complete degradation of the specimen occurs.

In NS attack, first stage is controlled by physical characteristics of specimen while the second stage is controlled by the chemical characteristics of the specimen and after chemical changes; the formation of cracks is again dependent on the available pore space which is a physical characteristic of the specimen. The time of initiation of attack depends on the length of first stage. The duration of first stage is increased with decrease in permeability of concrete that is achieved by lowering of water-to-binder ratio of the mix. That is why; the amount of compressive strength loss is less as the water-to-binder ratio is decreased. However, some investigators suggest that to evaluate deterioration degree of concrete in sulfate attack, influence of CH content is important *(Rasheeduzzafar et al 1990; Moon et al 2003).* In concrete specimens, the influence of CH content might gets counteracted by permeability of concrete because as the water-to-binder ratio is decreased, although CH content increases due to higher amount of cement used, lesser depth of concrete is susceptible to damage due to decreased permeability of the mix and hence decreasing the ultimate content of CH available for chemical reactions.

Also, once the chemical reaction has taken place, higher water-to-binder ratios have more space for the accommodation of expansive reaction products as compared to lower water-to-binder ratio, thus rendering lower water to binder ratios more susceptible to cracks. This must be the reason for higher weight loss in the case of lower water-to-binder ratio mixes although the compressive strength loss is not high.

The improvement in sodium sulfate resistance of concrete with mineral admixture addition seems to be due to their effect on both the stages of NS attack. Firstly, use of mineral admixtures lowers the permeability of concrete system. It occurs by the pore refinement process occurring due to the conversion of portlandite into secondary C-S-H gel by pozzolanic reaction. This secondary C-S-H is effective in filling the large capillary pores in concrete *(Al-Amoudi 2002, Moon et al 2003, Al-Amoudi 1995, Al-Dulaijan et al 2003).* Further, if the mineral admixture used is silica fume, the pore structure is further densified due to its finer size. All these effects tend to increase the duration of first stage. Secondly, the pozzolanic reaction leads to consumption of portlandite that is an essential ingredient for the chemical reaction leading to the formation of gypsum. The replacement of part of cement by the pozzolanic material also leads to reduction on C_3A content, thereby mitigating formation of ettringite. Along with this, since pozzolanic reaction consumes a significant portion of calcium hydroxide produced by hydration of cement and reduces pH, the ettringite that is formed is less expansive *(Al-Dulaijan et al 2003).* All these effects jointly reduce the chemical reaction taking place during the second stage of NS attack and hence increasing the overall efficiency of concrete in NS solutions.

5.4.6.2. Mechanism of Magnesium Sulfate Attack

The sequence of attack is schematically illustrated in Fig. 5.55 and it has following stages:

Stage I: Two counter ion flow

It is same as the first stage in NS attack. At early ages, concrete and solution system involves the flow of SO_4^{2-} from the solution to the specimen and diffusion of Ca^{2+} from inside the specimen to the solution *(Bonen 1993, Turker et al 1997, Irassar et al 2003).*

Stage II: Formation of gypsum and brucite

The sulfate ions react with portlandite leading to the formation of gypsum and magnesium hydroxide (called brucite)

$$CH + MS + 2H \rightarrow \underset{(gypsum)}{CSH_2} + \underset{(brucite)}{MH} \qquad \ldots (5.5)$$

The brucite so formed is insoluble (its solubility is 0.01 g/l as compared to 13.7 g/l for CH) and its alkalinity is low (pH<10.5) *(Dehwah et al 2003).* Due to its low solubility, a layer of brucite forms on the surface of the specimen. The layer of brucite is often complemented by a layer of gypsum that forms as a result of same reaction on the inside of brucite layer *(Santhanam et al 2003 b).* After the formation of these surface layers, the sulfate solution penetrates the interior of the specimen by diffusion.

Stage III Depletion of C-S-H

With the passage of time, the layer of brucite ultimately break down at several places due to expansion of gypsum and continued diffusion of solution. Once the layer is broken, direct attack on C-S-H occur. Due to low pH, secondary ettringite is not able to form. Instead, destabilization of C-S-H takes place. Since the magnesium and calcium ions associate well with each other due to their equal valance and similar radii, MS will react with C-S-H, thereby producing gypsum, brucite and silica gel.

$$\underset{(C-S-H\ gel)}{C_xSi_yH_z} + xMS + (3x+0.5y-z)H \rightarrow \underset{(gypsum)}{xCSH_2} + \underset{(brucite)}{xMH} + \underset{(silica\,gel)}{0.5ySi_2H} \quad \ldots (5.6)$$

The silica gel is less cementitious than the original C-S-H gel *(Rasheeduzzafar 1994; Al-Amoudi et al 1995).* Brucite and silica gel further reacts to form magnesium silicate hydrate, which is non cementitious.

$$4MH + SiH_n \rightarrow \underset{(M-S-H\,gel)}{M_4SiH_{8.5}} + (n-4.5)H \quad \ldots (5.7)$$

Therefore, ultimately C-S-H phase is converted into M-S-H phase which has no binding property *(Rasheeduzzafar 1994).* This attack is characterized by softening and deterioration of the superficial layer of hardened cement paste and more formation of gypsum and brucite. Therefore, the ultimate failure of specimens occur as a result of loss of strength and integrity due to transformation of C-S-H phase of the paste into M-S-H phase.

In concrete specimens, first stage, i.e., the diffusion of both hydroxide and sulfate ions, is controlled by the permeability characteristics of concrete. Second stage that involves the formation of double layer is controlled by chemical reactions and hence chemical characteristics of concrete. Once the double layer is formed, it protects the hardened cement matrix from further MS attack. However, the continuity of the brucite layer depends on the continuity of cement paste matrix which is broken by the presence of large coarse aggregates or by the large pores in the concrete system. Therefore, the continuity of brucite layer and protection provided from it is controlled by physical parameters of the concrete system. Also, the rate of diffusion of the solution from outside further inward into the concrete system depends on the thickness of brucite layer. Once the brucite layer is broken, further deterioration phenomenon of decomposition of C-S-H into M-S-H depends on chemical characteristics of concrete. Therefore, it can be concluded that MS attack depends equally on physical and chemical characteristics of concrete and presence of coarse aggregates play a major role in the resulting attack.

In the present study, it is found that with the decrease in water-to-binder ratio, the compressive strength loss decreases. Similar trend is observed by *Lee et al (2003)* in their research work. It can be due to the fact that at higher water-to-binder ratio, the rate of solution ingress is more due to higher permeability, thus reducing the time taken in first stage. Also, due to the presence of coarse aggregates and lesser cement content at higher water-to-binder ratio, the brucite layer that is formed is discontinuous and thin and hence the rate of diffusion of MS solution into the concrete specimens is high that makes C-S-H vulnerable to the sulfate attack. As the water-to-binder ratio is decreased, the pore space is reduced and the proportion of cement matrix in the whole system is increased that helps in making the brucite layer thicker and continuous and increases the time taken for diffusion of MS solution for further attack. Once this brucite layer is broken, it is expected that the deterioration will be more due to higher C-S-H present that leads to the formation of expansive products and reduces stiffness of the matrix. However, it seems that the attack will still be confined to the small area due to lesser permeability at lower water-to-binder ratio. In order to know about the advanced stages of attack longer studies on the concrete specimens must be carried out. Some studies in the literature indicate poor performance of dense hydrated cements in MS environments *(Al-Amoudi et al 1995, Hughes 1985).* Several factors are probably involved in this apparent discrepancy; some of them can be the difference in the paste and concrete specimens, the different exposure conditions etc. However, it is accepted in most of the studies that the MS attack is surfacial and the bulk of the specimen maintain their initial dense structure *(Al-Amoudi 2003, Al-Amoudi 1995, Al Amoudi 1998).*

At any water-to-binder ratio, with the addition of mineral admixtures, compressive strength loss is higher as compared to the corresponding control mixes. Actually, when mineral admixtures are used, the pozzolanic reaction leads to the consumption of calcium hydroxide. CH constitutes the first line of reaction with MS leading to the formation of brucite and gypsum and therefore, acts as a buffer and a retarded in the MS attack *(Rasheeduzzafar et al 1994).* Since the thickness of brucite layer is small that governs the ease of diffusion of sulfate ions, the reaction can proceed faster when mineral admixtures are used. The easier diffusion leads to quicker attack on C-S-H that leads to accelerated deterioration due to formation of M-S-H. This trend is supported by previous studies also *(Al-Amoudi 1995; Lee et al 2005; Santhanam et al 2002; Shannag and Shaia 2003; Cohen and Bentur 1988; Hekal et al 2002; Ganjian et al 2005).*

5.5. CHLORIDE INGRESS IN CONCRETE

5.5.1. General

Reinforced concrete is considered to be extremely durable material and is expected to have long service life. However, like all other materials, it deteriorates with time. Among the various factors that lead to decline in concrete durability, the penetration of chloride ions into concrete has been regarded as the major deterioration problem. Chlorides can be introduced into concrete by either internal sources (from aggregate, water etc) or external sources (by intrusion from the environment). Whatever may be the case, to cause damage, the chloride ions must be in contact with the reinforcement (called threshold chloride content) and also, there must be sufficient number of chloride ions to depassivate the reinforcement *(Ismail and Soleymani 2002; Mcpolin et al 2005; Thomas et al 1999; Alonso et al 2000).*

In the present study, chloride penetration mechanism is studied on some of the selected concrete mixes, prepared at the three water-to-binder ratios, when water-cured for 7 days followed by air curing till 90 days. Along with the study of chloride penetration profile, the objective is to develop a relation between free and total chlorides for mineral admixture concrete because it has already been established in the literature that the free chlorides are responsible for the initiation of corrosion. However, the chloride threshold value necessary to initiate corrosion of steel bars in concrete is mostly provided in terms of total chlorides *(Mohammed and Hamada 2003; Alonso et al 2000).* Therefore, the relationship between free and total chloride is necessary in order to judge the performance of mix under chloride exposure.

In order to study the chloride ingress, five mixes are chosen for each water-to-binder ratio. These include control mix for each water-to-binder ratio, binary mixes containing 5% and 10% of silica fume as partial replacement of cement, binary mix containing 30% fly ash as replacement of cement and ternary mix containing a combination of 5% silica fume and 15% fly ash as cement replacement. The binary mixes are taken in order to analyze the effect of silica fume and fly ash separately on chloride binding capacity of concrete and the ternary mix (TC1) is chosen because this mix has been found to be best in terms of strength development and impermeability characteristics of concrete. The study has been carried out with 5% sodium chloride and 5% calcium chloride solutions, as has been described in Chapter 3. The chloride penetration profiles for all the mixes subjected to sodium chloride salt are shown in Figs. 5.56 to 5.58 for water-to-binder ratios of 0.45, 0.35 and 0.25 respectively. The similar profiles under calcium chloride solution are presented in Figs. 5.59 to 5.61 respectively for water-to-binder ratios of 0.45, 0.35 and 0.25. The first graph in each figure represents the total chloride content while the second graph represents the corresponding free chloride profiles. The effects of different parameters on chloride penetration are discussed hereunder.

5.5.2. Effect of Water-to-Binder Ratio

From Figs. 5.56 to 5.61, it can be observed that for all types of concrete, the depth of chloride ingress decreases with the decrease in water-to-binder ratio. It is due to the pore refinement achieved due to relatively denser matrix and discontinuity of pores that occurs with the decrease in water-to-binder ratio that ultimately reduces the diffusion coefficient of chloride ingress. The reduced diffusion coefficient leads to lower chloride penetration through the pore system and therefore, results in lesser amount of total chloride and free chloride content in the concrete system at all depths for lower water-to-binder ratio as compared to higher water-to-binder ratio. The similar trend is observed by some previous researchers *(Ismail and Soleymani 2002; Chindaprasirt et al 2007).* However, if the relative effect of water-to-binder ratio and the presence of mineral admixtures are compared, it can be said that the decrease in water-to-binder ratio has lesser impact on the resistance to chloride penetration as compared to the effect of use of secondary cementitious materials.

5.5.3. Effect of Mineral Admixtures in Concrete

It is found that at all water-to-binder ratios, both the total and free chloride profiles of OPC mix is flat while the chloride penetration profile becomes steep for the blended mixes. This trend is due to relative change brought about both in the diffusivity characteristics and the chloride binding capacity by mineral admixtures in concrete. The only exception to this general behaviour is the binary mix containing only fly ash. In the case of fly ash, the slope of total chloride profiles is almost flat similar to the OPC mix. Although fly ash is considered to play a very effective role in improving the chloride binding of concrete because of its higher proportion of active alumina *(Dhir and Jones 1999)*, however in the present study, the curing has been provided for only a limited period of time that would have affected the porosity of the system adversely thus allowing the chloride to penetrate to a greater depth.

On the other hand, ternary mixes containing a combination of silica fume and fly ash performs equivalent to silica fume in chloride penetration profiles. The free chloride penetration profile of ternary mixes have maximum steepness and the depth to which chlorides have ingressed is minimum in ternary mixes indicating the combined effect of silica fume and fly ash is better than taking these admixtures alone as binary mixes. In the ternary system, silica fume reduces the diffusivity of the system even in short curing regime while fly ash helps in better chloride binding capacity due to its higher Al_2O_3 content.

5.5.4. Effect of Associated Cation

The trend of total chloride penetration profile for $CaCl_2$ is similar to that of NaCl with one general change, i.e., the depth to which chlorides have penetrated is more in the case of $CaCl_2$ solution and the initial chloride concentration is also somewhat higher in the $CaCl_2$ solution. In some of the mixes at the water-to-binder ratios of 0.45 and 0.35, the total chloride concentration even increases with depth. This increase of chloride concentration can be due to the increase in chloride binding capacity of the system when the associated cation is calcium instead of sodium.

5.5.5. Relationship between Free Chloride and Total Chloride

Based on the experimental results, linear relationships between free and total chlorides are prepared for various types of mixes in order to find the effect of various mineral admixtures on the relationship. Before finding the effect of mineral admixtures on chloride binding capacity of concrete, the effect of water-to-binder on chloride binding capacity is judged. For that, the linear plots are made between total chlorides and free chlorides for the control concrete. It is observed that the variation in chloride binding capacity is not significantly affected by water-to-binder ratio. The similar observation is made by *Pradhan and Bhattacharjee (2007)* while studying the role of steel and cement type on chloride induced corrosion of steel. Therefore, in order to judge the effect of mineral admixtures on chloride binding capacity of concrete, all the three water-to-binder ratios are taken together. The results are presented in Figs. 5.62 to 5.65 for NaCl solution and in Figs. 5.66 to 5.69 for $CaCl_2$ solutions. In the graphs, C_t represents the total chloride content in concrete and C_f represents corresponding free chloride content. In order to get the bound chlorides, the free chloride content can be subtracted from both sides of the equation representing the relation between free and total chlorides *(Mohammed and Hamada 2003).* The relationship between free and total chloride is of form $C_t = k_1 * C_f + k_2$, where k_1 and k_2 are constants. The term k_1 represents the rate of increase of free chloride with total chloride. Observing the values of k_1 in the figures, it can be concluded that the chloride binding ability of fly ash is highest among all mixes. Also, the chloride binding ability of the ternary mixes is almost similar but on the lower side of fly ash mixes. This trend is same irrespective of the type of associated cation with chloride ions. However, the relationship is steep when the associated cation type is calcium. It indicates that the chloride binding ability is affected by the associated cation type and the chloride binding ability of calcium chloride is more as compared to sodium chloride. The value of k_2 represents the total chloride content when the free chlorides present is zero. It is basically the bound chlorides present in concrete due to sources other than the external chloride ingress. The value of k_2 for all mixes is more or less same due to the similar materials used in casting.

5.6. INFERENCES ON DURABILITY ASPECTS

Firstly, the number of curing days required for all the mixes from the point of view of durability of concrete is established. The durability of concrete is dependent on permeability of the resultant concrete. Therefore, the requirement of minimum curing days is judged from the water impermeability studies on all the mixes. It is found that 7 days of curing is sufficient for all mixes except the one with 30% fly ash alone for the sedimentation of capillary pores, and therefore, achieving the desired durability of concrete. On comparing the correlation between impermeability, compressive strength and tensile strength, it is observed that the durability of concrete can be correlated better with the flexural strength of concrete.

After establishing the requirement of 7 days of initial water curing for silica fume concrete and ternary concrete, the rest of the durability studies are carried out on the mixes that are cured as per this curing regime. The durability studies are divided into three parts: acid attack, sulfate attack and chloride ingress in concrete. The acid attack on concrete is studied by subjecting the specimens to sulfuric acid, hydrochloric acid and nitric acid. The deterioration is judged in terms of compressive strength loss and weight loss of the specimens as compared to the corresponding values obtained before immersion in the aggressive medium. It is observed that under all aggressive solutions, with the decrease in water-to-binder ratio, weight loss and strength loss gives contradictory outcomes. While the weight loss increases with the decrease in water-to-binder ratio, the compressive strength loss increases. This contradiction is explained considering that the weight loss is a surface phenomenon and compressive strength loss reflects the properties on whole concrete matrix. It further shows that the acids affect the surface of concrete while the interior core of the specimen is still intact. This leads to the conclusion that weight loss is not a reliable index to durability of concrete in acid attack and must be supplemented by strength studies. Considering the effect of mineral admixtures on the resistance to acid attack, it is found that the presence of mineral admixtures lowers the detrimental effect of all types of acids and further, ternary mixes are found to perform better than the binary mixes containing only silica fume as mineral admixture. It is also observed that the mechanism of concrete deterioration under acid attack is of two types: mass loss type and strength loss type. The first course of action is adopted when the salt formed is soluble in water and hence can be leached out, leading to major effect on mass loss without having much affect on strength. This course of action is adopted by hydrochloric acid attack and nitric acid. The second course of action is the one in which reaction products are not soluble, therefore, they get deposited in the voids and cause internal stresses leading toe disruption and strength loss of the matrix. This course of action is adopted by sulfuric acid.

The sulfate attack in concrete is studied in terms of compressive strength loss, weight loss, visual observations and ultrasonic pulse velocity test. It is observed that lowering of water-to-binder ratio tends to mitigate the deterioration process. However, it is found that the degree of deterioration in sulfate attack is highly dependent on the type of cation associated with sulfate ions. The deterioration process is faster in the case of magnesium sulfate solution as compared to sodium sulfate solution. The use of mineral admixtures is found to be effective when the associated cation is sodium, but is highly detrimental if the associated cation is magnesium. It is because in magnesium sulfate solution, if calcium hydroxide is not present, the attack starts directly on C-S-H gel, leading to the formation of non cementitious M-S-H and hence ultimate strength loss. Presence of mineral admixtures leads to reduction in calcium hydroxide content due to secondary hydration reaction, leaving the concrete matrix highly vulnerable to magnesium sulfate attack. Among all mixes, ternary mixes are found to perform best in sodium sulfate solution, while OPC concrete is better in magnesium sulfate solution.

Regarding the effect of mineral admixtures and water-to-binder ratio on the chloride ingress in concrete, it is observed that for all types of concrete, the depth of chloride ingress decreases with the decrease in water-to-binder ratio and with the presence of mineral admixtures in concrete. If the relative effect of these two factors is considered, it is found that the decrease in water-to-binder ratio has lesser impact on the resistance to chloride penetration as compared to the effect of use of mineral admixtures in concrete. This is due to the effect of mineral admixtures on the improvement in diffusivity characteristics of concrete and their higher chloride bonding capacity. Among the mineral admixtures, ternary mixes containing a combination of silica fume and fly ash have least free chloride content. It is due to the fact that silica fume reduces the diffusivity of concrete even in short curing regime while fly ash helps in better chloride binding capacity of concrete. Out of two chloride salts studied, it is found that chloride penetration depth is higher when calcium chloride is used as compared to the chloride ingress in sodium chloride solution. Comparing the chloride binding capacity of various mixes, it is observed that the chloride binding capacity of fly ash concrete is highest. The chloride binding capacity of ternary mixes are also near to the values obtained by fly ash concrete. The chloride binding capacity is found to be dependent on the associated cation type, calcium chloride being more effective in binding chlorides as compared to sodium chloride.

