# EFFECT OF MIXING TIME ON THE PROPERTIES OF SELF-COMPACTING CEMENT PASTE SYSTEMS USING SUPPLEMENTARY CEMENTITIOUS MATERIALS

## FINAL YEAR PROJECT UG 2012

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has been accepted towards the
requirements for the undergraduate
degree

**in**

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# ABSTRACT

This study focuses on the effect of mixing time on the properties of self-compacting paste systems using supplementary cementitious materials (SCMs) such as Marble Powder (MP), Fly Ash (FA) and Limestone Powder (LSP). These SCMs are industrial waste products of the marble, coal and limestone industry, respectively and their use as replacements of cement aids in their effective disposal while making concrete production more economical and environment friendly. Furthermore, replacement of cement with SCMs results in the reduction of environmental pollution causes by cement production.

The parameters studied include powder particle size characterization, flow, strength development, water absorption and calorimetry.

In earlier stages, tests were carried out at 3 minute mixing time to determine the optimum replacement levels for all SCMs by replacing cement with 15%, 30% and 45% SCMs by weight. A replacement level of 15% for all SCMs resulted in the highest strengths and was, thus, selected for latter experimentation though in an earlier project, it was estimated at 20%. An increased replacement level for SCMs caused a fall in water demand, in terms of water-powder ratio, but increased superplasticiser demand. An increase in flow was recorded with increasing replacement levels of SCMs except for MP which retarded flow due to increased internal friction and possible early hydration. Increased replacement levels delayed setting times and reduced both water absorption and final strengths of the self-compacting paste systems. Addition of SCMs also resulted in reduced and delayed hydration.

The self-compacting pastes containing optimum replacements of 15% SCMs were subjected to varying mixing times of 5 and 10 minutes. Results show a

considerable improvement in strength with increasing mixing time along with greater water absorption. MP exhibits the greatest compressive strength.

It can be concluded that higher mixing time results in better compressive strength (though reduced flow and increased flow times) as well as earlier and faster hydration which proves that the use of SCMs can produce concrete that is workable, strong, economical and environment-friendly.

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| | |
|---|---|
| SCCS | Self-Compacting Cementitious System |
| SCP | Self-Compacting Paste |
| SCPS | Self-Compacting Paste Systems |
| SCC | Self-Compacting Concrete |
| SRM | Secondary Raw Materials |
| SCM | Supplementary Cementitious Materials |
| OPC | Ordinary Portland Cement |
| FA | Fly Ash |
| LSP | Limestone Powder |
| MP | Marble Powder |
| HRWR | High Range Water Reducers |
| WD | Water Demand |
| w/c | Water to Cement Ratio |
| w/p | Water to Powder Ratio |
| SP | Super-plasticizer |
| PSD | Particle Size Distribution |
| PSC | Particle Size Characterization |
| SEM | Scanning Electron Microscopy |
| XRD | X-Ray Diffraction |
| XRF | X-Ray Fluorescence |
| CH | Calcium Hydroxide |
| CSH | Calcium Silicate Hydrate |
| ACI | American Concrete Institute |
| ASTM | American Society for Testing and Materials |

# CHAPTER 1

# INTRODUCTION

## 1.1 General:

Concrete is the most common artificial material on earth. The word “concrete” does not refer to just a single building material. It can be any substance that holds a combination of rocks and gravel together via a binding material.

Most concretes use hydraulic cement such as Portland cement as a binder. Portland cement concrete is a mix of aggregates, water, cement and other mineral admixtures. This mix of ingredients forms a flowable, semi-liquid substance that can be poured into molds and shaped into anything using appropriate formwork.

The discovery of concrete can be traced back two thousand years to the port city of Pozzuoli where the locals witnessed hardening of volcanic ash when it came in contact with water. The reaction occurred due to the combination of decarbonated lime ($CaCO_3$) with silica-rich ash at the surface which created cement-forming particles.

The ancient Romans first noticed this Pozzolanic ash harden when it mixed with the sea-water. They experimented with this naturally-occurring cement paste by adding small pieces of Pumice to it, planting roots of modern day concrete.

Today, concrete is a $100 billion dollar industry. Adding to that, concrete is the most widely-used material on the planet after water. Humans use more concrete today than steel, wood, plastics and aluminium combined.

Concrete is a revolutionary building material. Prior to setting, concrete exhibits workability which allows it to fill molds with relative ease. Chemical additions to the concrete mix can also alter its setting time. Modern day science has allowed us to alter the properties of concrete to construct structures like dams, reservoirs, runways, overpasses, underpasses, bridges and buildings, which would be impossible to build in ancient times.

There are many modern-day varieties of concrete available today, the most common of which is reinforced concrete. As concrete on its own exhibits little to no resistance to tension, it is commonly reinforced using steel bars. This reinforcement allows concrete to sustain much more loads as opposed to the non-reinforced variety.

Furthermore, special varieties include high performance concrete (HPC), self-compacting concrete (SCC) and pervious concrete which allows water to seep through to the underlying surface. Water can directly flow through the pavement without compromising the structural integrity of the urban environment as well as providing a solution to the age old problem of surface drainage.

## 1.2 Self-compacting Concrete:

Self-compacting concrete (SCC) was first introduced by Prof. Okamura of Tokyo University in 1988 with the name of “High Performance Concrete”. Its creation was spurred on by a decrease in the availability of skilled labour along with the problems caused by inadequate compaction.

SCC is a mixture of concrete that is capable of consolidating under its own weight. This fluid nature of SCC means that it can be placed in difficult conditions and in sections with congested reinforcement with relative ease.

A lack of external consolidation through vibration results in a considerable reduction in hearing-related damages. Furthermore, a significant amount of time is saved while placing SCC into the designated formwork as well as the energy required for mechanical consolidation. Structural elements ideally suited to the use of SCC are tunnels, underwater concrete placements and congested reinforcement works.

The constituents of SCC include the usual cement, aggregates and water along with High Range Water Reducers or Superplasticizers (HRWRs or SPs) and Viscosity Modifying Agents (VMAs). SCC requires a specific range of rounded aggregates as the shape of aggregate directly affects the flowability of the mix. The addition of SPs and VMAs in a calculated amount ensures adequate flow without problems such as bleeding and segregation which can diminish inter-layer bonding, reduce strength and make the concrete much harder to pump.

### 1.2.1 Self-compacting Paste Systems:

Self-compacting paste (SCP) refers to all the constituents of Self-compacting concrete excluding the inert aggregates. The cement paste plays a vital role in maintaining the fluid nature of the SCC by virtue of the chemical reactions between the Superplasticizers and Viscosity Modifying Agents. Consequently, the behavior of the cement paste directly results in both the physical and chemical properties of the concrete it essentially acts a binder in.

## 1.3 Superplasticizers:

The amount of water has a drastic effect on many characteristics of the cement paste, such as mix density, paste quality, compressive strength, flexural strength, permeability, weathering resistance, bond strength with reinforcement, shrinkage and workability. The water-to-cement ratio (w/c) required to complete hydration generally ranges from 0.22 to 0.25 but there is a need for additional water to overcome frictional resistance and enhance workability.

The use of HRWR or Superplasticizers solves this problem by reducing the amount of water by 12% to 30% while maintaining a desired consistency.

## 1.4 Mixing of Concrete:

The mixing of concrete and its constituents is carried out to achieve a homogenous, amalgamated and fluid product. Homogeneity of the mix results in the consequent homogeneity of the hardened properties of concrete. Thus, certain mixing regimes have to be established to attain the final properties. However, mixing time can also have a drastic effect on the fresh and hardened properties of concrete such as flow, workability, strength, setting time and hydration rate. Therefore, it is of utmost importance that the mixing regime is such that it allows for thorough mixing as well as being able to avoid all the ills that accompany improper mixing of concrete.

### 1.4.1 Mixing of Cement Paste Systems:

Given that concrete is just a mix of aggregates within a cement paste matrix, the mixing of cement paste holds the most importance for attaining the desired fresh and hardened properties of concrete. The mixing time and regime of the cement paste directly influences the setting time, flow, workability and strength of the concrete. The used mixing times for this research are 3 minutes, 5 minutes and 10 minutes.

## 1.5 Supplementary Cementitious Materials (SCMs):

Supplementary Cementitious Materials (SCMs) are being widely used world-wide to form partial replacement of cement individually or in form of blends. Different percentages of SCMs are used to replace the cement content and they contribute to and enhance the properties of cement through hydraulic or pozzolanic activity.

Supplementary Cementitious Materials(SCMs), also widely known as Secondary Raw Materials, Pozzolans, and fillers can be defined as fine materials that are used as replacements of cement which do not possess cementitious properties within themselves but in the presence of water and cement they react with cement to form compounds that possess cementitious properties.

Supplementary Cementitious Materials (SCMs) used in construction industry as cement replacements can be of natural or artificial origin. Naturally occurring SCMs include volcanic ashes or pumice. Artificial SCMs are by-products of different industrial processes and include Fly Ash (FA), Silica Fumes (SF), Blast Furnace Slag, Marble Powder (MP), Limestone Powder (LSP) and Rice Husk, etc. All the artificial SCMs are waste products and their use in replacements of cement makes the whole process economical and environmental-friendly as it reduces the green-house effect formed due to production of cement.