Table 5.1. Levels of deterioration used for evaluating visual distress in concrete

(Irassar and Soleymani 2003)

Deterioration No.	Level of deterioration
0	No sign
1	Slight attack on corners and edges
2	moderate attack on corners and edges
3	severe attack on corners and edges
4	cracking of corners
5	cracking on the surfaces
6	disintegration of surface

Table 5.2. Deterioration rating judged by visual appearance of specimens when exposed to 5% sodium sulfate solution

Exposure cycles	Level of deterioration for various mixes											
	W/B = 0.45				W/B = 0.35				W/B = 0.25			
	M1	BS1	BS2	TC1	M2	BS1	BS2	TC1	M3	BS1	BS2	TC1
2	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	1	0	0	0	2	1	0	0
8	1	0	0	0	2	2	0	0	3	1	1	0
10	2	1	1	1	2	2	2	1	3	2	2	1
12	3	2	2	1	3	3	2	1	4	3	2	2

Table 5.3. Deterioration rating judged by visual appearance of specimens when exposed to 5% magnesium sulfate solution

Exposure cycles	Level of deterioration for various mixes											
	W/B = 0.45				W/B = 0.35				W/B = 0.25			
	M1	BS1	BS2	TC1	M2	BS1	BS2	TC1	M3	BS1	BS2	TC1
2	0	0	0	0	0	0	0	1	0	1	1	1
4	0	1	1	2	1	2	2	2	1	2	3	3
6	1	2	2	2	2	3	3	3	2	3	4	4
8	2	2	3	3	3	3	4	4	4	4	4	4
10	2	3	3	3	4	4	4	5	4	4	4	5
12	3	4	4	4	4	4	5	5	4	5	6	6

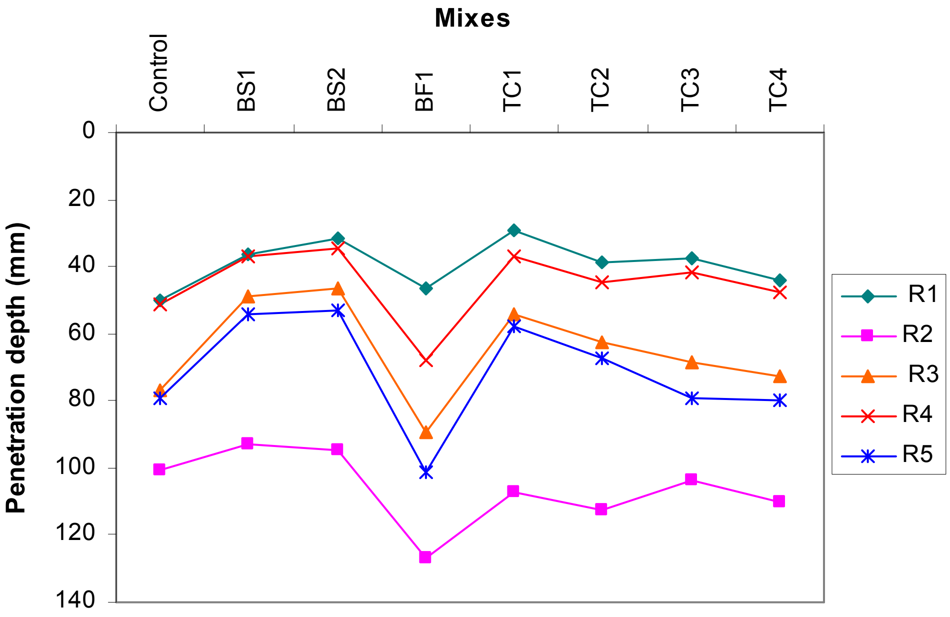


Fig. 5.1. Water penetration depth of all mixes prepared at the water-to-binder ratio of 0.45 when subjected to different curing regimes

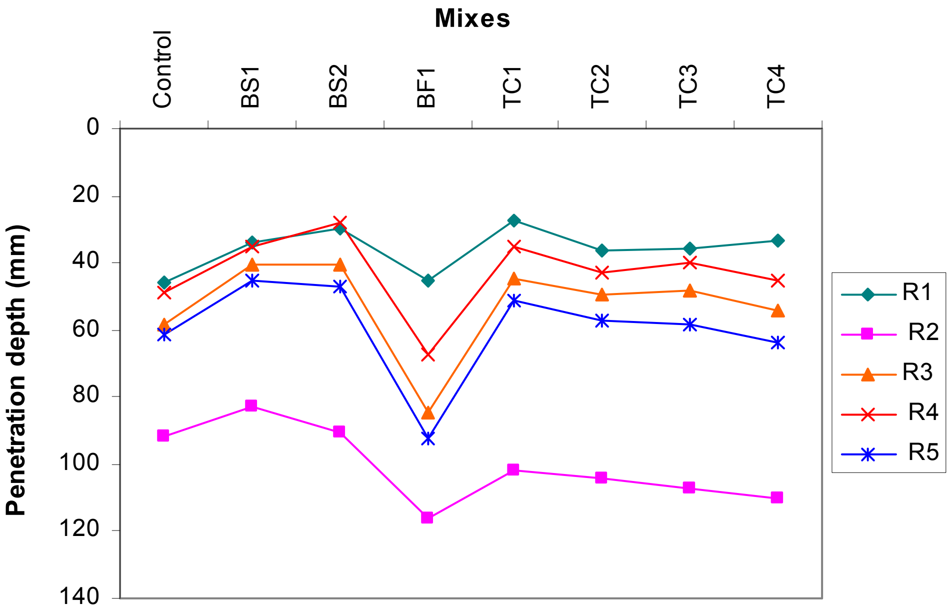


Fig. 5.2. Water penetration depth of all mixes prepared at the water-to-binder ratio of 0.35 when subjected to different curing regimes

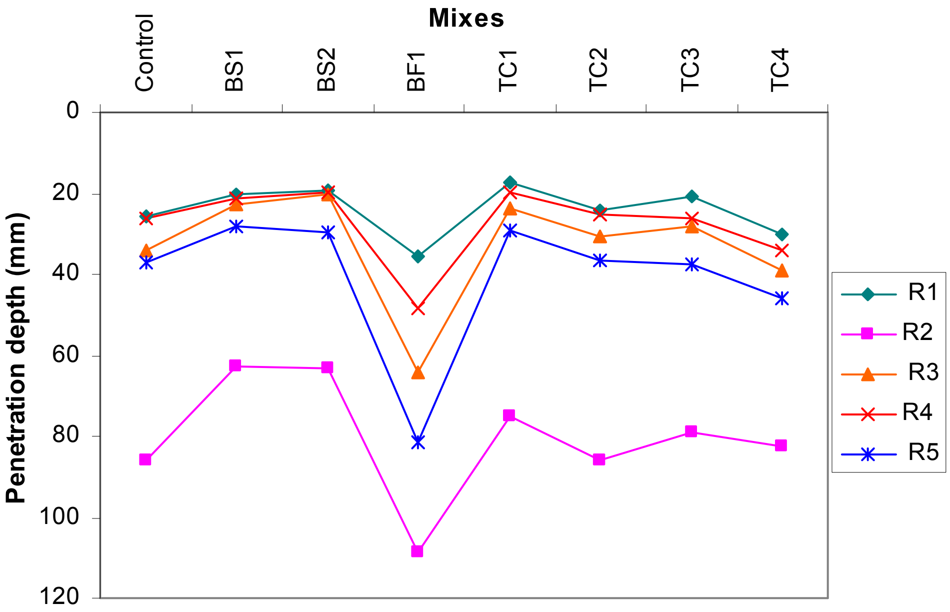


Fig. 5.3. Water penetration depth of all mixes prepared at the water-to-binder ratio of 0.25 when subjected to different curing regimes

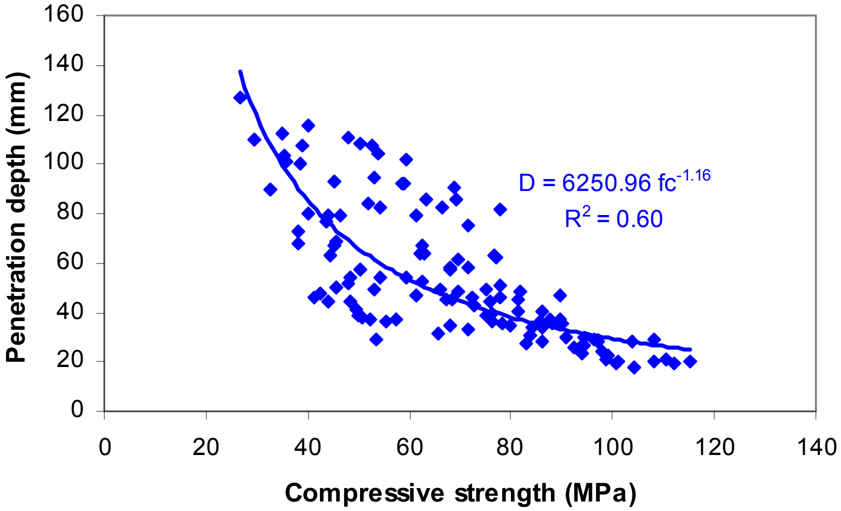


Fig. 5.4. Relationship between penetration depth and compressive strength of concrete

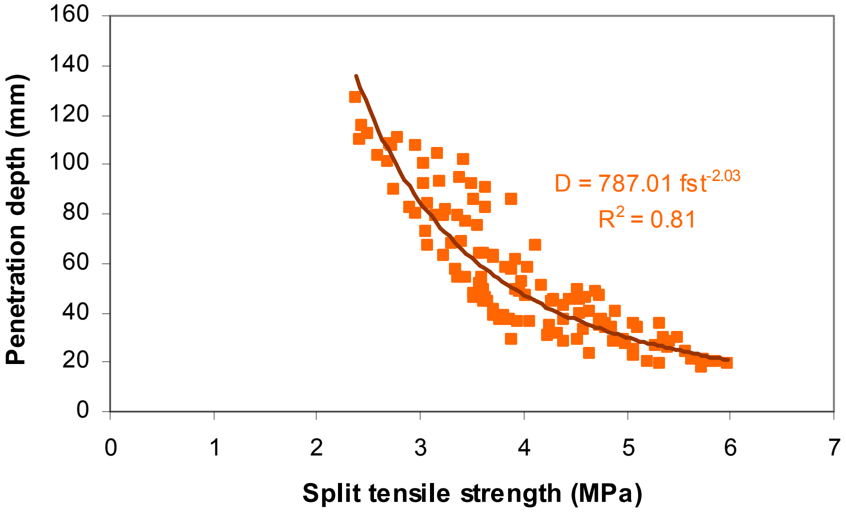


Fig. 5.5. Relationship between penetration depth and split tensile strength of concrete

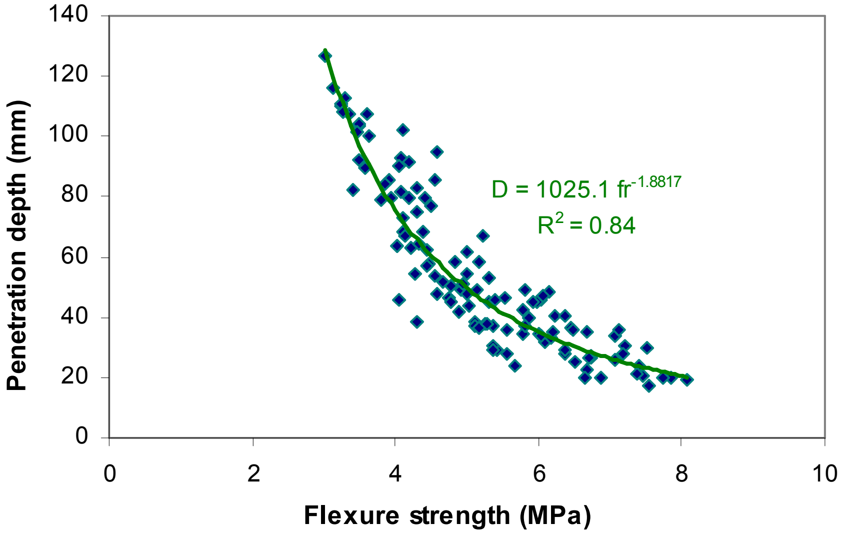


Fig. 5.6. Relationship between penetration depth and flexure strength of concrete

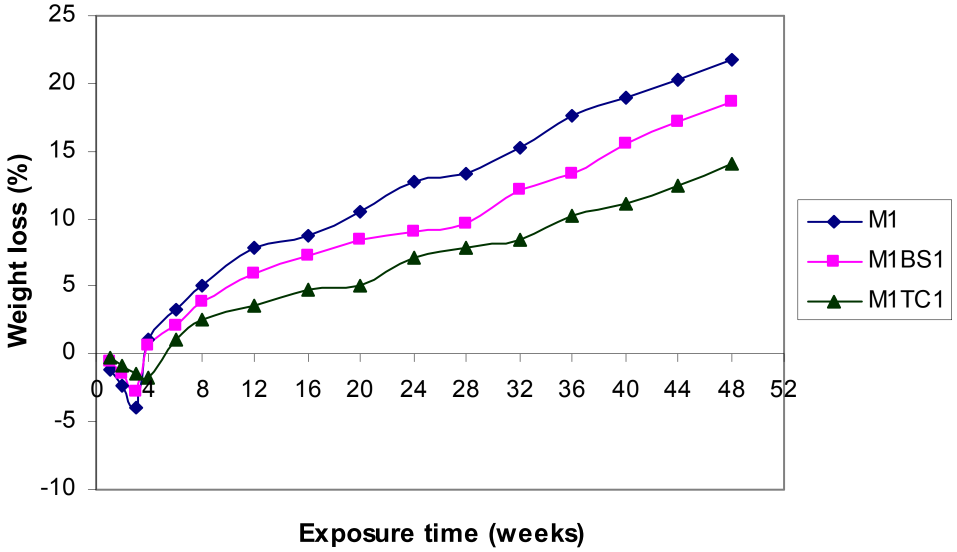


Fig. 5.7. Weight loss of specimens prepared at water-to-binder ratio of 0.45 under sulfuric acid exposure

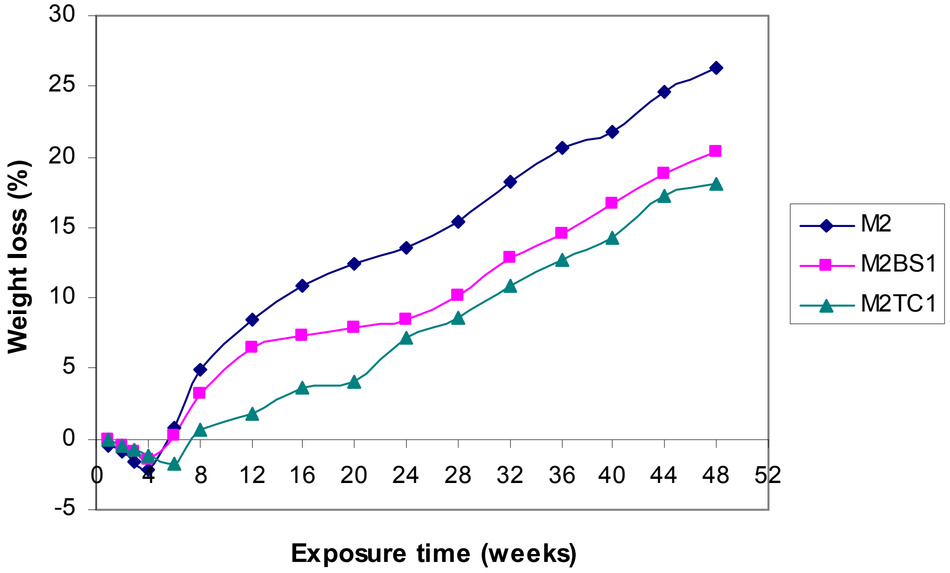


Fig. 5.8. Weight loss of specimens prepared at water-to-binder ratio of 0.35 under sulfuric acid exposure

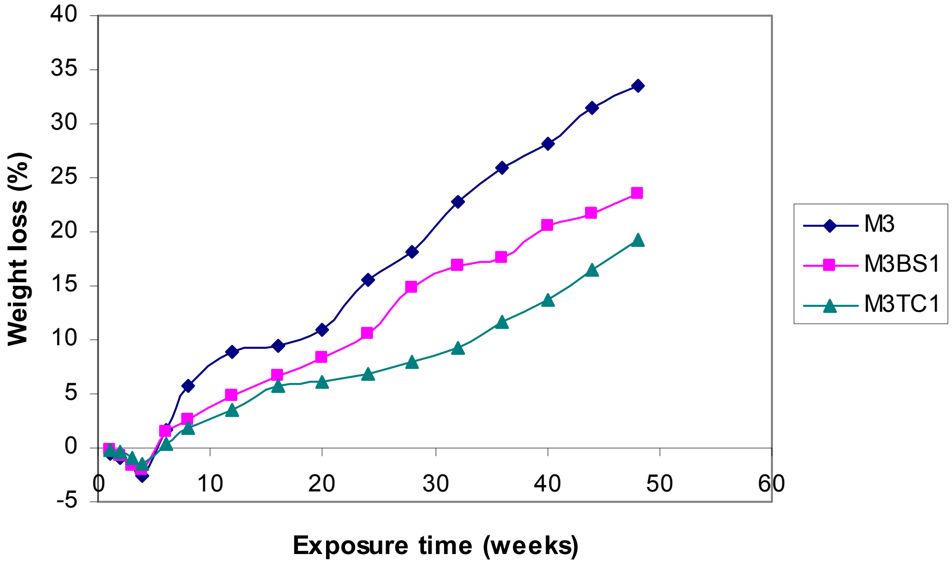


Fig. 5.9. Weight loss of specimens prepared at water-to-binder ratio of 0.25 under sulfuric acid exposure

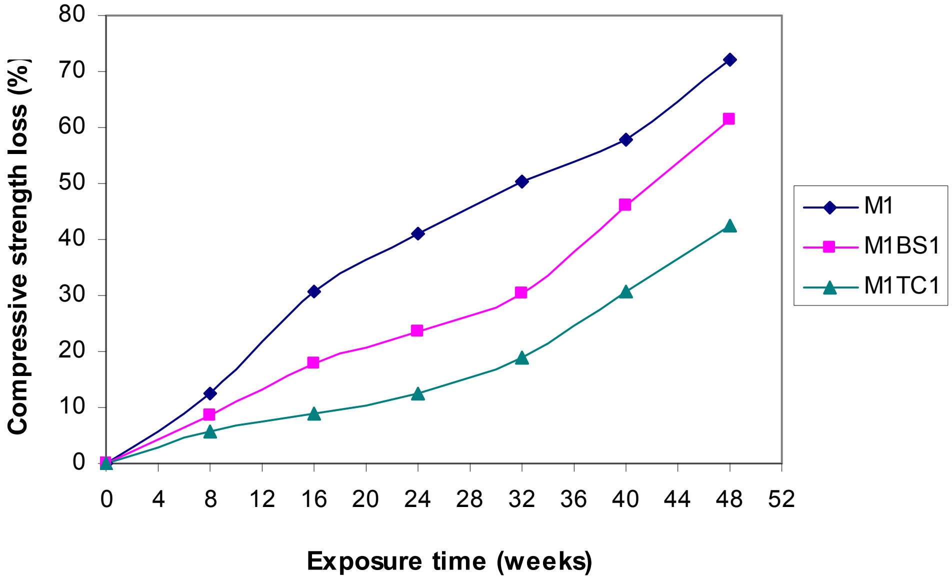


Fig. 5.10. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.45 under sulfuric acid exposure