The main advantages associated with the increased use of Supplementary Cementitious Materials (SCMs) other than their contribution to sustainable development is the improvement in durability and transport properties of the cement mix when used in controlled dosages. Other advantages may include reduced water demand (WD), increased flow and strength and reduced shrinkage, depending on amount and types of SCMs used. SCMs of their reactions products an act as fillers in the pores and thus reduce permeability. Thus the use of SCMs increases economy, durability, performance and sustainability.

### 1.5.1 Fly Ash (FA):

Fly Ash (FA) is the by-product of combustion of pulverized coal in furnaces of thermal-power generation plants and are one of the most widely used Supplementary Cementitious Materials (SCMs). The particles of FA are spherical in shape and range in size from 0.5 µm to 300 µm. FA particles are transported and captured through flue gases in the furnace and thus the particles are non-combustible.

Fly Ash (FA) mainly consists of silicates, aluminates, carbon oxides and iron oxides but their composition may vary according to the type of coal used in their formation. The two main types of FA are Class F Fly Ash which is produced due to combustion of anthracite and bituminous coal and Class C Fly Ash that is produced due to combustion of lignite or sub-bituminous coal.

Use of Fly Ash (FA) as Supplementary Cementitious Material (SCM) reduces pollution as FA is not disposed into the air but collected to replace cement, thus reducing the greenhouse effect. The main effect of FA on the cement mix is enhanced workability of the system. Other advantages that FA may have are increase in long-term strength, increase in permeability and durability and reduction in the potential of sulfate attack and heat of hydration. Type and quantity of FA used as a replacement to cement determine the effect of FA on the properties of the system.

### 1.5.2 Marble Powder (MP):

Marble is a metamorphic rock that has been used as a building material since ancient times and continues to have a very high demand today. This high-demand results in bulk of waste produced by marble stone industry which can cause environmental problems. Waste is generated in solid form as well as stone slurry. Marble Powder (MP) used in this research as a replacement of cement comes mainly from cutting and shaping of marble and is in the form of stone slurry. This slurry consists of marble particle of very high fineness and is dried so that Marble Powder can be used as a Supplementary Cementitious Material (SCM).The chemical composition of pure MP is very similar to that of cement.

The main advantage of using Marble Powder (MP) as a SCM is the control of pollution by re-using the waste of marble stone industry. Other advantages include high strength development with lower costs thus making the construction process economical and energy efficient.

### 1.5.3 Lime Stone Powder (LSP):

Limestone is a sedimentary rock found across the world and it has been used as a construction material since old times. Limestone (LSP) is a by-product of limestone crushers which is produced in large quantities and thus is an environmental hazard. LSP has been used as a filler in concrete for many years now but it has been recently discovered that it can be used as a Supplementary Cementitious Material (SCM) too as its compounds in moist conditions impart cementitious properties.

Limestone Powder (LSP) has calcite as its main constituent and has a chemical composition very similar to that of cement. The particle size of LSP depends upon its origin or the method used in its production. LSP used as a replacement of cement has very fine particle size.

The use of Limestone Powder (LSP) as a Supplementary Cementitious Material (SCM) has the main advantage of reducing the environmental hazard by reusing the waste of limestone industry and also decreasing the carbon dioxide emissions produced from cement manufacture. Thus, the use of LSP makes concrete production economical, environmental friendly and also has positive effect on the cement system.

## 1.6 Research Objective:

The aim of this study carried out on Self-Compacting Paste Systems (SCP) was to observe the effect of varying mixing times on the response of SCPs using Supplementary Cementitious Materials (SCMs), with varying replacement levels of such SCMs. The properties studied were strength, flowability, and calorimetry using standard procedures. The study focuses on the use of a combination of OPC with Limestone Powder, Fly Ash and Marble Powder while bringing change to the mixing times and studying the resulting effects on the aforementioned properties.

# CHAPTER 2

## LITERATURE REVIEW

### 2.1 Introduction of Study:

The use of blended cements to enhance the properties of self-consolidating concrete is on the rise around the world. The objective of this study is to contribute to this development as well as reducing $CO_2$ emissions, energy consumption and costs using multiple replacement levels. This research aims to study the effects of varying mixing times on self-compacting cement paste systems using Supplementary Cementitious Materials while modifying replacement levels of such SCMs. The properties to be studied are Strength, Flow ability and Calorimetry using standard procedures.

The study focuses on the use of a combination of Ordinary Portland Cement with Limestone Powder, Fly Ash and Marble Powder while bringing change to the mixing times and studying the resulting effects on the aforementioned properties.

### 2.2 Self-Compacting Concrete (SCC):

Self-compacting concrete also known as self-consolidating concrete is a highly flow able, non-segregating concrete that completely encapsulates even the most congested reinforcement arrangements without the need for any additional mechanical vibration. The European Federation of Specialist Construction Chemicals and Concrete Systems (EFNARC) defines SCC as "Concrete that is able to flow under its own weight and completely fill the formwork, even in the presence of dense reinforcement, without the need of any vibration, whilst maintaining homogeneity."[1]

Even though with great research and advancements in concrete there was still a problem with producing durable concrete structures in which concrete could fully cover the reinforcement. This problem was greatly felt in Japan where the gradual reduction of skilled labour led to a similar reduction in the quality of construction work which led to the inception of self-compacting concrete, which flows to every corner of formwork and is compacted under its own weight without the need of mechanical vibration.

The prototype of self-compacting concrete was first completed in 1988 using materials already on the market. It was called "High Performance Concrete." and was defined as follows at the three stages of concrete [2];

(1) Fresh: self-compactable

(2) Early age: avoidance of initial defects

(3) Hardened: protection against external factors

At almost the same time, "High Performance Concrete" was defined as a concrete with high durability due to low water-cement ratio by Professor Aitcin. Therefore, the name for the proposed concrete was changed to "Self-Compacting High Performance Concrete."[2]

From its inception in Japan in 1980s, research, development and use of SCC has spread throughout the world. With the formation of organizations such as American Concrete Institute (ACI) and American Society for Testing and Materials (ASTM) specific guidelines, standards and specification for Self-Compacting Concrete are now available.

### 2.2.1 Self-Compacting Paste Systems (SCPS):

Self-compacting Paste (SCP) systems are the agents that transport the aggregate particles and therefore define the properties of self-compacting mortar (SCM) systems and self-compacting concrete (SCC) systems [6]. Use of different secondary raw materials in paste systems help improve the properties of the Self-Compacting Cementitious System (SCCS) considerably and can only be achieved by the optimization of its major components self-compacting paste (SCP) and self-compacting mortar (SCM).

## 2.3 Characteristics of Ordinary Portland Cement (OPC):

Cement can be defined as a powdered binding material which has both cohesive and adhesive properties allowing it to combine and bind different construction material (sand and coarse aggregate mixed with water) in a relatively uniform matrix structure.

ASTM C150[3] defines Portland cement as "hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers which consist essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulphate as an inter ground addition."

Typical composition of main oxides present in ordinary Portland clinker are:

- $CaO$ (60-70%),
- $SiO_2$ (18-22%),
- $Al_2O_3$ (4-6%)
- $Fe_2O_3$ (2-4%)

Remaining 5 % includes $MgO$, $Mn_2O_3$, $SO_3$, $K_2O$, $Na_2O$, and $TiO_2$.

The typical composition of main compounds these oxides form are:

| | | | |
|---|---|---|---|
| Alite | 3CaO.SiO2 | C3S | 55-65% |
| Belite | 2CaO.SiO2 | C2S | 15-25% |
| Aluminate | 3CaO.Al2O3 | C3A | 8-14% |

## 2.4 Characteristics of Self-Compacting Concrete (SCC):

Self-consolidating concrete, also referred to as self-compacting concrete, is "highly flow able, non-segregating concrete that can spread into place, fill the formwork, and encapsulate the reinforcement without any mechanical consolidation" (ACI 237 2007) [4]

Self-compacting concrete must have sufficient fluidity and flow so that it consolidates under its own weight without the requirement of external vibration, completely filling the formwork easily flow through congested reinforcement while maintaining sufficient resistance to segregation. Along with this SCC should also meet the strength and durability criteria while maintaining the required level of workability.

The two properties specific to effective performance of SCC are its flowability and stability. The high flowability of SCC is obtained through the use of high range water reducing (HRWR) admixtures and not by addition of extra water in the mix. The resistance to segregation of plastic concrete mixture can be attained by increasing total quantity of fines in concrete mix or by using VMAs which effect the viscosity of water in the concrete mix. Percentage fines of a concrete mix can be increased by increasing content of cementitious material or by using mineral fines. The ability of flow of SCC is also effected by internal friction between various solids such as sand, coarse aggregate or powder materials. This inter particle friction increases resistance to flow and the ability to deform. However the use of HRWR helps to reduce this internal friction by spreading out cement particles and maintaining flow ability even with reduction in water content.

The ability to self-compact of SCC depends upon the yield stress which is the applied stress that must be exceeded in order to make a fluid flow. Viscosity of the mix in turn controls the homogeneity and ability to flow through reinforcement. Self-compacting nature of SCC requires paste or mortar to deform while providing resistance to separation of coarse aggregate and mortar. During pumping and placement, the concrete mix is not as stable as it is during mixing. As concrete deforms around and moves between reinforcement, stability of concrete becomes a point of concern. As the mortar deforms, some aggregate particles might not deform and begin to segregate, creating a blockage for effective flow of concrete [5]. This can be controlled by limiting aggregate content and size (or both) which provides sufficient distance between aggregate particles limiting the collisions between them, eventually lowering the internal stress during concrete deformation.