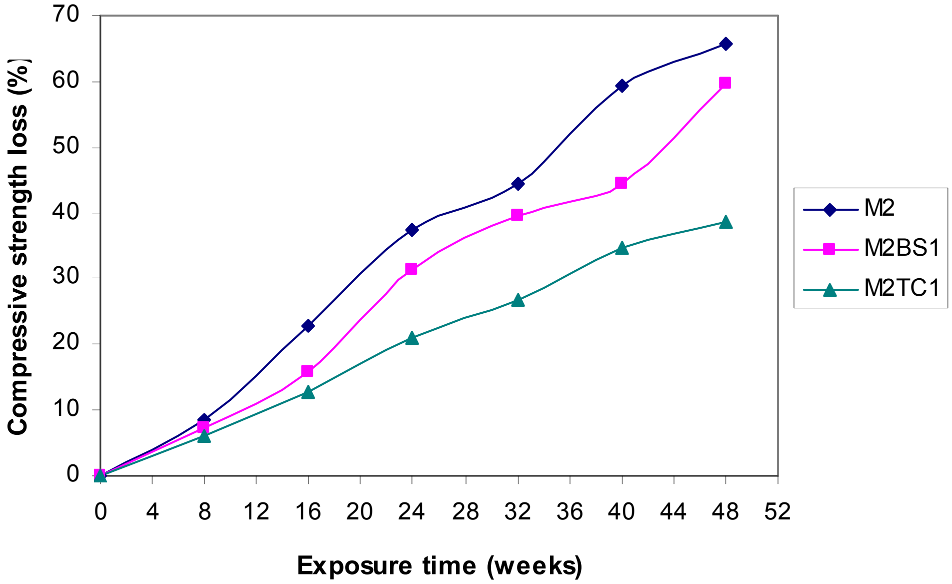


Fig. 5.11. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.35 under sulfuric acid exposure

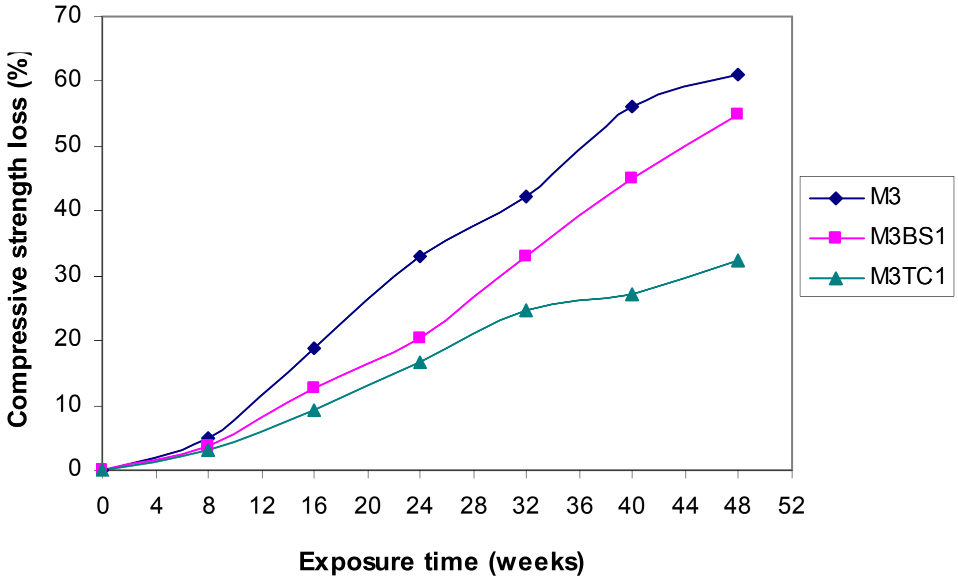


Fig. 5.12. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.25 under sulfuric acid exposure

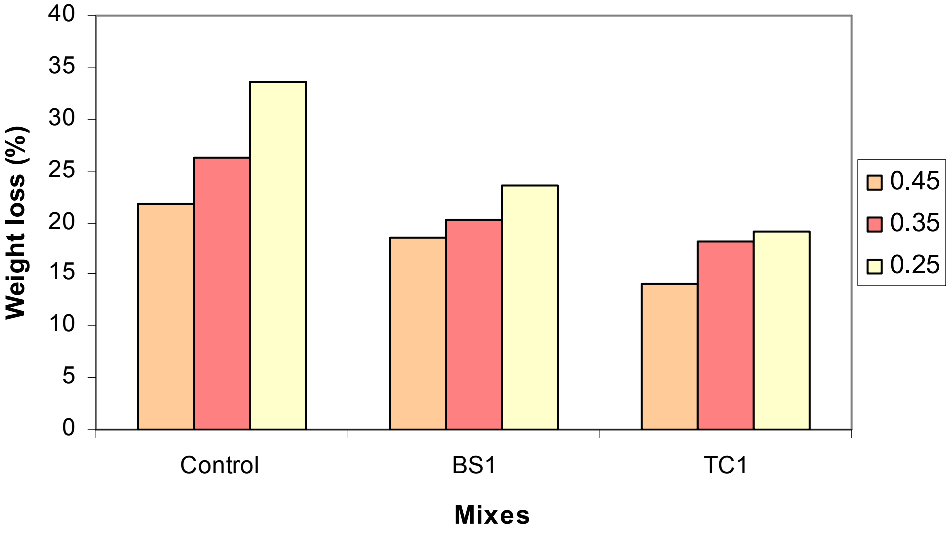


Fig. 5.13. Final weight loss at the end of 48 weeks of all the mixes at different water-to-binder ratios

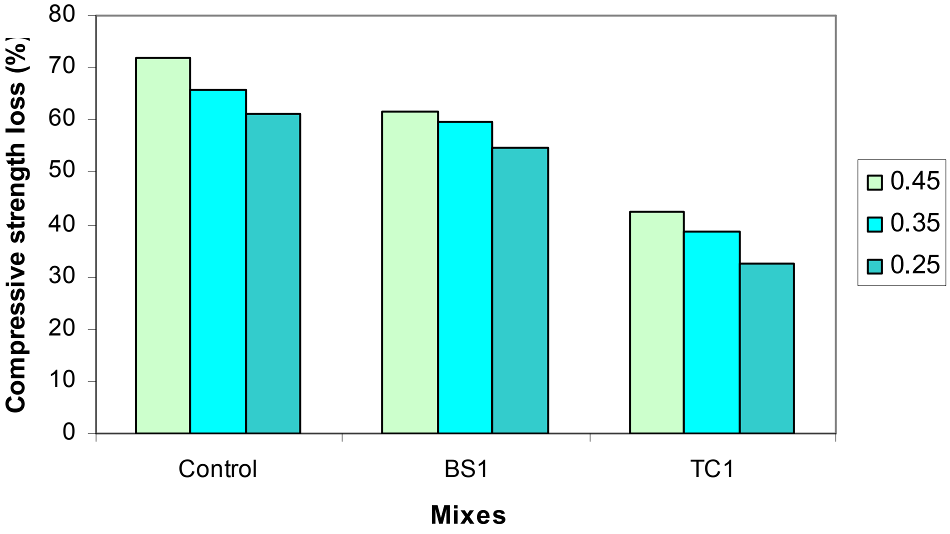


Fig. 5.14. Compressive strength loss of all the mixes at the end of 48 weeks for different water-to-binder ratios

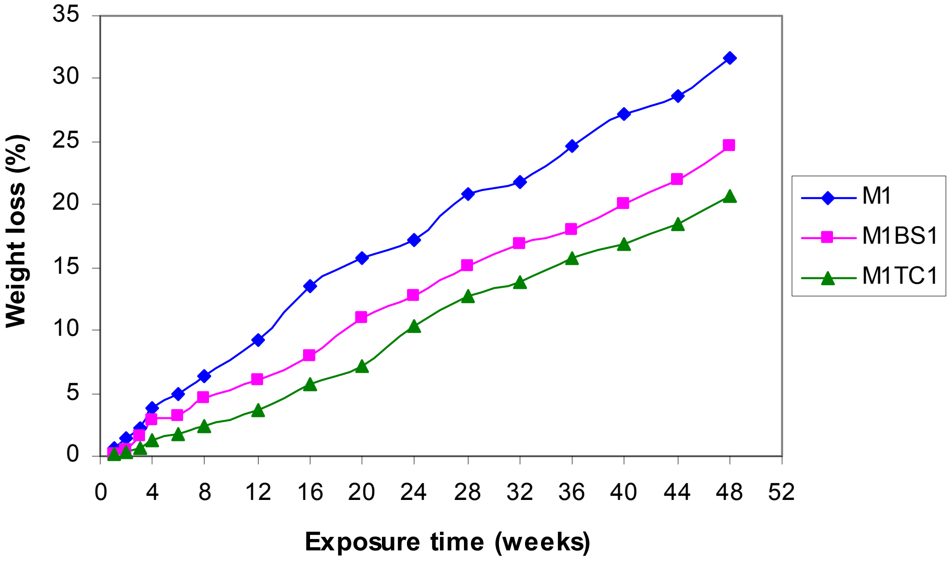


Fig. 5.15. Weight loss of specimens prepared at water-to-binder ratio of 0.45 under hydrochloric acid exposure

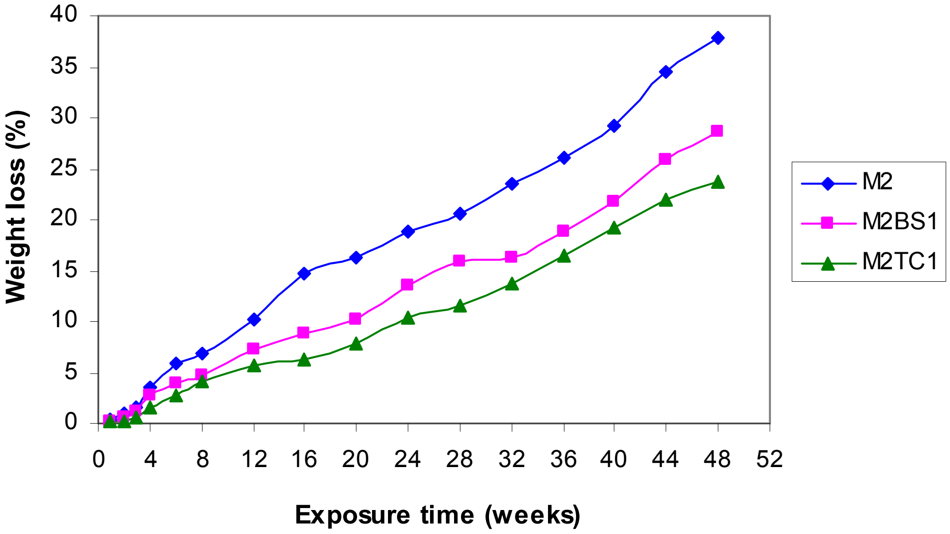


Fig. 5.16. Weight loss of specimens prepared at water-to-binder ratio of 0.35 under hydrochloric acid exposure

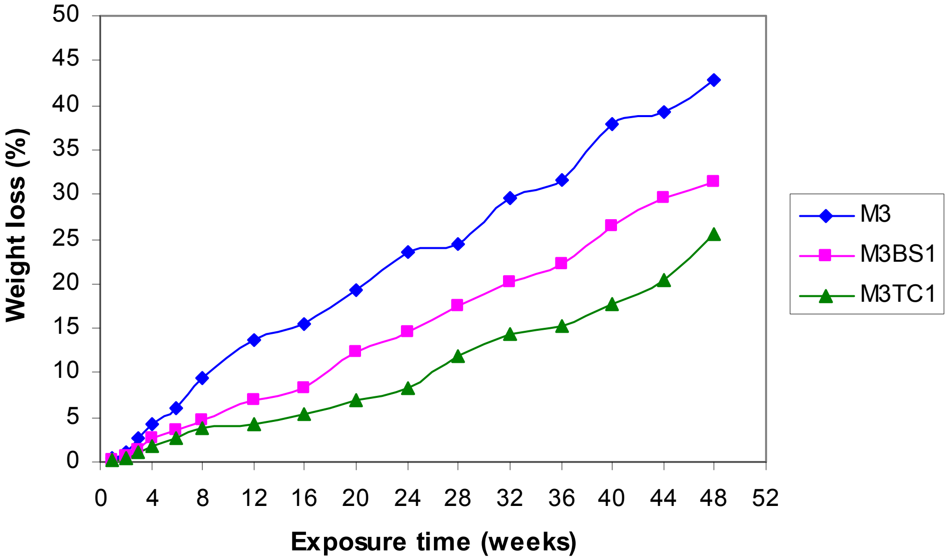


Fig. 5.17. Weight loss of specimens prepared at water-to-binder ratio of 0.25 under hydrochloric acid exposure

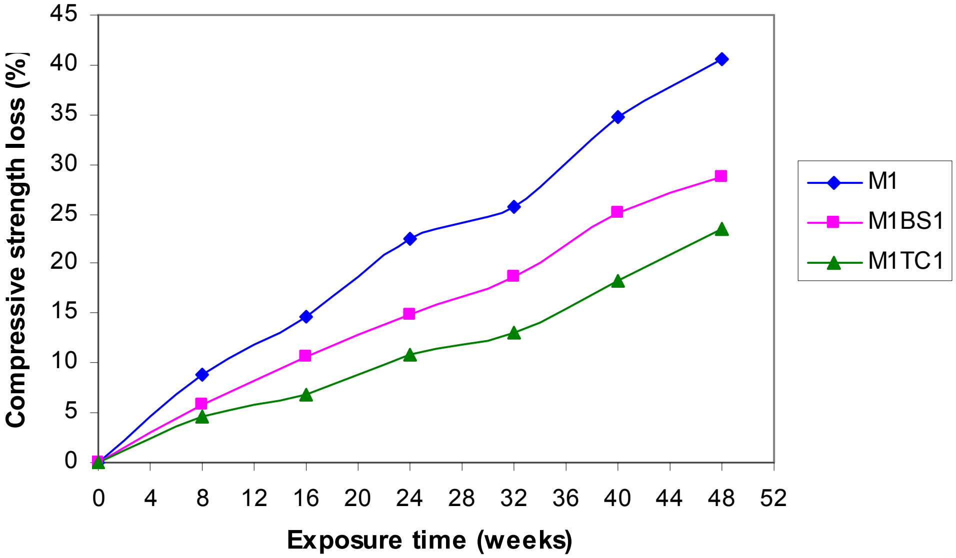


Fig. 5.18. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.45 under hydrochloric acid exposure

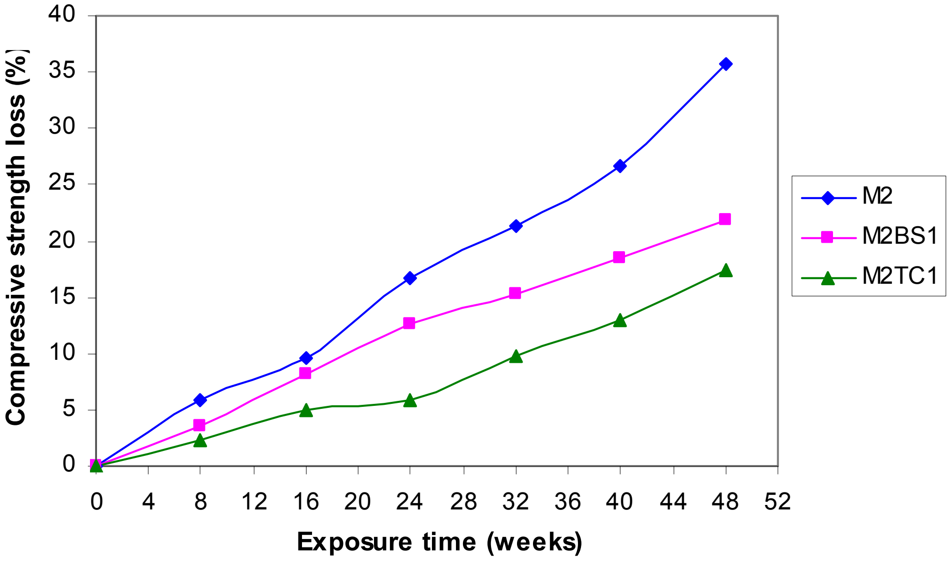


Fig. 5.19. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.45 under hydrochloric acid exposure

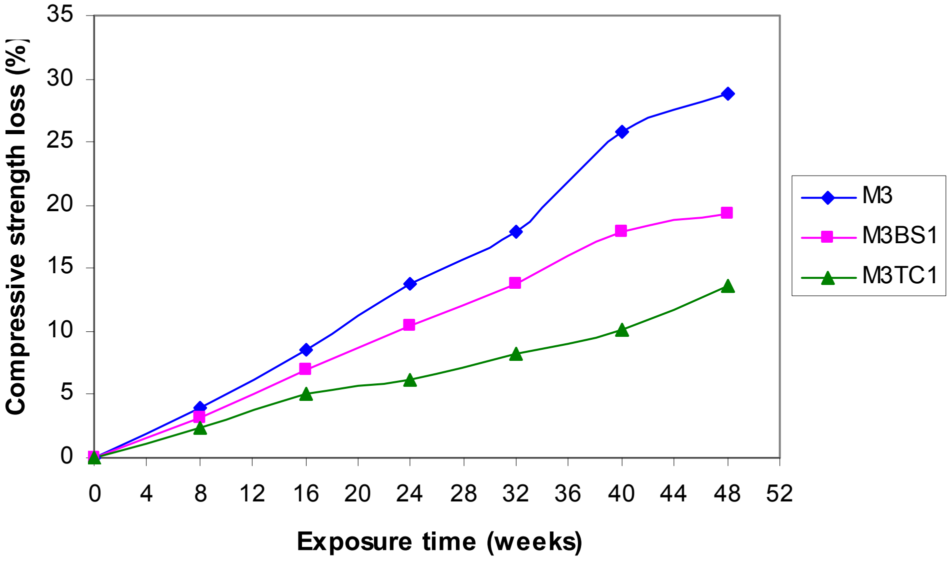


Fig. 5.20. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.45 under hydrochloric acid exposure

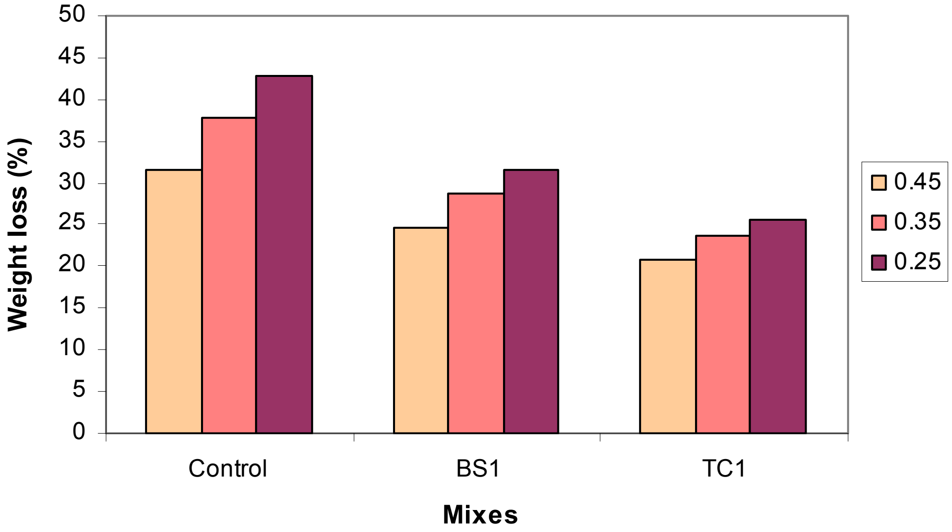


Fig. 5.21. Final weight loss at the end of 48 weeks of all the mixes at different water-to-binder ratios