## 2.5 Properties of Self-Compacting Concrete (SCC):

Self-compacting concrete (SCC) is a new technology that does not require vibration for placing and compaction. It is able to flow under its own weight, completely filling formwork and achieving full compaction, even in the presence of congested reinforcement. The hardened concrete is dense, homogeneous and possesses the same engineering properties and durability as traditional vibrated concrete. [7] SCC flows without any external or internal compaction. [8]

The three key properties of SCC are: [9]

- The filling ability of SCC where SCC completely fills the formwork under its own weight.
- The passing ability where SCC wan overcome obstacles such as reinforcement under its own weight without hindrance
- The segregation resistance where SCC maintains its homogenous composition during the whole process of concreting.

The use of SCC reduces the internal segregation between solid particles and the adjoining liquid which results in less porous transition zones, and thus increases the durability of concrete. There is an increase in allowable reinforcement rate and overall construction rate, increasing the overall quality of the system.

SCC also enhances overall productivity of construction and reduces the overall cost by eliminating external work, thus making the whole process economical. SCC are environmentally sustainable because their production includes less energy consumption which improves the work environment and makes the whole process energy efficient. [8]

## 2.6 Supplementary Cementitious Materials (SCMs):

The production of cement is very energy-consuming and environmentally unfriendly requiring about 4 GJ per tonne of finished product in addition to producing 0.8-1.3 ton of $CO_2$ per ton of cement produced [10].Thus, after considerable efforts to replace cement with other materials, Supplementary Cementitious Material (SCMs) were discovered as a replacement that not only make the process energy efficient and environmentally friendly by reduction of $CO_2$, but also help reduce pollution by the reuse of some of the industrial waste products.

Supplementary Cementitious Materials(SCMs) can be defined as "materials that possess in themselves little or no cementitious value but will in finely divided form and in the presence of moisture react with cement at ordinary temperatures to form compounds possessing cementitious properties" [11]. Thus, an SCM requires $Ca(OH)_2$ to impart strength to the mix, whereas a cementitious material itself contains CaO content. [12]

### 2.6.1 Reaction Kinetics of SCMs:

Addition of Supplementary Cementitious Materials (SCMs) in the cement mix enhance both fresh and hardened properties of the mix. The clinker phases hydrate at various rates resulting mainly in theformation of C–S–H, C–H, ettringite and AFm phases. Theblending of SCMs with cement leads to a more complicatedsystem where the hydration of the Portland cement and hydraulicreaction of the SCM occur simultaneously and may also influence thereactivity of each other [13]. The effect of SCMs on the system can be divided into two categories which are "the filler effect" (4) and "the hydration activity". Following is how both these mechanisms effect the properties of cement mix:

#### 2.6.1.1 The Filler Effect:

The reactivity of SCMs is largely dependant on the alkalinity of pore solution and that develops over time, thus in the first few days, SCMs enhance the reaction kinetics solely on the basis of the filler effect. The two mechanisms causing the filler effect are:

- The presence of small sized SCMs reduce internal voids.
- Because of the enhanced fineness of SCM particles, the act as nucleation sites and provide extra surface for the hydration products of clinker phase. [13]

#### 2.6.1.2 The Hydration Activity:

The reaction of SCMs is not as fast as the reaction of cement and difficult to follow as many SCMs consist of X-ray amorphous glasses. The kinetics of the SCM reaction depends on the chemical composition, the fineness, and on the amount of reactive phases such as glass or zeolites of the SCM used as well as on the composition of the interacting solution.[13].

As we know that the hydration products of cement are C–S–H, C–H, ettringite and AFm phases. The SCMs generally have a lower calcium content that cement, thus there is a difference in the hydrates formed by the two. One important difference is in the composition of C–S–H phase. Silica-rich SCMs result in the formation of C–S–H with a lower C/S ratio, which leads to an increased uptake of aluminium: C–A–S–H[13]. Depending on the composition and the reactivity of the SCM, also the amount of ettringite and the amount and kind of AFm phases are also determined [13].

### 2.6.2 Effects of SCMs:

Other than the obvious impacts such as making the process energy efficient, environmentally-friendly and economical, the use of SCMs as a replacement of cement reduces the cement content which results in reduced shrinkage and heat of hydration[10]. As a result of this, shrinkage cracking is also reduced.

SCMs have a major role in the improvement of transport properties of the system. Initially it was assumed that fine particles increase the water demand (WD) of the mix, but in the case of SCMs the fine particles act as a filler and reduce the WD, increase paste volume and thus stability, improve finished surfaces and increase workability and flowability of the system [10]. The SCMs also reduce permeability and enhance the particle packing of the mix. This results in higher durability and compressive strength [14] [15].

## 2.7 Fly Ash:

Fly Ash or pulverized fuel ash is driven out of boilers by flue gas in thermal power plants. FA is generally collected by electrostatic precipitators or other particle filtration systems before the flue as escapes to save the environment from pollution. In this process, the ash that falls on the bottom of the boiler is called bottom ash. Characteristics of FA depend upon the type of coal burnt or the combustion mechanism. The temperature during the combustion is as high as 1200° C and under such high temperatures, FA particles assume a spherical shaped glass particles. The final product ash is as fine as less than 100$\mu$m in diameter.

The two basic types of FA based on the type of coal used and their composition are Class-F FA and Class-C FA. ASTM-168 states that for Class-F Fly Ash the sum of SiO2, $Al_2O_3$ and $Fe_2O_3$ should be greater than or equal to 70%. While for Class-C Fly Ash the above Oxides content should be at least 50% [10].

The degree of reactiveness of FA depends upon its particle size and the smaller the particle, the more reactive it is. The water-binder ratio is related to water-cement ratio by the following relation in a cement system containing FA: [16]

$$\frac{W}{C+F} = \frac{W}{C}\left(1 - \frac{F}{F+C}\right)$$

Where W, C and F are water, cement and Fly Ash respectively. This means that if the water-binder ratio is kept constant, higher the FA, more effective the w/c ratio. [10]

### 2.7.1 Hydration of FA:

FA is inert at the early stages of its reaction and the hydration effects depend mainly on the amount of water available. FA depresses the calcium concentration in the initial hours and thus delays C–H and C–S–H crystallization and eventually retards the hydration process. [17]

The effect on hydration kinetics of cement because of FA depends upon he levels of replacement and curing temperatures and at normal temperatures, FA acts as a retarder in the dormant and acceleration stages of hydration but acts as an accelerator after the acceleration phase. The addition of FA facilitates water diffusion through the C-S-H layer in the later stages, and consequently contributes to an acceleration of the cement hydration [18]. The higher the w/c ratio, the greater the retardation effect of FA in early stages.[19]

Fly Ash mainly consists of $SiO_2$ and also contains $Al_2O_3$ in significant amounts, and the limited amount of CaO depends upon the type of FA. The blend of cement and FA produces a reduced amount C–H in the hydration mixture as compared to that of pure cement. If the FA is rich in aluminium, such as in the case of Class-F FA, hydration mix will have high amounts of Al-rich phases. As fly ashes contain significant quantities of $Al_2O_3$ but little

$SO_3$, the blending of PC with fly ash results in a decrease of ettringite and in an increase of AFm content. When the replacement of FA in the cement exceeds 40%, ettringite are calculated to become unstable. The C–S–H formed in OPC–FA blends has a lower C/S ratio and contains more Al. [13]

## 2.8 Marble Powder:

During the cutting and finishing of marble, almost 20-30% of the weight of marble stone worked is wasted in the form of marble slurry and the residues are deposited in landfills or water bodies, causing pollution [20]. To overcome this and to reuse the waster product, replacement of cement with MP was initiated. Also, MP has a chemical composition which is quite comparable to that of cement.

Different researchers have concluded that the use of MP of content more than optimum has a negligible negative effect on concrete compressive strength where compressive strength of concrete increased almost 15% on addition of marble dust up to optimum replacement [21] [22]. MP also have no adverse effects on the value of pH and doesn't speed up or effect the process of carbonation. [21]

Marble powder also improves the durability and workability of the system and reduces permeability, without decreasing the compressive strength [23]. Although, increasing the replacement of MP over the optimum dosage can lead to segregation aggregates and decreased resistance of concrete [24]. Different researchers have established different optimum amounts for MP replacement such as 10% and 15%.

The SEM investigations show that C–H morphology in specimens with and without MP are different from each other. The differences between the appearances of CH crystals prove that the MP has also played a noticeable role during the hydration process. [25]

## 2.9 Limestone Powder:

Limestone is a sedimentary rock of calcium carbonate, found in the remains of marine. Limestone powder interacts with the cement system in two way, it acts as a filler and it also takes part in the hydration reaction.

The use of cement containing LSP as a filler is a quite common practice. Limestone filler improves the hydration rate and increases the strength of cement compounds at early ages [26]. The addition of limestone filler in to cement results in increase in cement fineness of the cement which provide higher rate of hydration and hence faster development of the early strength [27]. LSP physically improve the denseness of hardened Portland cement paste due to its filling effect, improves workability, controls bleeding and reduces shrinkage and water demand (WD).[28][29]

LSP accelerates the hydration rate of Portland cement in an early stage [28]. According to some researchers, LSP reports an acceleration of the $C_3S$ and an incorporation of the calcium carbonate into the C–S–H. Additionally, limestone is known to interact with AFm and AFt phases [30]. The particle size of LSP must be considered in the mix design because the early strength of the concrete depends on blended cement composition and LSP fineness, since interaction between gypsum and limestone during early C3A hydration interferes with setting time. The catalytic effect results from the high specific surface area of LSP, which produces nucleation sites for cement hydration products [29].