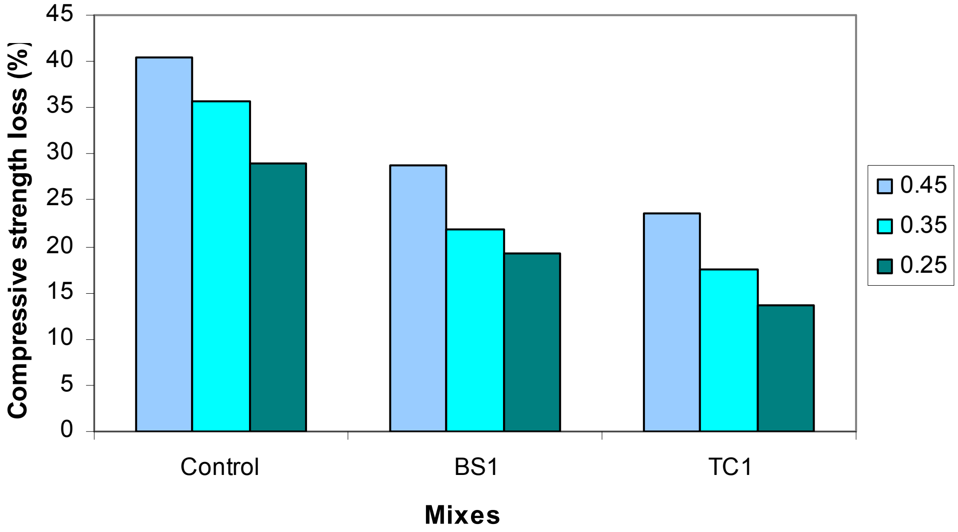


Fig. 5.22. Compressive strength loss of all the mixes at the end of 48 weeks for different water-to-binder ratios

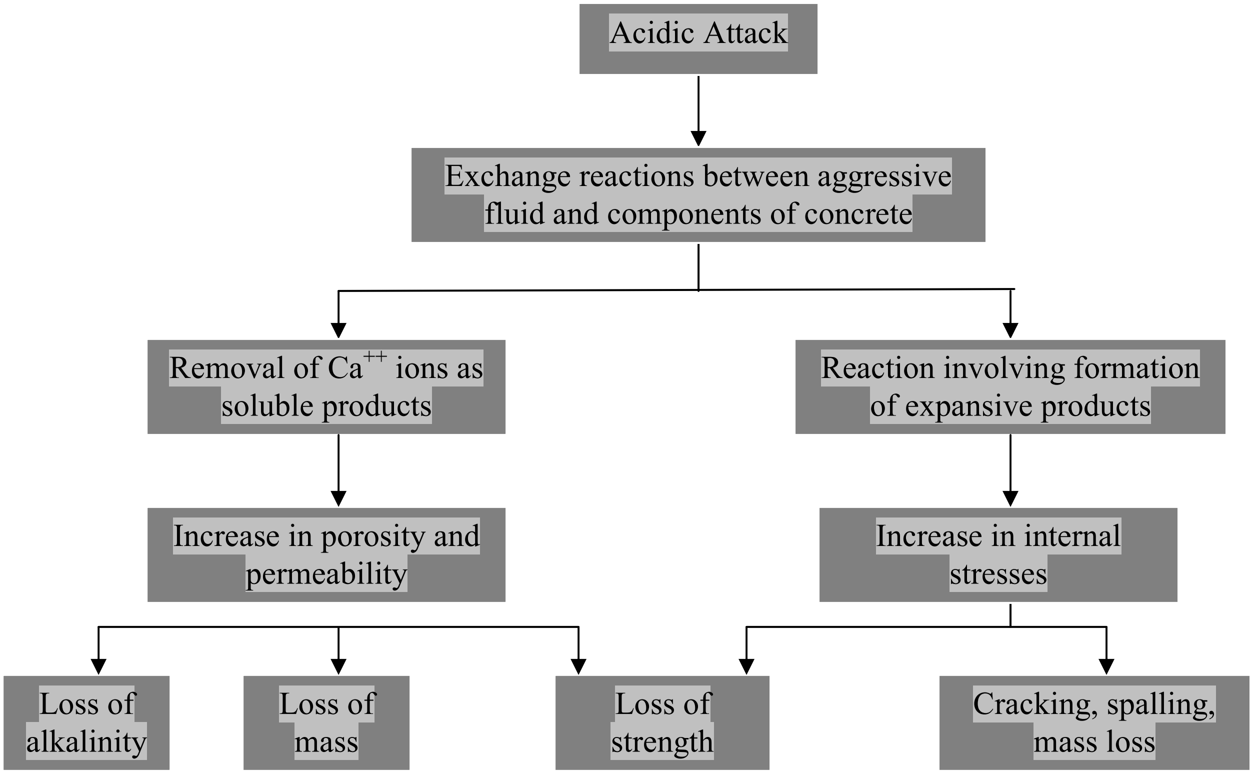


Fig. 5.23. Schematic deterioration mechanism of concrete under acid attack

(Zivica 2001)

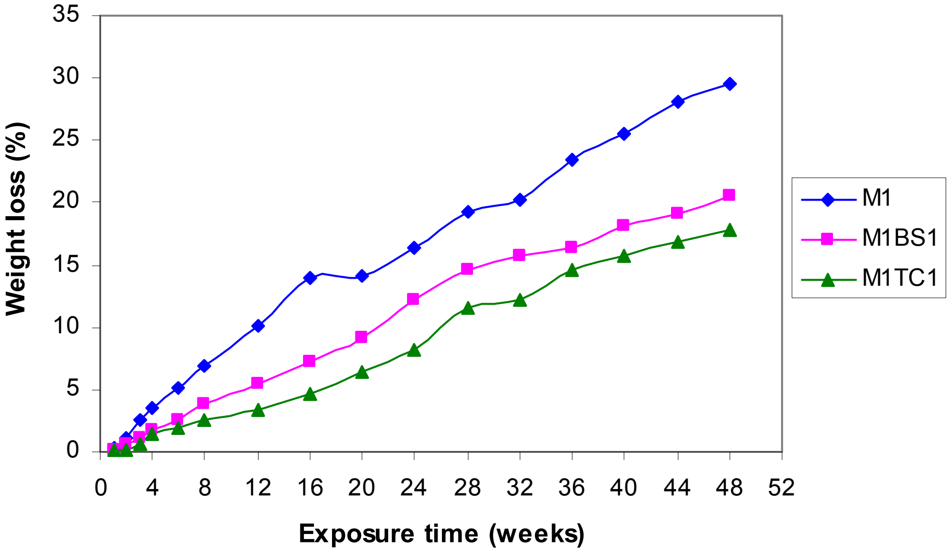


Fig. 5.24. Weight loss of specimens prepared at water-to-binder ratio of 0.45 under nitric acid exposure

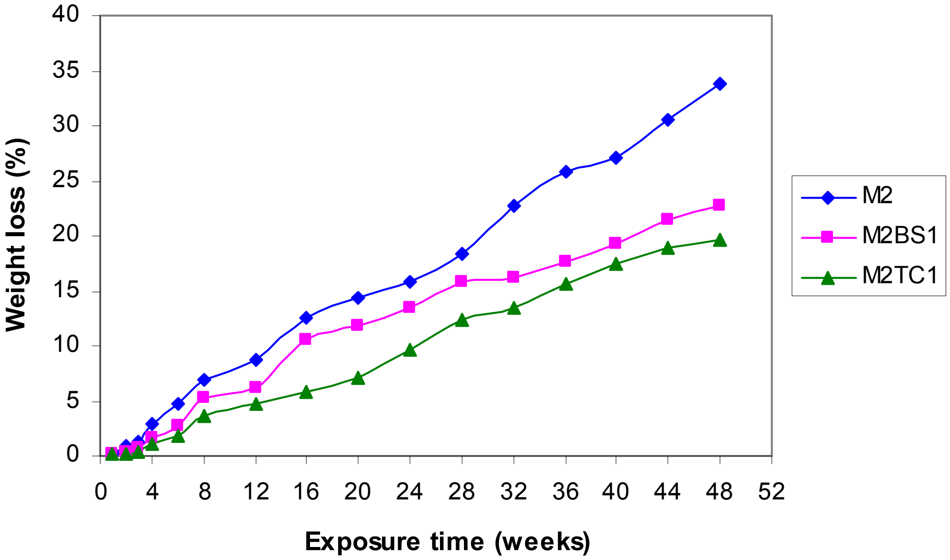


Fig. 5.25. Weight loss of specimens prepared at water-to-binder ratio of 0.35 under nitric acid exposure

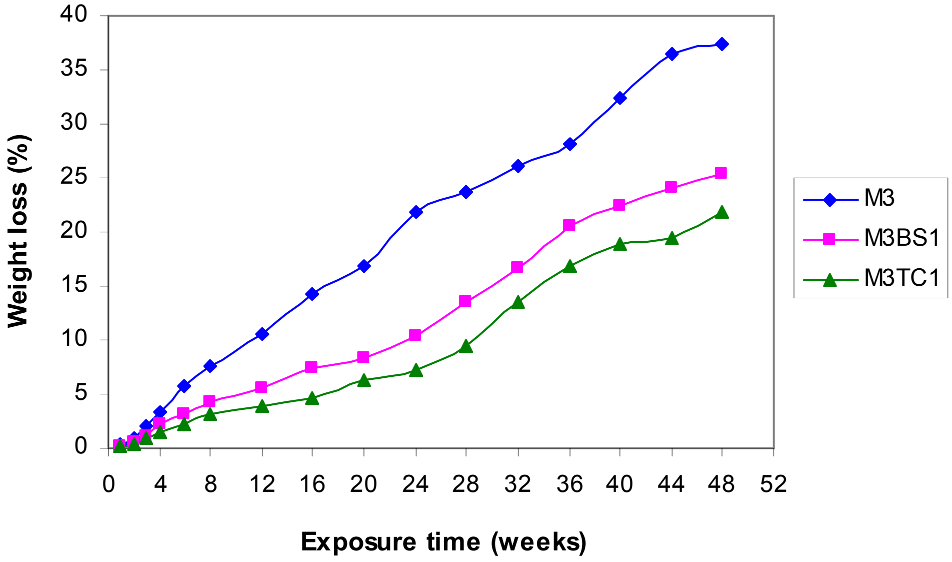


Fig. 5.26. Weight loss of specimens prepared at water-to-binder ratio of 0.25 under nitric acid exposure

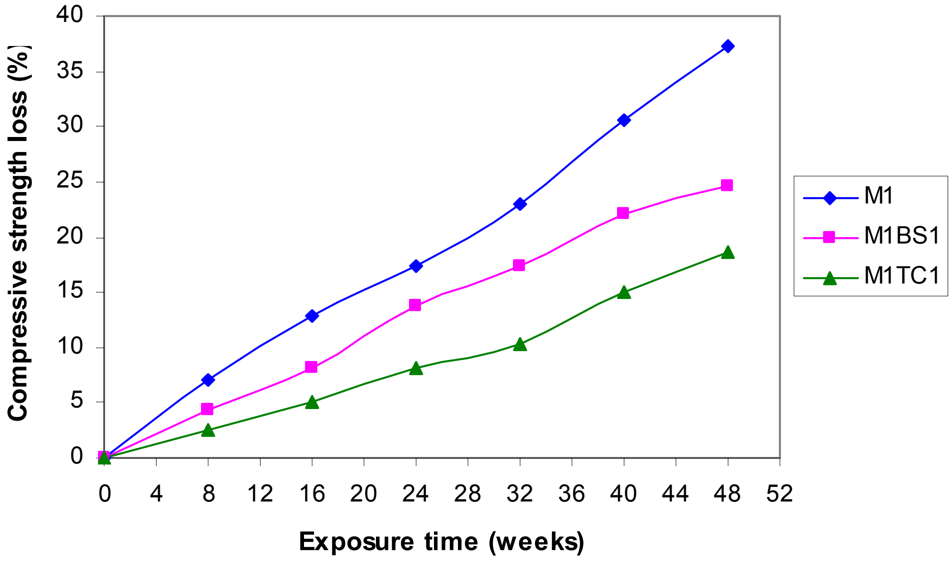


Fig. 5.27. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.45 under nitric acid exposure

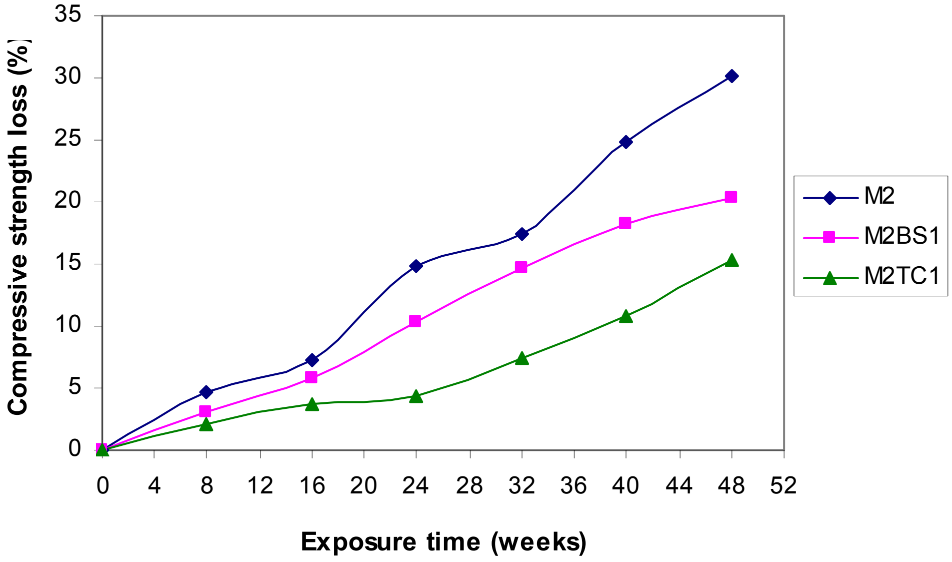


Fig. 5.28. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.35 under nitric acid exposure

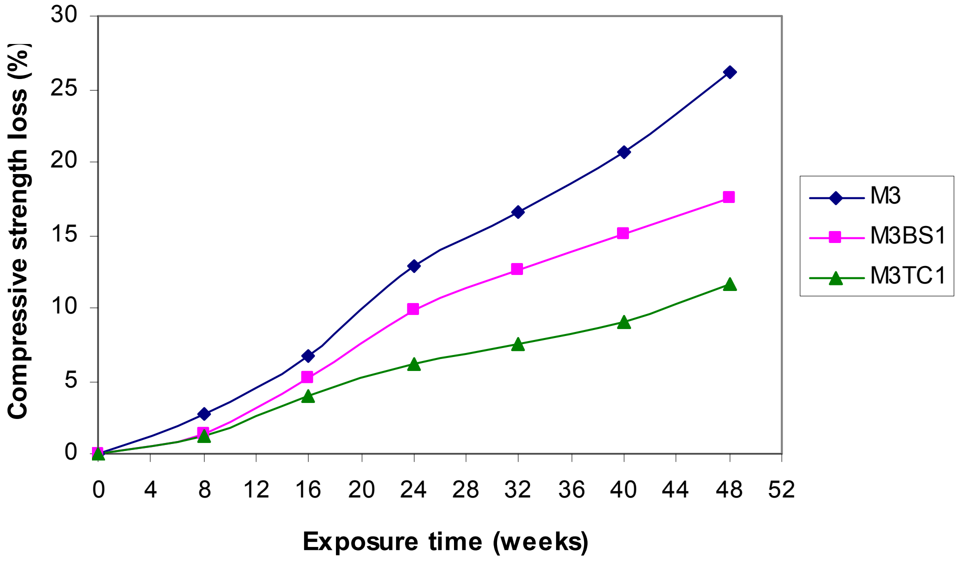


Fig. 5.29. Compressive strength loss of specimens prepared at water-to-binder ratio of 0.25 under nitric acid exposure

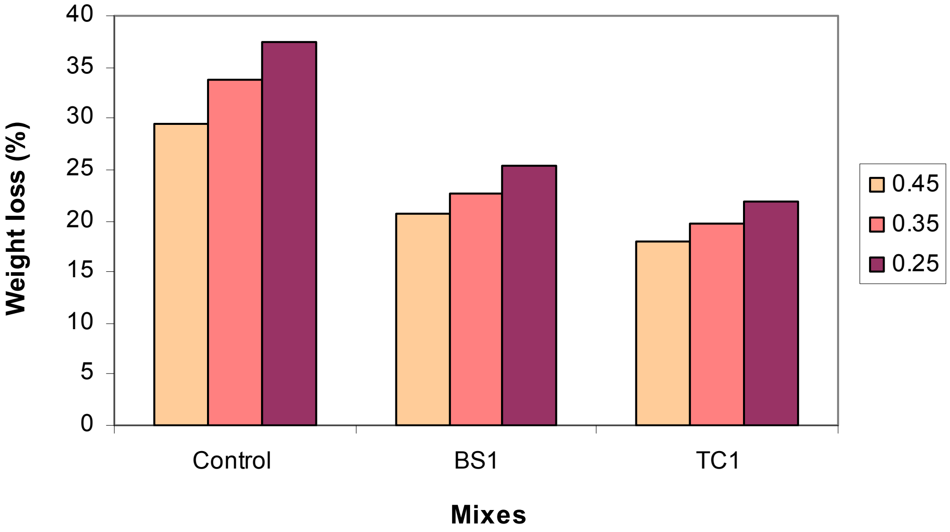


Fig. 5.30. Final weight loss at the end of 48 weeks of all the mixes at different water-to-binder ratios

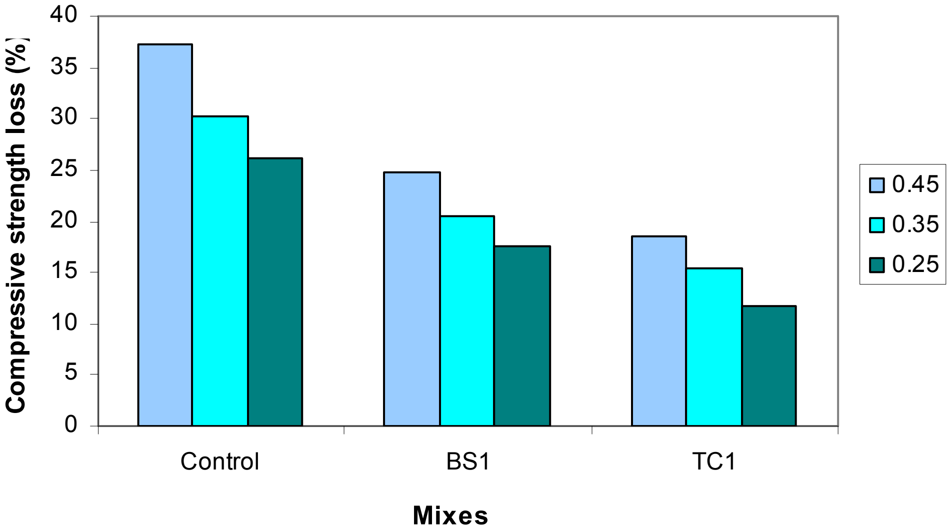


Fig. 5.31. Compressive strength loss of all the mixes at the end of 48 weeks for different water-to-binder ratios

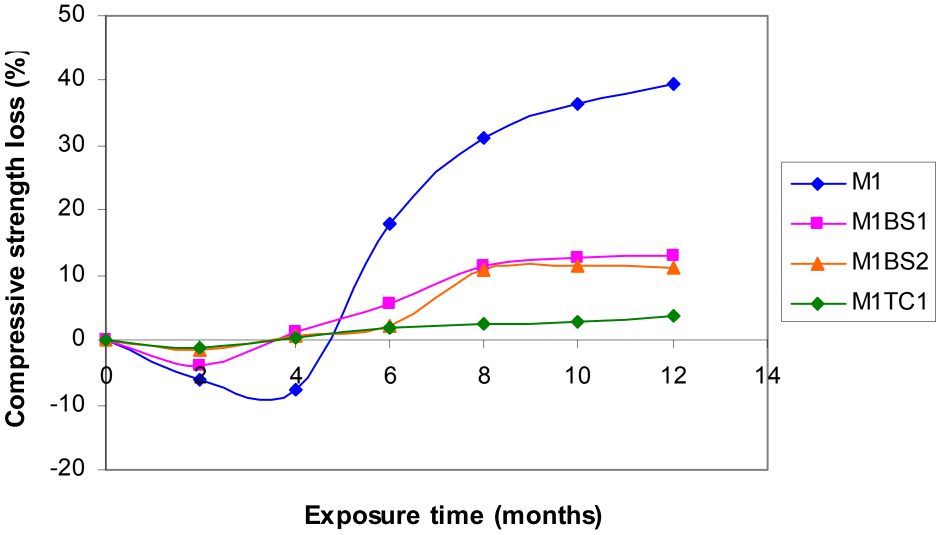


Fig. 5.32. Compressive strength loss of concrete prepared at water-to-binder ratio of 0.45 and subjected to 5% sodium sulfate solution