Thus, other than making the whole process of replacement energy efficient and economical, LSP addition to cement causes an increase of hydration at early ages inducing a high early strength, but it can reduce the later strength due to the dilution effect [31].

## 2.10 Superplasticizers (SP):

A super plasticizer is a type of water reducer which is artificially prepared water soluble organic material, used as an ingredient of concrete along with water cement and aggregates added immediately before or during the mixing to increase the workability of the cementitious mix at low water mixing content. Superplasticizers are chemical admixtures that are essential for Self-Compacting Cementitious Systems (SCCS) [10].

Superplasticizers effect many fresh and hardened properties of the system and the following factors are involved to cause these effects: [32] [33]

- Reduction in interfacial tension.
- Multi-layered adsorption of Organic molecule.
- Release of water trapped amongst the cement particles.
- Retarding effect of cement hydration.
- Change in morphology of hydrated cement.

Superplasticizers are known to work in one of the following ways: [34]

- They produce high workability concrete with constant cement content and strength
- produce concrete with normal workability, but lower water requirement
- production of concrete with combination of high workability and low water content
- and designing a normal strength and workability concrete with less cement content

### 2.10.1 Types of Superplasticizers:

ASTM C494 classifies superplasticizers or High Range Water Reducing Agents (HRWR) as "an admixture that reduces the quantity of mixing water required to produce concrete of a given consistency by 12% or greater and retards the setting of concrete."

There are three main generations of plasticizers, of which first generation or lignosulfonates (LF) doesn't qualify as SP because they reduce water requirement by just 5%.

Second generation of SP include Sulfonated melamine-formaldehyde condensate or Sulfonated naphthalene-formaldehyde condensate (SNF/ SMF) and these reduce the water demand by atleast 12%. The third generation polycarboxylatesesters (PCE) type SP reduces the water demand upto 40%. These are essential components of Self-Compacting Systems as they bring down the water demand and regulate the setting time. [10]

### 2.10.2 Mechanism of SP Action:

Of the four main phases of cement namely $C_2S$, $C_3S$, $C_4AF$ and $C_3A$, the first two have a negative zeta-potential and the other two have a positive zeta-potential. Attractive forces exist between particles due to opposite charges and this leads to very fast coagulation of the grains of cement.

SP directly absorbs on the surface of these phases and changes their characteristics. SP which is negatively charged, permits the adsorption on the positively charged particles, thus changing the zeta-potential of positive particles. SP molecule binds on the surface and decreases charges so that all of them become negative. Repulsion is created and thus the agglomeration of different particles is prevented and entrapped water is released. [35] [10]

When SP is added along with mixing water, SP interacts with $C_3A$ mainly and very small quantity is left to disperse the silicates, but when SP is added a few minutes later, $C_3A$ had already hydrated and thus SP is left for silicates, this enhancing the workability. [10]

### 2.10.3 Effects of SP on Concrete:

The effects of SP on the fresh properties of concrete include increased workability, reduced water demand, regulated water demand and no undue segregation and bleeding. SP also helps escape the entrained air, thus reducing the air content by 1-3%.

Of the hardened properties, it is observed that SP reduces porosity, increases durability, results in early volume stability and a higher compressive strength due to improvement in interfacial zone. [10]

## 2.11 Experimental Techniques:

### 2.11.1 Particle Size Distribution (PSD):

Particle size distribution (PSD) is an index that specifies the size of the particles being studied individually and also their percentage relative to the total sample group to be measured. Accurate PSD results are vital to predicting the performance of cementitious materials. ASTM C 115-96 is presently the only available standard method for determining particle size [36]. However, this method has a lower particle size limit of 7.5μm which limits its capability to accurately cover the entire particle range. Other experimental techniques are being employed to overcome this obstacle including the laser diffraction method that measures particle size by measuring the angular variation in the intensity of light scattered as a laser beam passes through a dispersed particulate sample. This method gives a better range to accurately measure size with the added benefit of taking substantially less time than the previous method. An index known as the refractive index of the material under scrutiny must be known prior to performing the experiment [37]. The laser diffraction method has been implemented during the course of this study.

### 2.11.2 X-ray Fluorescence (XRF):

X-ray fluorescence (XRF) is a non-destructive technique used to conduct the chemical analysis of minerals, rocks and construction materials. This technique makes use of an objects ability to emit a characteristic X-ray when bombarded with high energy rays. These characteristic X-rays aid in the identification of chemical substances present in the material. Furthermore, it calculates and consequently, displays the relative percentages of distinct chemical compounds present in the material. X-ray fluorescence helps identify chemical compounds inside cement and other cementitious materials to predict the chemical reactions that they might undergo in a cement paste system.