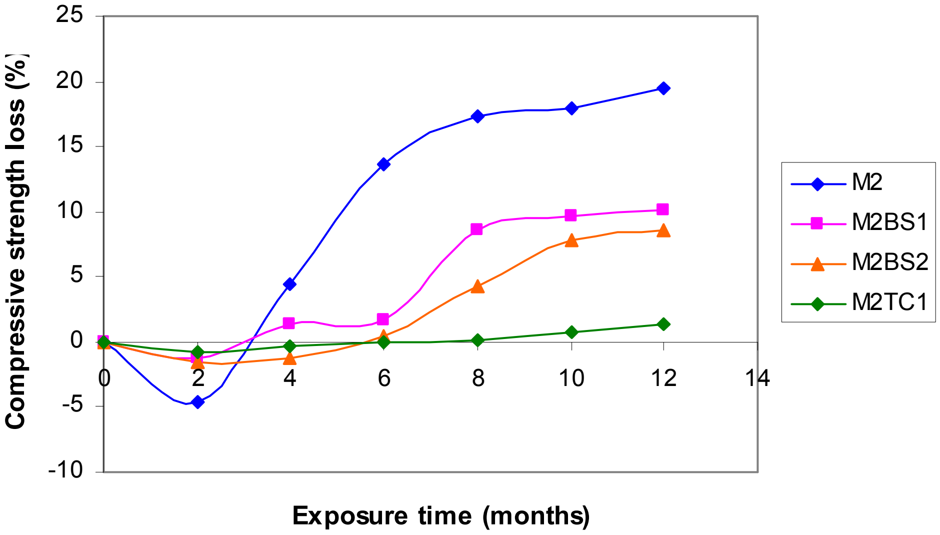


Fig. 5.33. Compressive strength loss of concrete prepared at water-to-binder ratio of 0.35 and subjected to 5% sodium sulfate solution

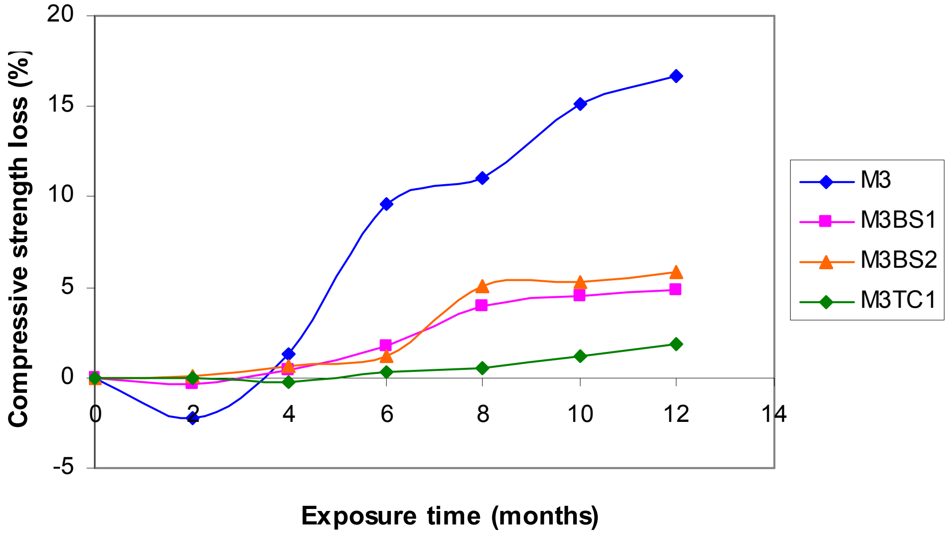


Fig. 5.34. Compressive strength loss of concrete prepared at water-to-binder ratio of 0.25 and subjected to 5% sodium sulfate solution

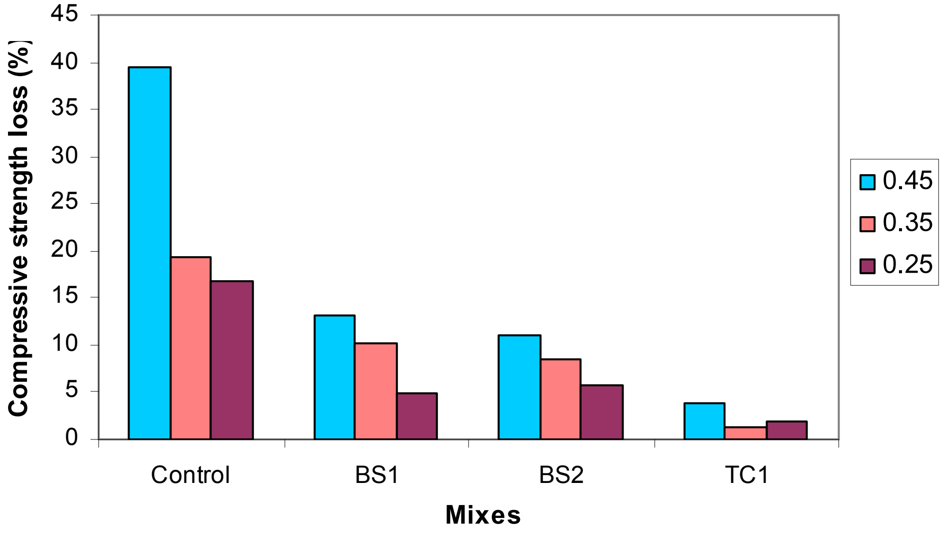


Fig. 5.35. Compressive strength loss of all the mixes at the end of 12 monthly cycles for different water-to-binder ratios

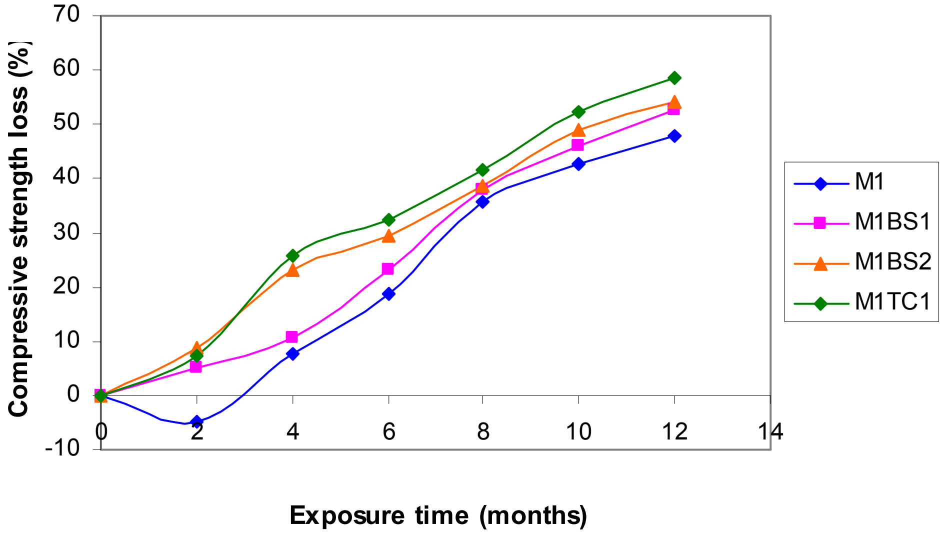


Fig. 5.36. Compressive strength loss of concrete prepared at water-to-binder ratio of 0.45 and subjected to 5% magnesium sulfate solution

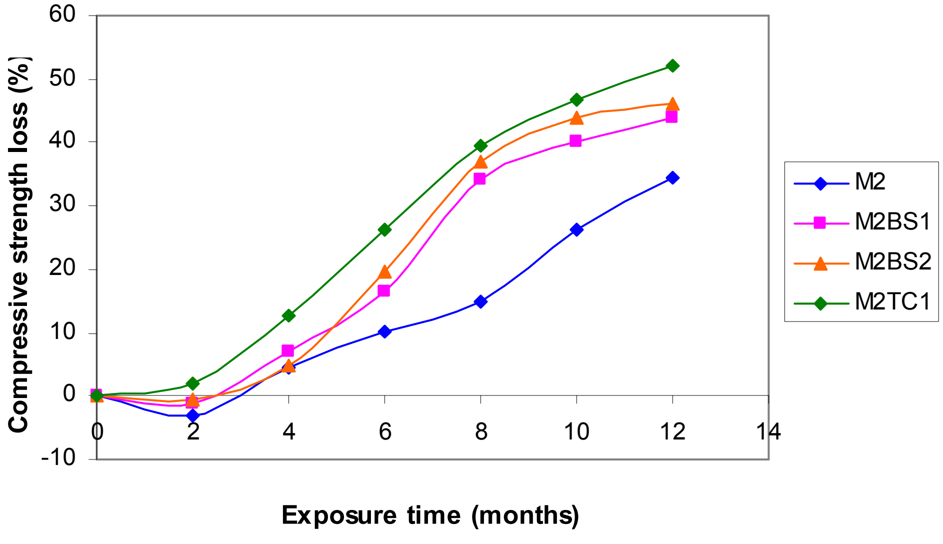


Fig. 5.37. Compressive strength loss of concrete prepared at water-to-binder ratio of 0.35 and subjected to 5% magnesium sulfate solution

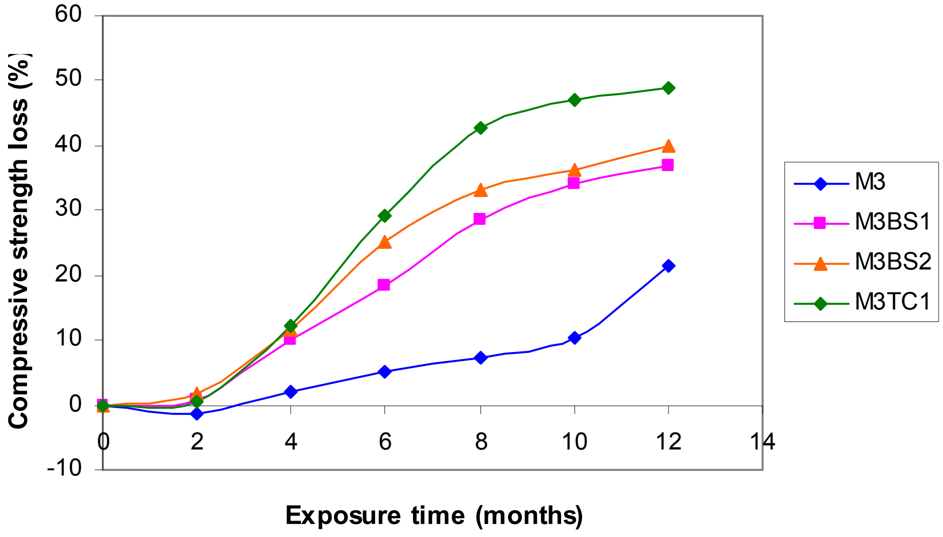


Fig. 5.38. Compressive strength loss of concrete prepared at water-to-binder ratio of 0.25 and subjected to 5% magnesium sulfate solution

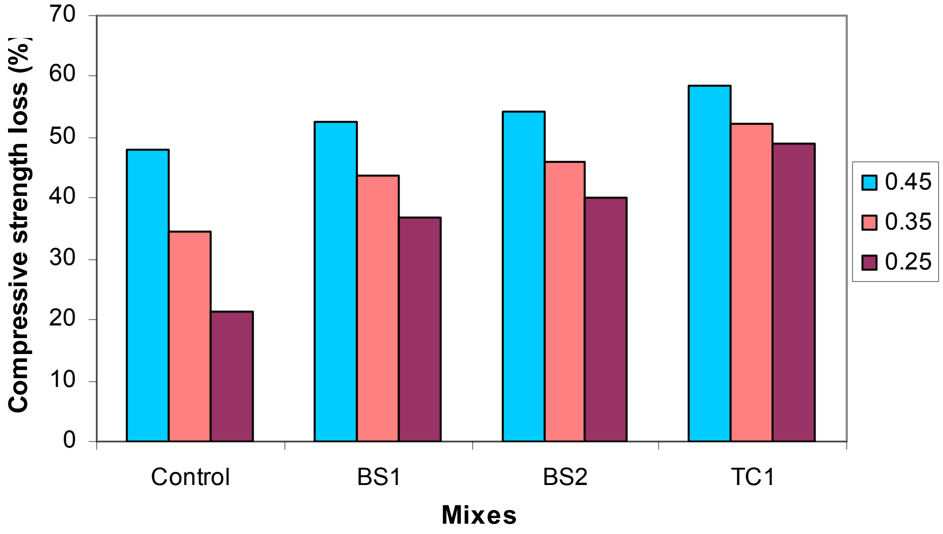


Fig. 5.39. Compressive strength loss of all the mixes at the end of 12 monthly cycles for different water-to-binder ratios

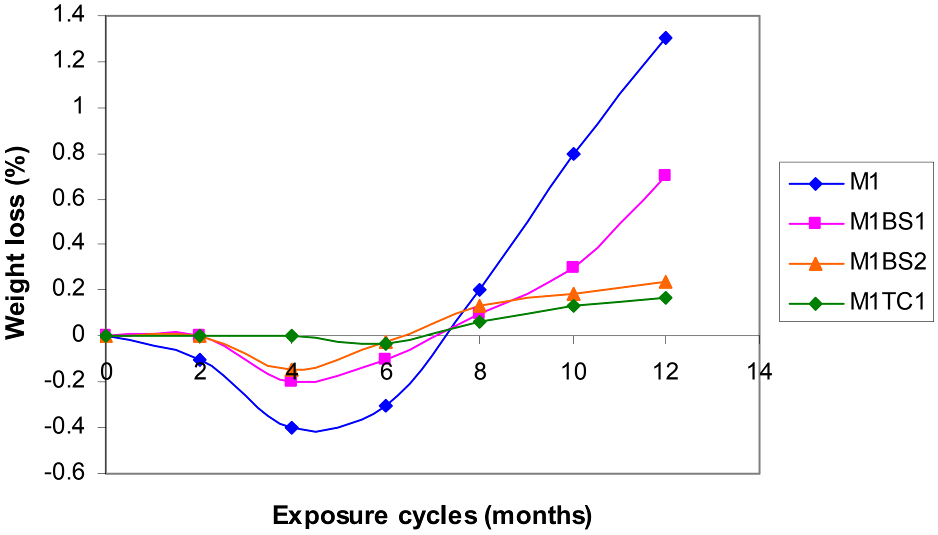


Fig. 5.40. Weight loss of concrete specimens prepared at water-to-binder ratio of 0.45 and subjected to 5% sodium sulfate solution

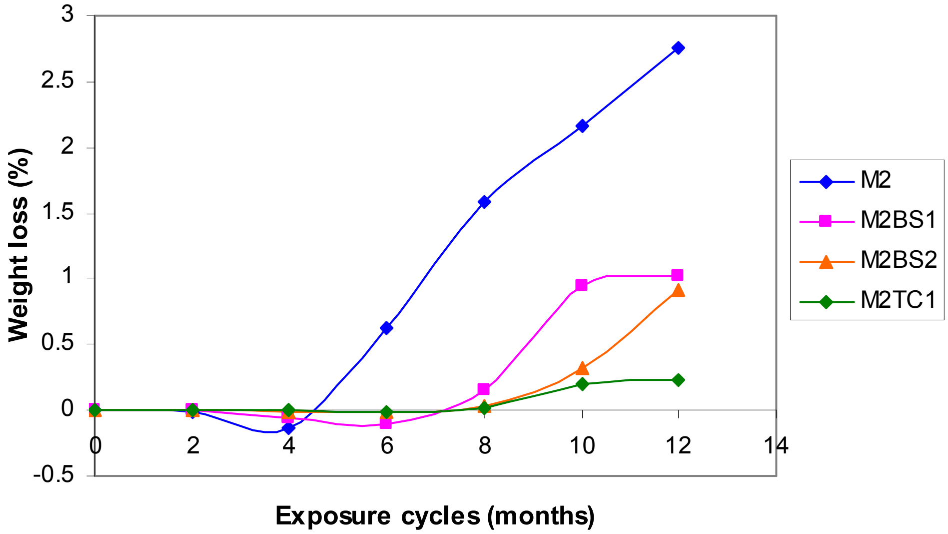


Fig. 5.41. Weight loss of concrete specimens prepared at water-to-binder ratio of 0.35 and subjected to 5% sodium sulfate solution

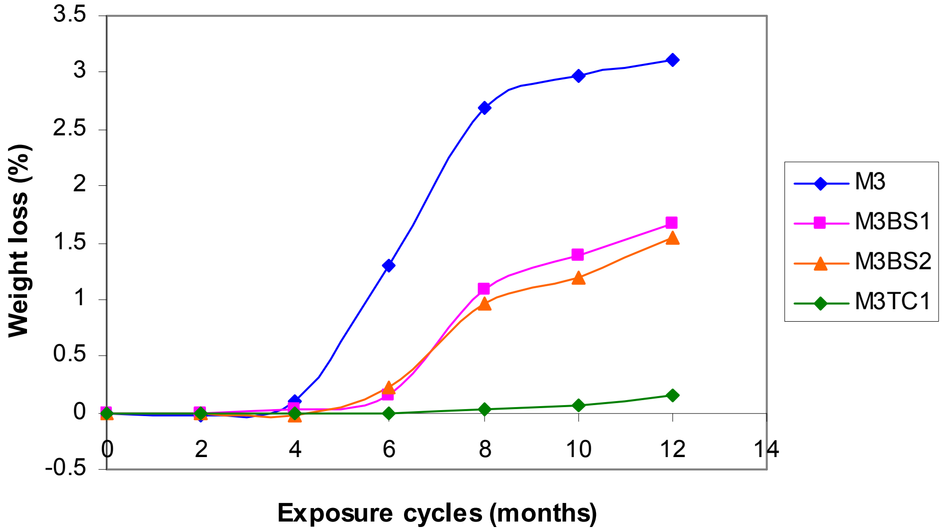


Fig. 5.42. Weight loss of concrete specimens prepared at water-to-binder ratio of 0.25 and subjected to 5% sodium sulfate solution

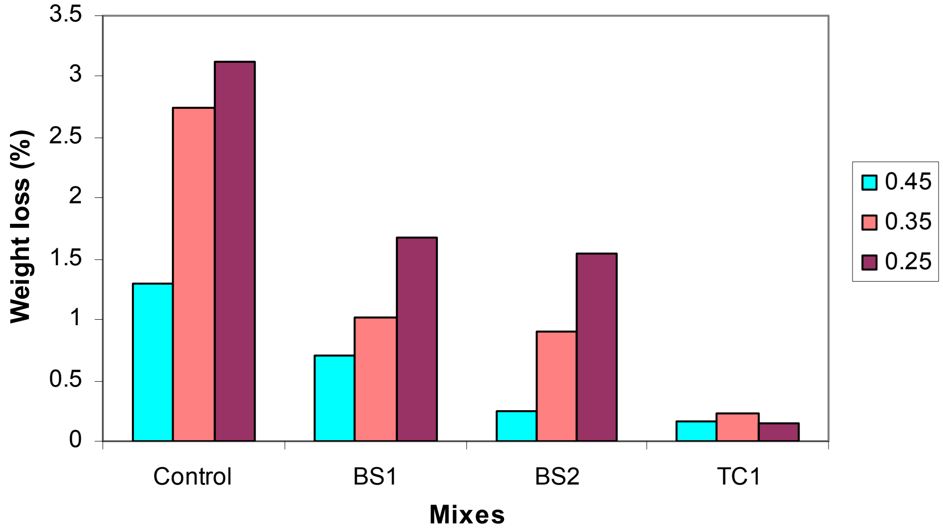


Fig. 5.43. Weight loss of all the mixes at the end of 12 monthly cycles for different water-to-binder ratios under sodium sulfate exposure

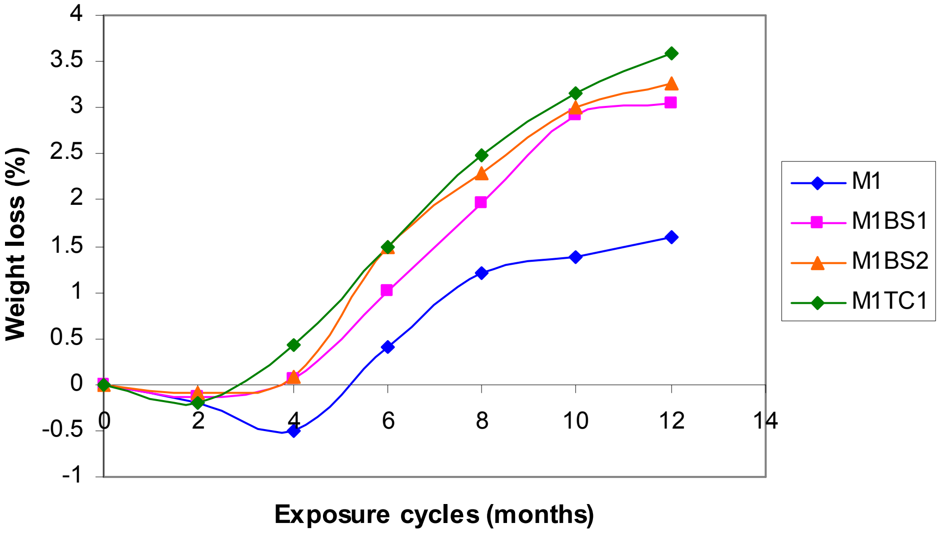


Fig. 5.44. Weight loss of concrete specimens prepared at water-to-binder ratio of 0.45 and subjected to 5% magnesium sulfate solution

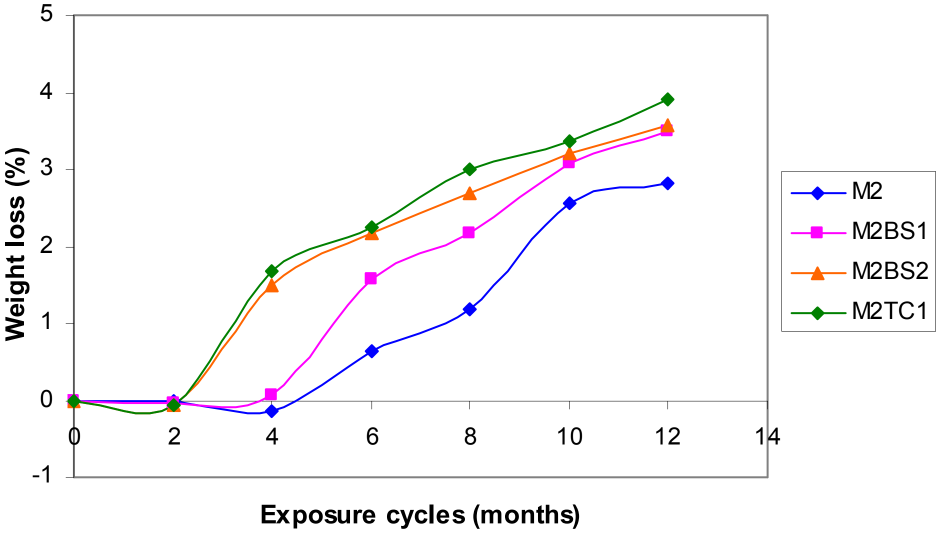


Fig. 5.45. Weight loss of concrete specimens prepared at water-to-binder ratio of 0.35 and subjected to 5% magnesium sulfate solution

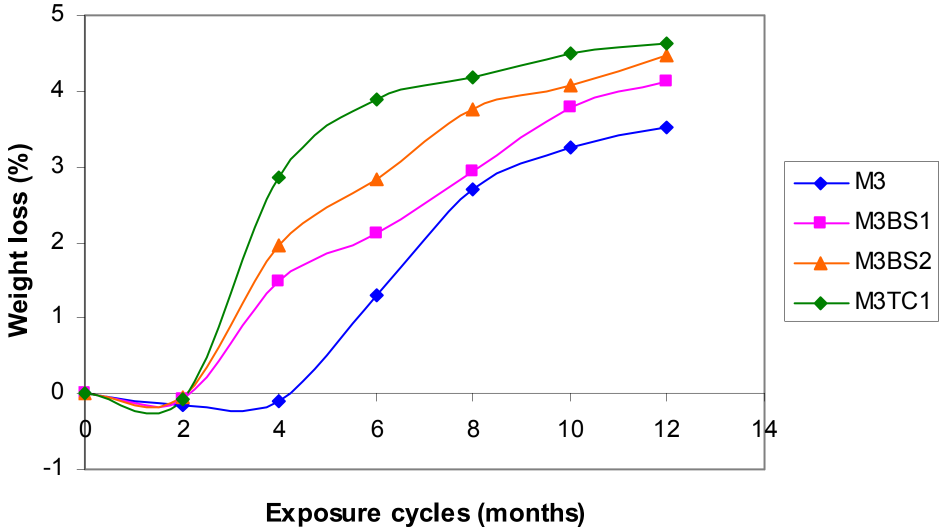


Fig. 5.46. Weight loss of concrete specimens prepared at water-to-binder ratio of 0.25 and subjected to 5% magnesium sulfate solution

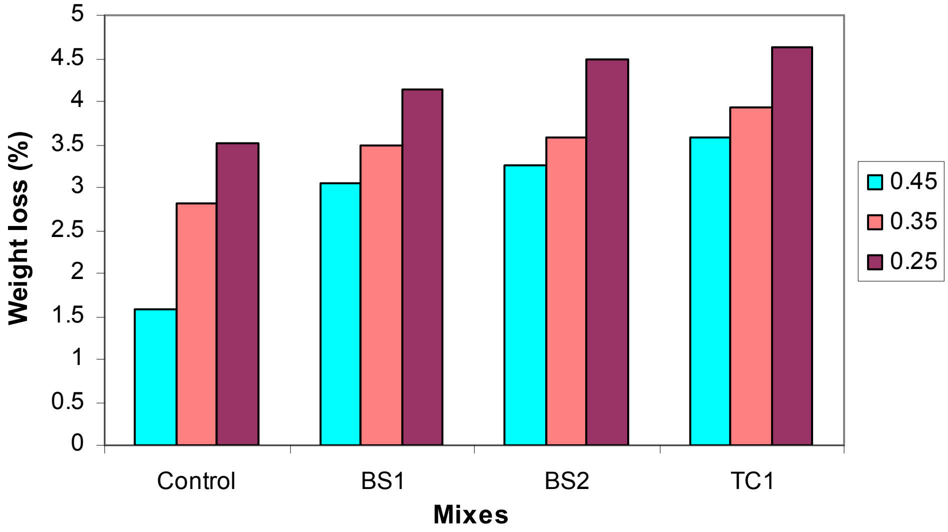


Fig. 5.47. Weight loss of all the mixes at the end of 12 monthly cycles for different water-to-binder ratios under magnesium sulfate exposure

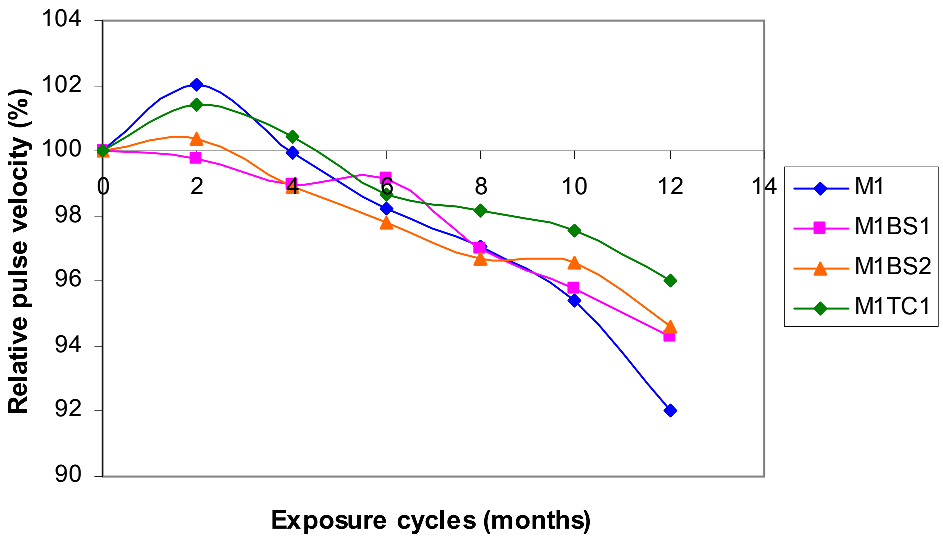


Fig. 5.48. Relative pulse velocity of concrete specimens prepared at water-to-binder ratio of 0.45 and subjected to 5% sodium sulfate solution

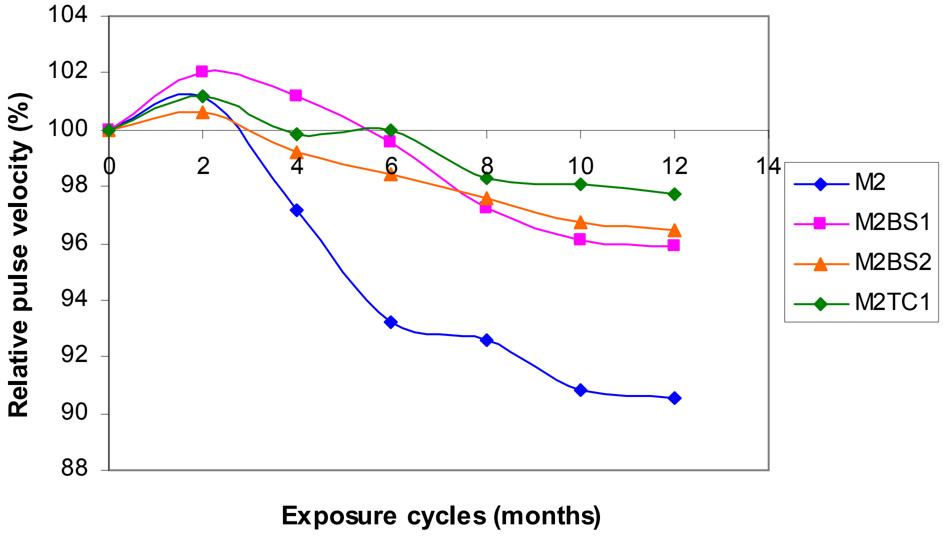


Fig. 5.49. Relative pulse velocity of concrete specimens prepared at water-to-binder ratio of 0.35 and subjected to 5% sodium sulfate solution

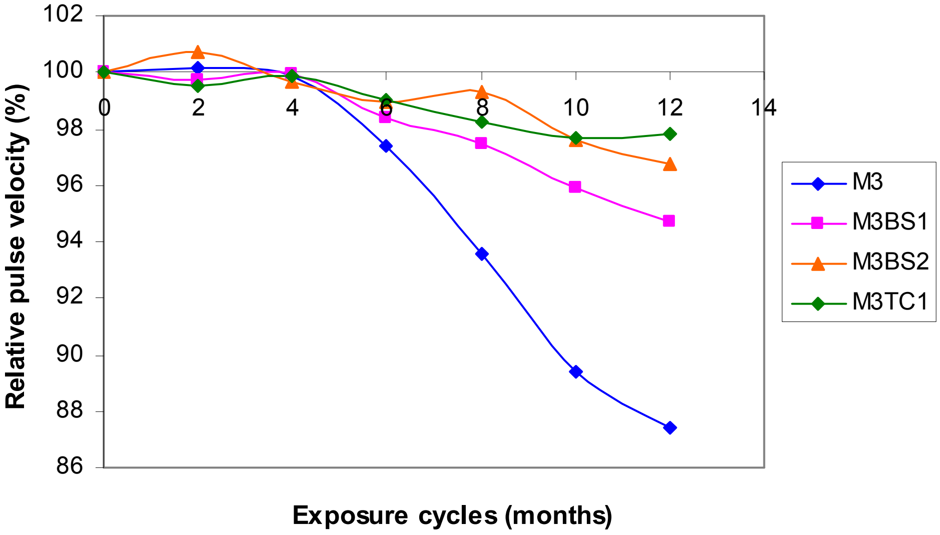


Fig. 5.50. Relative pulse velocity of concrete specimens prepared at water-to-binder ratio of 0.25 and subjected to 5% sodium sulfate solution

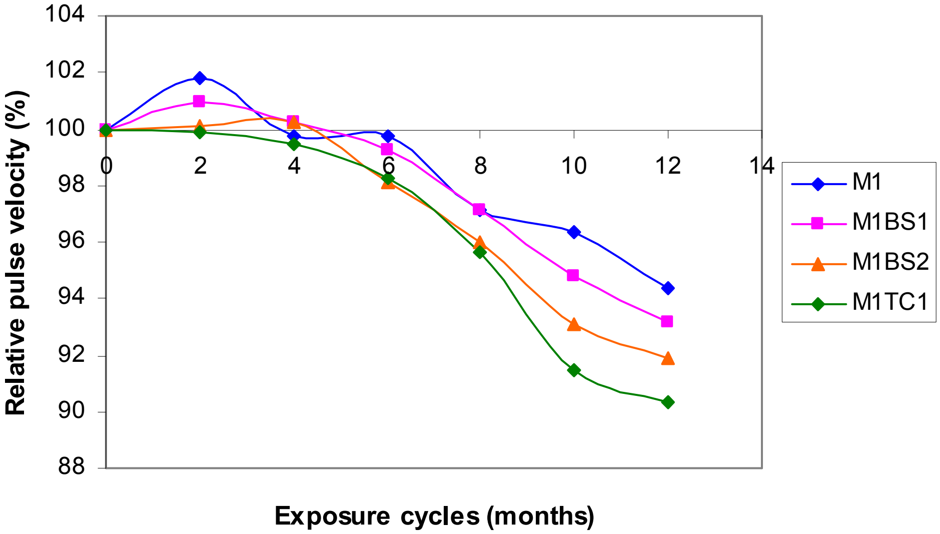


Fig. 5.51. Relative pulse velocity of concrete specimens prepared at water-to-binder ratio of 0.45 and subjected to 5% magnesium sulfate solution

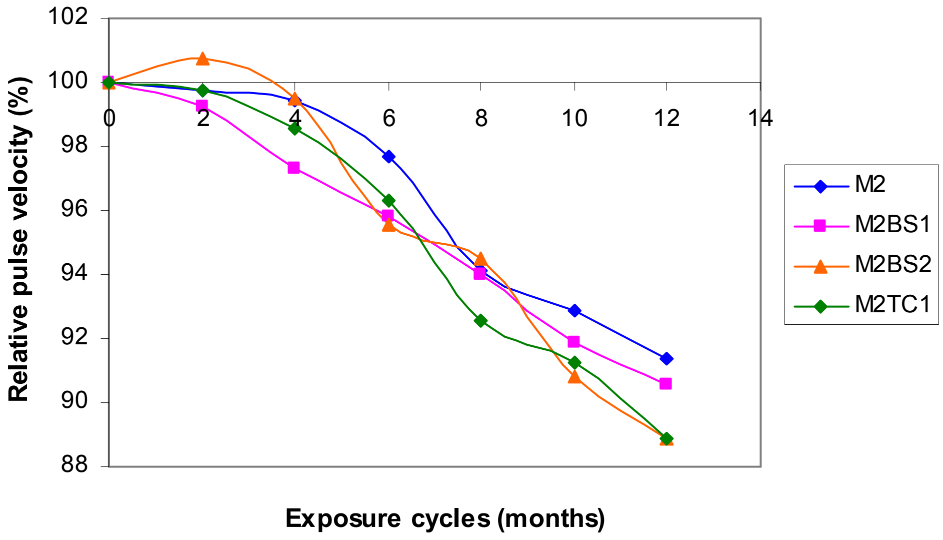


Fig. 5.52. Relative pulse velocity of concrete specimens prepared at water-to-binder ratio of 0.35 and subjected to 5% magnesium sulfate solution

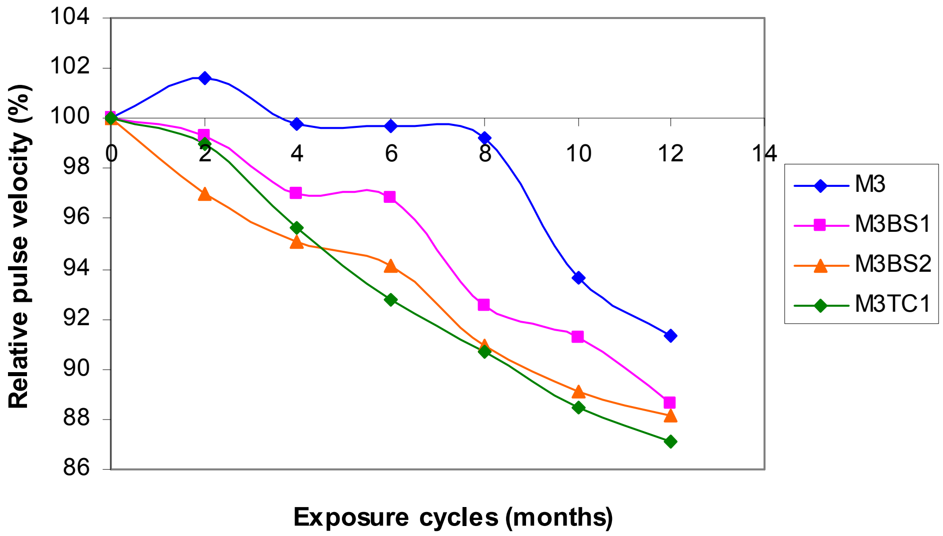


Fig. 5.53. Relative pulse velocity of concrete specimens prepared at water-to-binder ratio of 0.25 and subjected to 5% magnesium sulfate solution

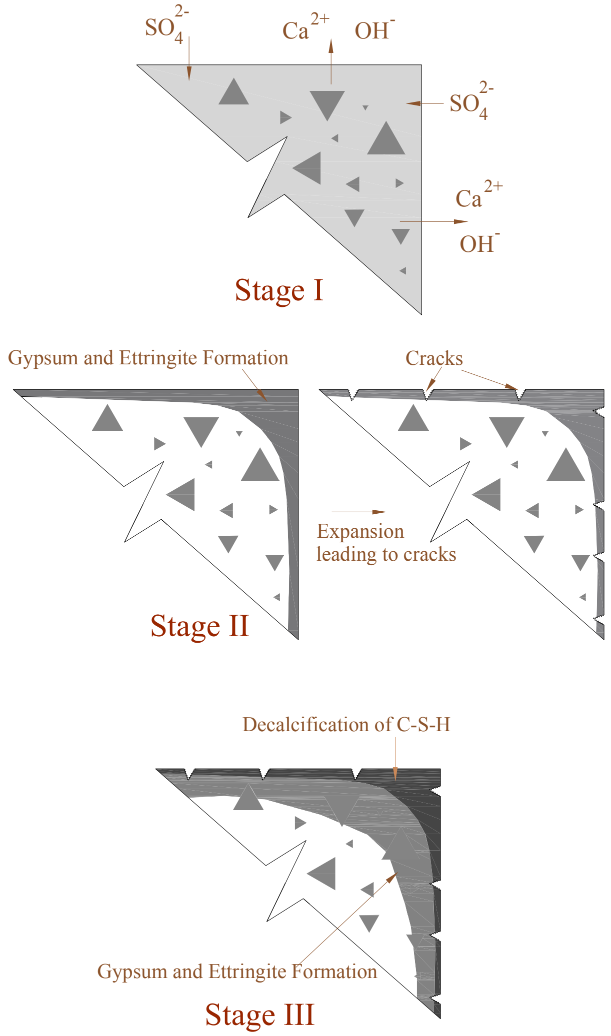


Fig. 5.54. Mechanism of sodium sulfate attack

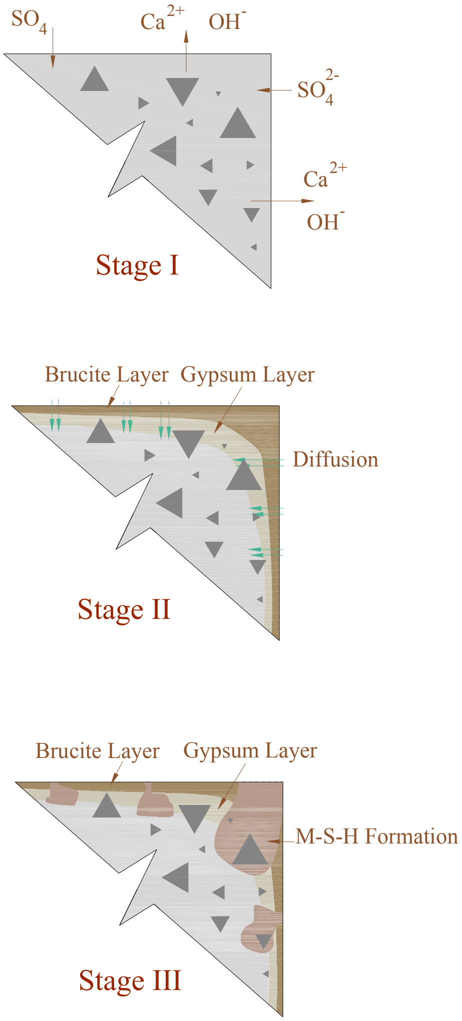
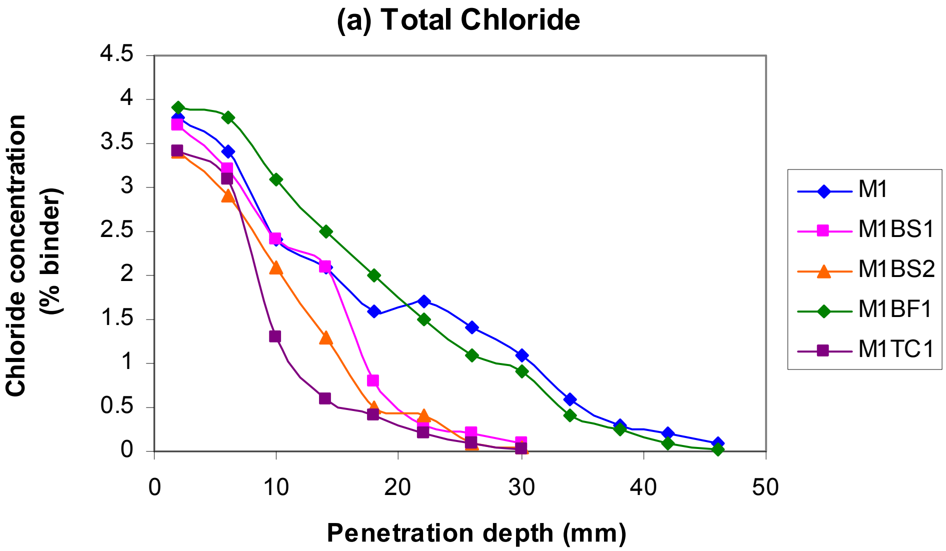


Fig. 5.55. Mechanism of magnesium sulfate attack



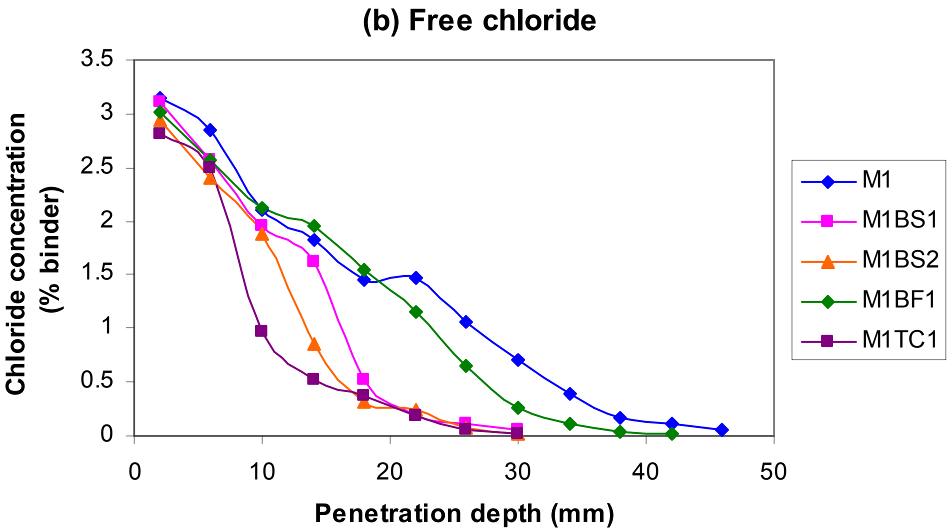
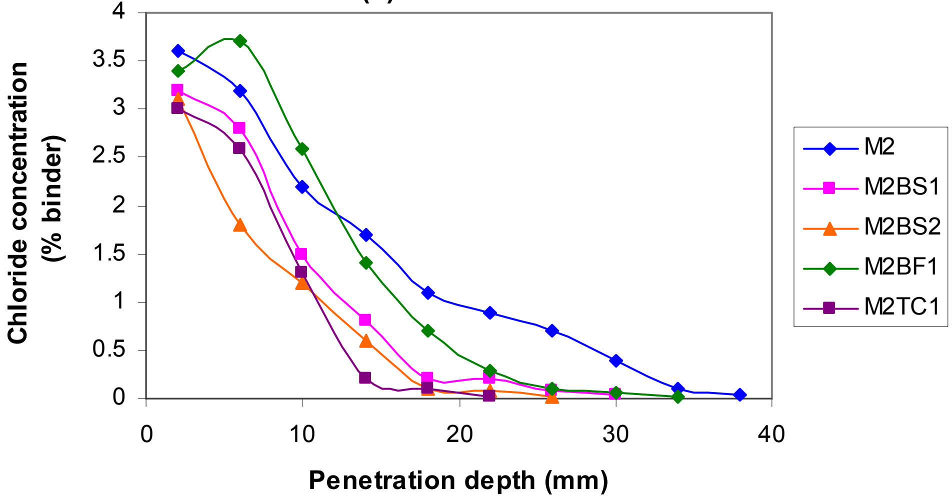
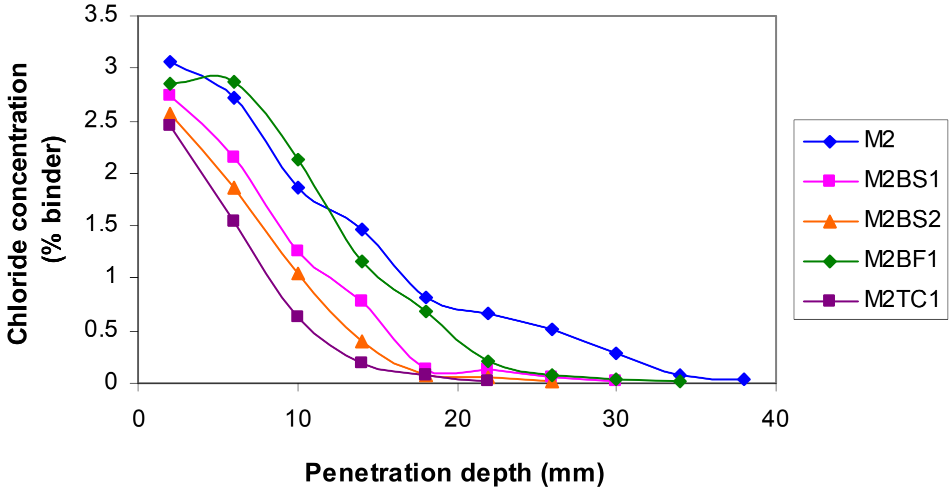


Fig. 5.56. Chloride penetration profiles of specimens prepared at water-to-binder ratio of 0.45 and exposed to 5% sodium chloride solution

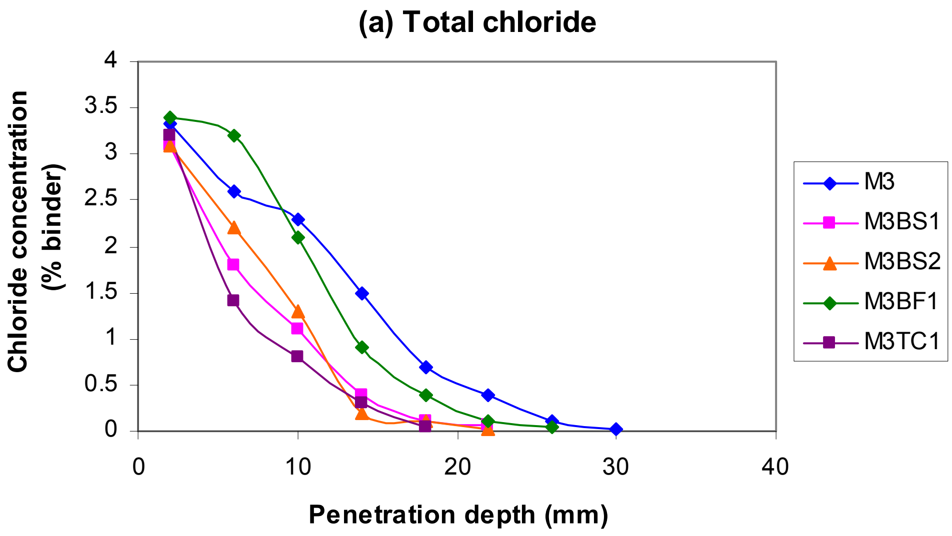


(a) Total chloride



(b) Free chloride

Fig. 5.57. Chloride penetration profiles of specimens prepared at water-to-binder ratio of 0.35 and exposed to 5% sodium chloride solution


(a) Total chloride

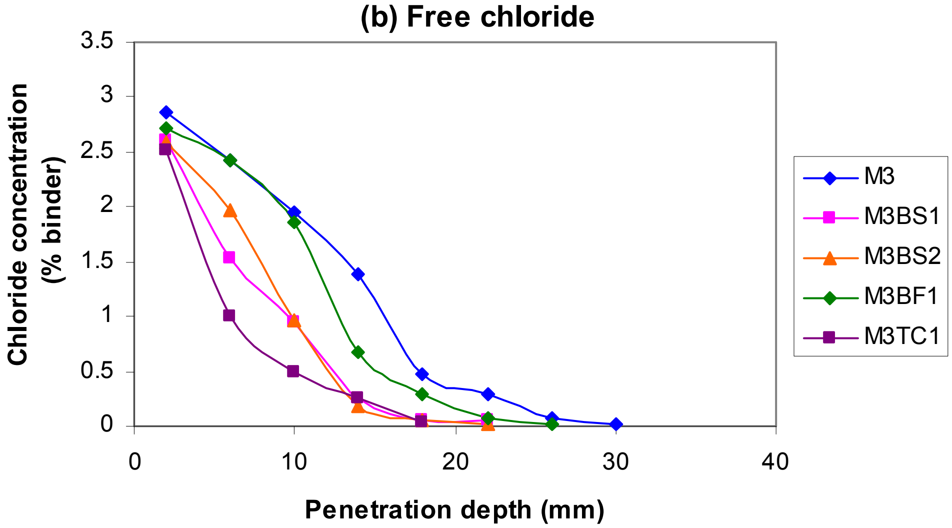
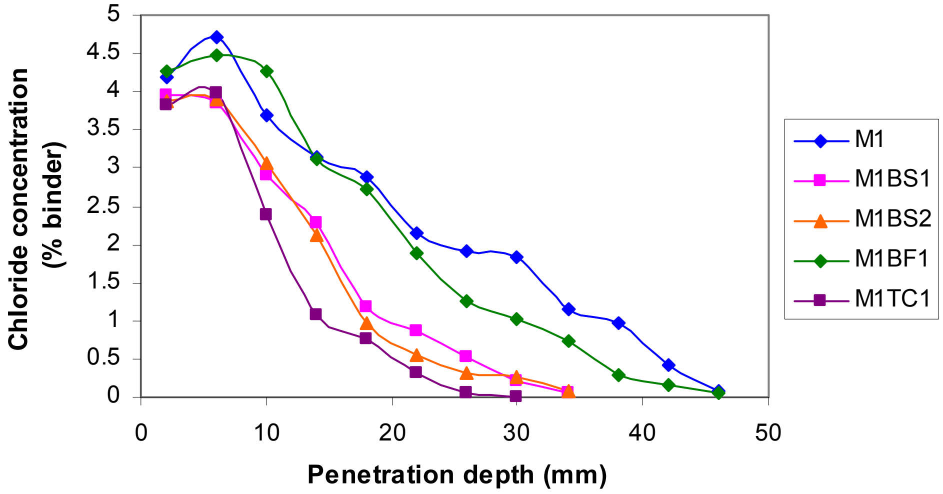
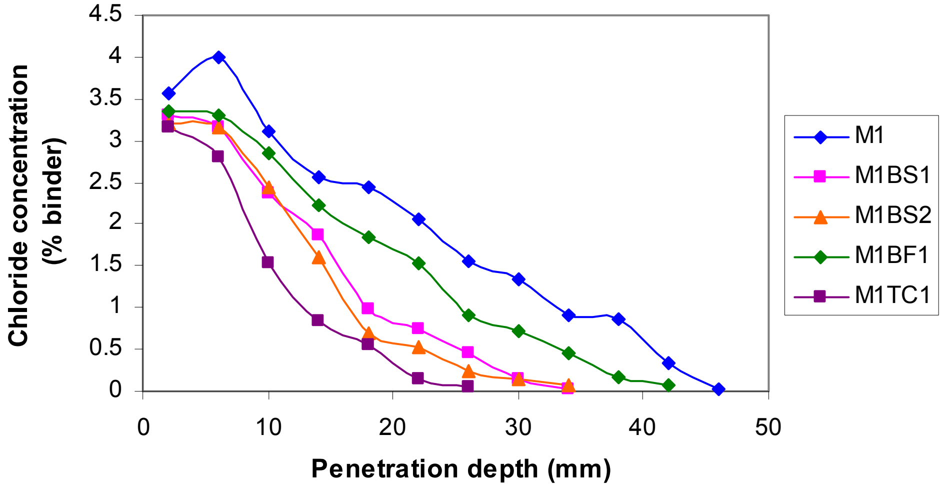

(b) Free chloride

Fig. 5.58. Chloride penetration profiles of specimens prepared at water-to-binder ratio of 0.25 and exposed to 5% sodium chloride solution

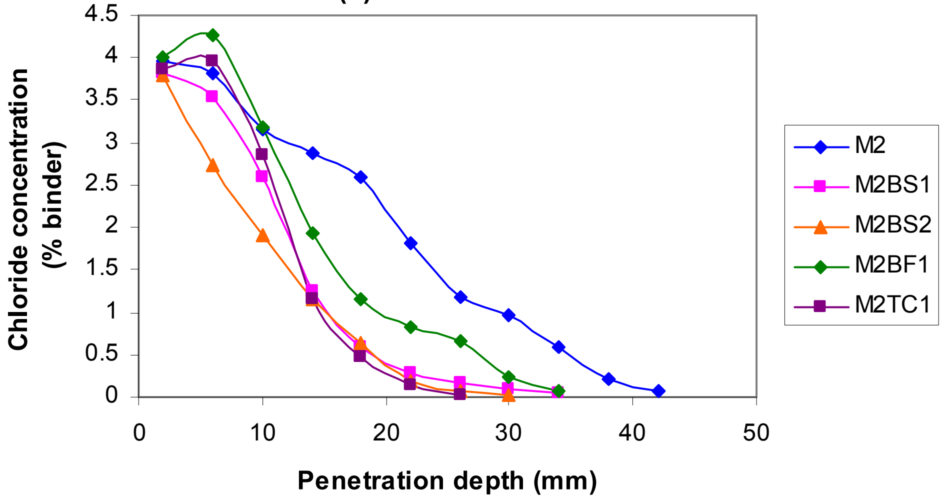


(a) Total chloride



(b) Free chloride

Fig. 5.59. Chloride penetration profiles of specimens prepared at water-to-binder ratio of 0.45 and exposed to 5% calcium chloride solution


(a) Total chloride

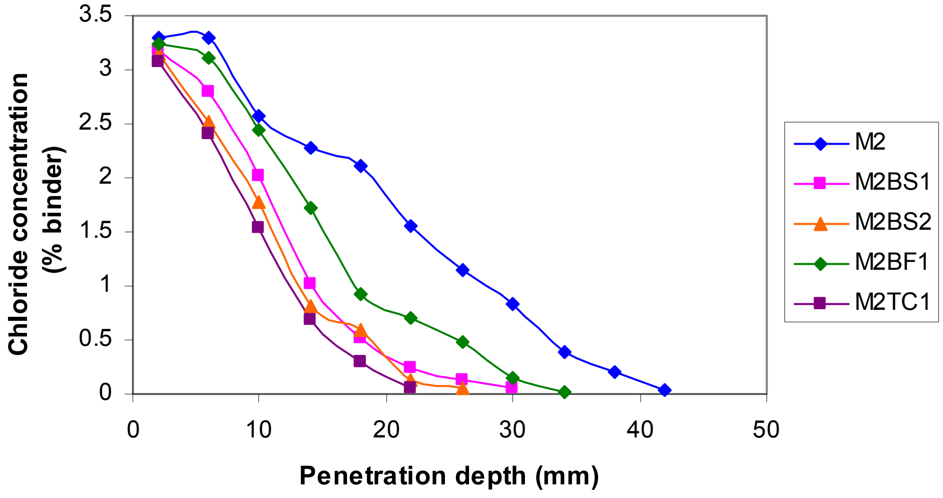
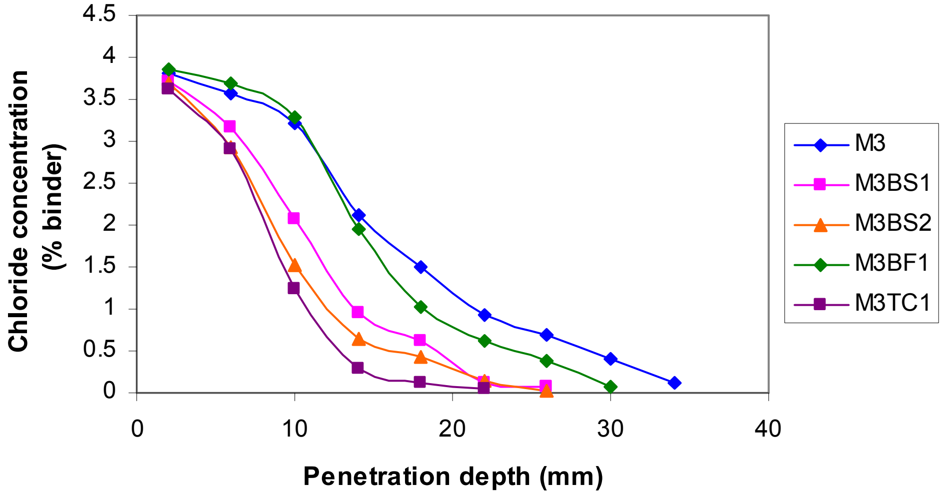

(b) Free chloride

Fig. 5.60. Chloride penetration profiles of specimens prepared at water-to-binder ratio of 0.35 and exposed to 5% calcium chloride solution


(a) Total chloride

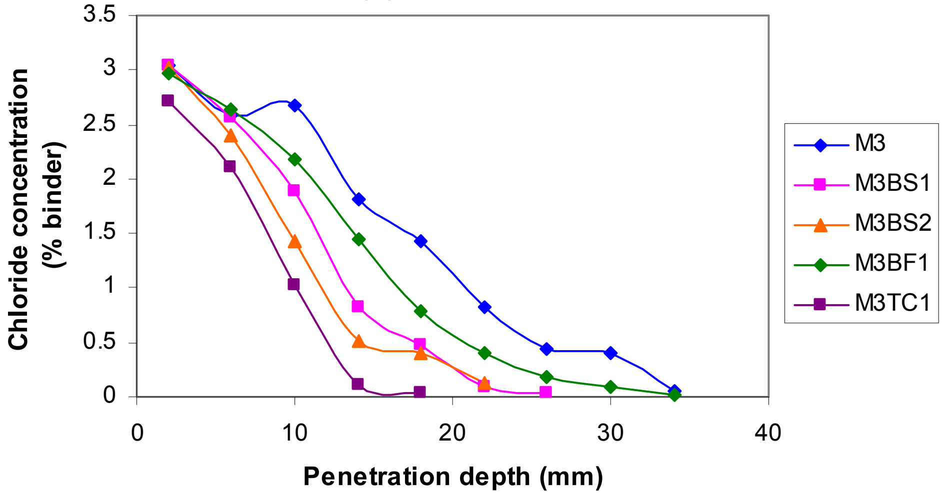

(b) Free chloride

Fig. 5.61. Chloride penetration profiles of specimens prepared at water-to-binder ratio of 0.25 and exposed to 5% calcium chloride solution

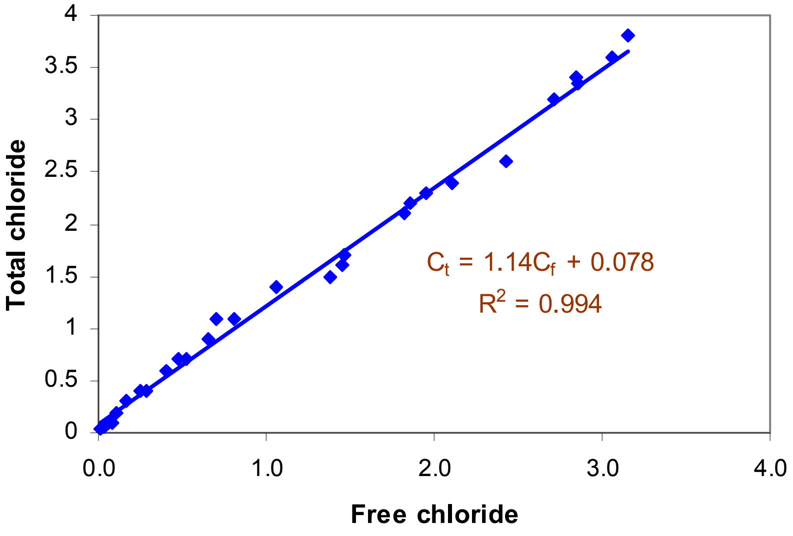


Fig. 5.62. Relationship between free and total chlorides for OPC concrete exposed to sodium chloride solution

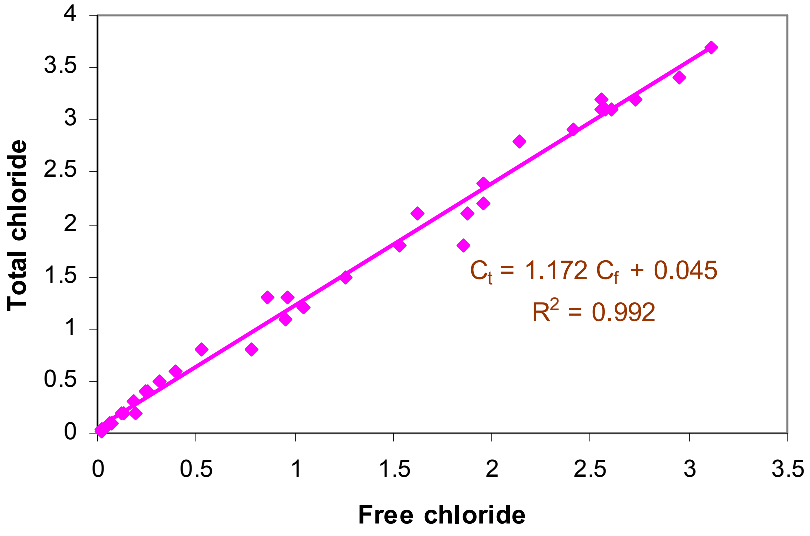


Fig. 5.63. Relationship between free and total chlorides for silica fume concrete exposed to sodium chloride solution

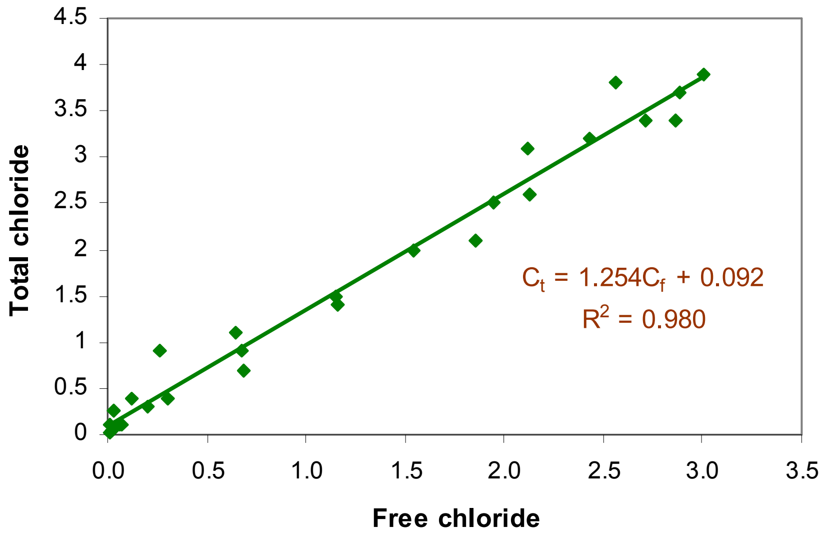


Fig. 5.64. Relationship between free and total chlorides for fly ash concrete exposed to sodium chloride solution

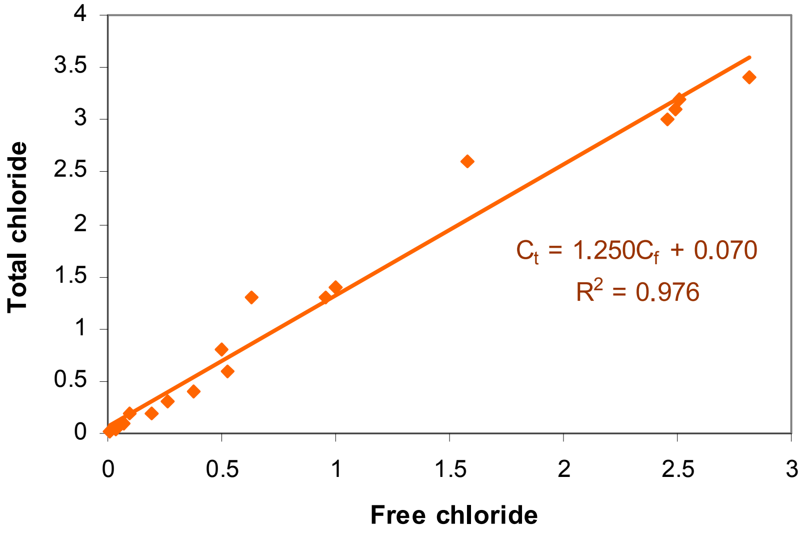


Fig. 5.65. Relationship between free and total chlorides for ternary concrete with silica fume and fly ash exposed to sodium chloride solution

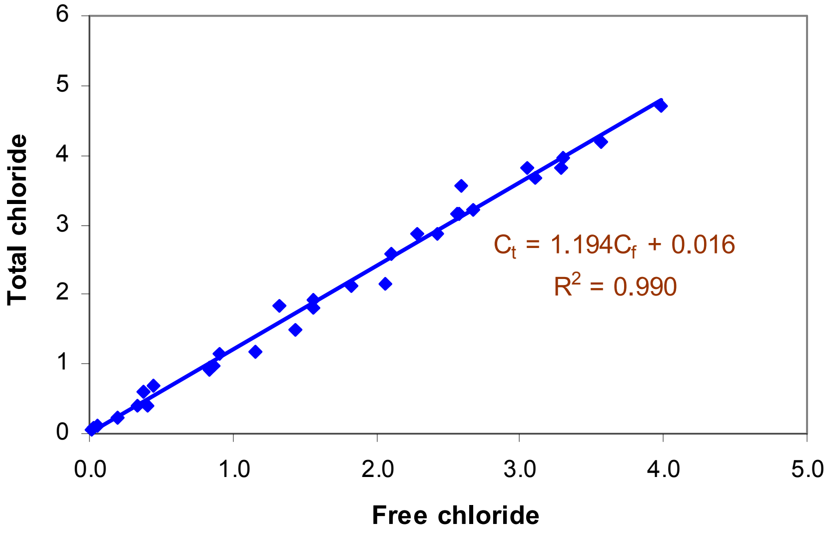


Fig. 5.66. Relationship between free and total chlorides for OPC concrete exposed to calcium chloride solution

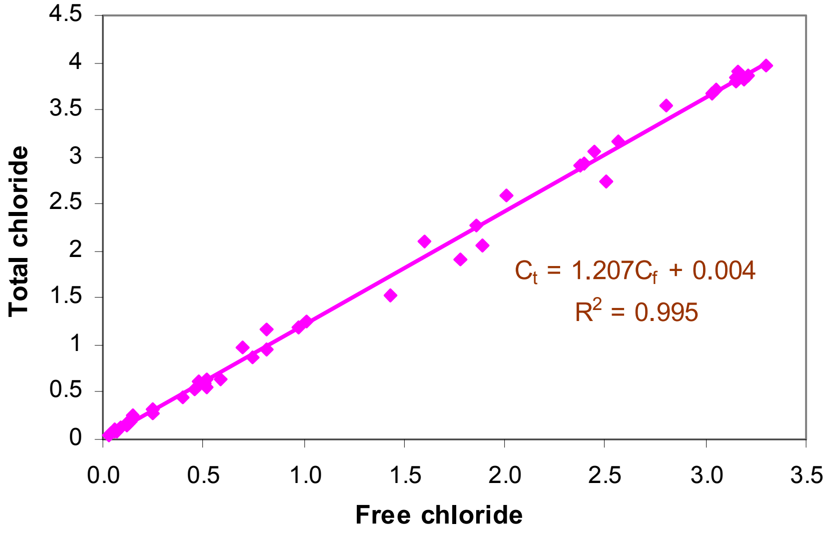


Fig. 5.67. Relationship between free and total chlorides for silica fume concrete exposed to calcium chloride solution

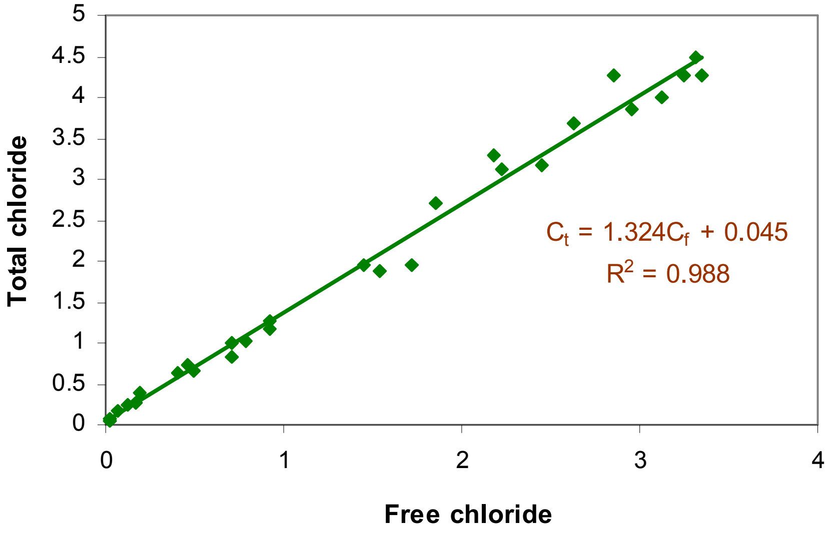


Fig. 5.68. Relationship between free and total chlorides for fly ash concrete exposed to calcium chloride solution

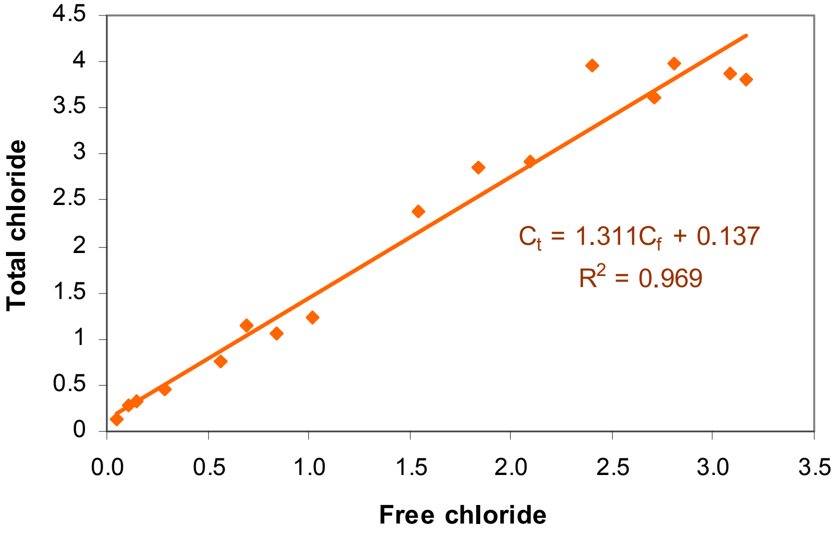


Fig. 5.69. Relationship between free and total chlorides for ternary concrete with silica fume and fly ash concrete exposed to calcium chloride solution

Plate 5.1. Brownish belt that appeared on the specimens exposed to hydrochloric acid attack

Plate 5.2. Condition of the specimens that are exposed to hydrochloric acid attack showing complete peeling off of the surface

Plate 5.3. White deposits on the surface of specimens exposed to magnesium sulfate solution

CHAPTER 6

CONCLUSIONS

6.1. GENERAL

The strength and durability characteristics of concrete having a combination of cement, silica fume and fly ash as cementing material, are investigated in the present study. On the basis of the various tests conducted for evaluating the performance of mixes and the mathematical models developed, the following conclusions are drawn.

6.2. FRESH PROPERTIES OF ADMIXTURE CONCRETE

1. In ternary mixes, inclusion of fly ash in the silica fume concrete system helps in compensating the increased demand of super-plasticizer, rendered due to the presence of silica fume alone, thereby reducing the optimum percentage of super-plasticizer required for desired workability.

2. The increase in optimum dosage of super-plasticizers increases with decrease in water-to-binder ratio. This increase is very sharp when the water-to-binder ratio is decreased from 0.35 to 0.25 as compared to the increase when the shift is from 0.45 to 0.35. This is attributed to the fact that at very low water – binder ratios, cement particles are closely packed, and hence to overcome inter particle friction and inter particle forces of attraction, higher optimum dose of super-plasticizer is required.

6.3 STRENGTH ASPECTS OF ADMIXTURE CONCRETE

3. In ternary system, inclusion of silica fume along with fly ash helps in compensating the decrease in early strength development caused by presence of fly ash alone, thereby leading to overall increase in compressive strength at all ages.

4. From the strength development aspect of concrete, the full potential of mineral admixture is utilized when a combination of 80 percent cement, 5 percent silica fume and 15 percent fly ash is used. It is further substantiated by stochiometric equations of cement hydration in concrete.

5. The strength development of pozzolanic concrete is more adversely affected by poor curing practices than ordinary Portland cement concrete.

6. For silica fume concrete and for ternary concrete mixes having a proper combination of silica fume and fly ash, 7 days of initial water curing is both necessary and sufficient to explore the pozzolanic activity and for reaching the required compressive as well as tensile strength level.

7. For concrete mixes having larger percentage of fly ash (beyond 15 percent), a long initial moist curing period is necessary to fully benefit from the addition of these supplementary cementing materials.

8. In terms of the overall economy achieved by using mineral admixtures, ternary concrete mixes using silica fume and fly ash in combination are the most suitable. For the same strength level, use of some percentage of fly ash in silica fume concrete reduces the cement requirement and also the amount of super-plasticizer required for achieving desired workability, leading to overall economy of the system. On the other hand, use of small amount of silica fume in fly ash concrete helps in reducing the number of curing days required to obtain a desired strength level, thus reducing the cost incurred on curing, also leading to overall economy of the system.

9. The beneficial effect of incorporation of mineral admixtures is more pronounced in tensile strength development as compared to the compressive strength development. On the other hand, the detrimental effect of adverse curing regimes is also more pronounced in tensile strength development.

10. Using the data of compressive strength and tensile strength (flexure strength and split tensile strength), a multiple regression mathematical model relating tensile strength and compressive strength of concrete is developed, incorporating parameters like water-to-binder ratio, concrete age and curing conditions. The model is validated by Integral absolute error (IAE) and the average value of the experimental/observed ratio $(O/P)_{avg,}$ with reasonable accuracy. The developed model is applicable to all kinds of concrete ranging from immature to fully developed, regardless of mix proportions and shape and size of specimens used for testing.

11. The combined relationship between non-destructive tests, which include ultrasonic pulse velocity and rebound number, and the destructive compressive strength test is obtained and validated with reasonable accuracy in terms of integral absolute error index.

6.4. DURABILITY ASPECTS OF ADMIXTURE CONCRETE

12. Seven days of initial water curing is sufficient for silica fume concrete and for ternary concrete, having a combination of silica fume and fly ash, to achieve desirable water impermeability, and hence increased durability of concrete.

13. Weight loss is not a reliable index to measure the durability of concrete in acid attack and must be supplemented by strength studies.

14. The presence of mineral admixtures lowers the detrimental effect of all types of acids on concrete. Among binary and ternary mixes, ternary mixes perform better than the binary mixes containing only silica fume as mineral admixture.

15. The course of action of acid attack is dependent on the type of acid present. In the case of hydrochloric acid and nitric acid attack, the calcium salt formed is soluble in water, leading to higher mass loss. On the other hand, in the case of sulfuric acid attack, the calcium salt formed is not soluble in water, getting deposited in the voids and causing internal stresses leading to disruption and strength loss of the matrix.

16. In the case of sulfate attack, the lowering of water-to-binder ratio tends to mitigate the deterioration process.

17. The degree of deterioration in sulfate attack is highly dependent on the type of cation associated with sulfate ions. The deterioration process is faster if the cation associated is magnesium as compared to sodium.

18. In sulfate exposure, the use of mineral admixtures is highly effective when the associated cation is sodium, but is highly detrimental if the associated cation is magnesium. It is attributed to the fact that during magnesium sulfate exposure, in mineral admixture concrete, the attack starts directly on C-S-H gel due to non-availability of calcium hydroxide, leading to the formation of non cementitious M-S-H and hence ultimate strength loss.

19. Among all mixes, ternary mixes perform best in sodium sulfate solution, while the performance of ordinary Portland cement concrete is comparatively better in magnesium sulfate solution.

20. In general, the depth of chloride ingress decreases with the decrease in water-to-binder ratio and with the presence of mineral admixtures in concrete. The decrease in water-to-binder ratio has lesser impact on the resistance to chloride penetration as compared to the effect of use of mineral admixtures in concrete as the mineral admixtures improve the diffusivity characteristics of concrete due to higher chloride binding capacity.

21. Ternary mixes containing a combination of silica fume and fly ash have least free chloride content among all the mixes. In the ternary combination, silica fume reduces the diffusivity of concrete even in short curing regime while fly ash helps in better chloride binding capacity of concrete.

22. Chloride diffusion process is a strong function of cation type. The chloride penetration depth is higher in calcium chloride solution as compared to the chloride ingress in sodium chloride solution.

23. The chloride binding capacity of concrete is independent of water-to-binder ratio but depends on the type of mineral admixture present. The binding capacity of fly ash concrete and the ternary mixes are almost similar, followed by silica fume concrete and is minimum for OPC concrete. The chloride binding capacity is also dependent on the associated cation type, calcium chloride being more effective in binding chlorides as compared to sodium chloride.

6.5. SUGGESTIONS FOR FURTHER WORK

1. The work can be extended to study the synergistic effect of other locally available mineral admixtures and by using higher percentages of fly ash.
2. The chemical resistance of concrete need to be studied after exposing the specimens to aggressive chemicals for longer durations.
3. The extensive study of the behaviour of ternary mixes in stress and cracking is required to be undertaken as future work.

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