### 2.11.3 Calorimetry:

A substance undergoes a change in energy levels when it changes its chemical composition during a reaction. This energy change is often expressed as heat. Calorimetry is the science of studying this heat flow during a physical or chemical change and the equipment used to observe and record these changes are called calorimeters. There are many forms of calorimeters but a semi-adiabatic calorimeter has been used in this research which limits the heat losses to 100 J/(h.K) [38]. It provides a rough estimate of the heat evolution in the cement paste systems. This calorimeter works on the principle of conservation of heat. The curve of heat flow versus time can be a great indicator of the rate of hydration as well as the effects of adding unconventional materials such as Supplementary Cementitious Materials and Admixtures to the cement paste.

The hydration of cement is an extremely exothermal process which takes place in the following steps as stated by Young in 1985:

- Rapid Initial Process
- Dormant Period
- Acceleration Period
- Retardation Period
- Long-term Reactions

The heat of hydration of cement holds great importance due to its influence on the workability, setting time, pore structure, development and long term properties of concrete. The initial high heat can be credited to the hydration of the Aluminate $C_3A$ that result in Aft (Alumina, Ferric oxide and tri-sulphate) phases. This is followed by the dormant phase where hydration decreases to a minimum in about 2-3 hours. The pozzolanic activity and precipitation of Calcium Silicate Hydrate (C-S-H) gel comes next which causes another second peak. This process slows down and there are minor peaks which lead to the long term reactions. Many factors affect the heat liberated one of which is the addition of a superplasticizer. Rizwan et al state that their addition to cementitious systems delays the peaks during calorimetry [39].

## 2.12 Mixing of Cement Paste Systems:

### 2.12.1 Standard Mixing:

The constituents of concrete require thorough mixing to achieve the desired homogeneity. While this mixing takes place, the cement paste system experiences shear which has an effect on the rheological properties, hydration kinetics and the fresh state microstructure of the mix. This shearing rate needs to be accurately reproduced for the response of cement paste systems to be studied. Therefore, a standardized mixing practice is implemented that seeks to replicate the conditions faced during mixing of concrete.

The ASTM standards C305 and C1738 state practices for mixing of cement paste while the EN 196-1 represents the European Standard [40-42]. EN

196 and ASTM C305 have similar characteristics as they implement the usage of a Hobart mixer with low shearing rates (140-285rpm) while C1738 employs a high-shear mixer which has substantially higher shearing rates (up to 12000rpm). Furthermore, Williams et al, upon evaluation of the effects of hand mixing, mixing with a Hobart mixer and a Ross high shear mixer concluded that the shear rate experienced by the cement paste in the concrete mixture is most similar to the shear rate supplied through a Ross high-shear mixer. [43]

### 2.12.2 Effect of Mixing on Cement Paste:

Different types of mixing affect the fresh state and rheological properties of the cement paste as well as causing a change in the microstructure and hydration kinetics. As Han et al discovered through studying the effects of increasing shear, an increase in plastic viscosity was discovered while prolonging the high-shear protocol whereas the extension of the low-shear protocol yielded no such result. Furthermore, the high mixing intensity affected the dispersing action of Superplasticizers as well as the development of early age fresh state microstructure. Lastly, high intensity mixing caused for accelerated hydration kinetics. This acceleration was further amplified when the duration was elongated, compensating for the retarding effect of SP on the cement paste system [44].

### 2.12.3 Effect of Mixing Time:

The length of the mixing is also a very important factor for consideration due to its effect on the rheological properties as well as the microstructure of concrete. The addition of admixtures to concrete also creates a need for additional mixing time for proper dispersal. Self-consolidating concrete may require up to 90 seconds more mixing time than conventional concrete [45].

Prasittisopin and Trejo [46] observed a change in the hardened state microstructures of mortars as well as an increased 28-day porosity of mortars when they were subjected to increased mixing times and increased mixer revolutions.

M. M. Rahman et al investigated the effects of mixing time on self-compacting concrete (SCC) to discover that increased mixing also increased the amount of water required to maintain constant workability. In addition, the tensile and compressive strength of the concrete decreased as the cohesion between the constituents was affected by the heightened water/cement ratio. Furthermore, elongated mixing increased the pores in concrete, leading to high water absorption and greater chloride ion permeability [47].

Ali Raza Khalid et al observed the effects of prolonged mixing time on self-compacting cement paste systems incorporating SCMs such as Limestone, Silica Fume and Marble powder [48]. Prolonged mixing of neat cement paste was found to show little effect on its spread, showing that the yield stresses in neat cement are independent of mixing time.  However, longer mixing times increased the compressive strengths of the pastes incorporating neat cement and Fly Ash. An intermediate time of mixing gave maximum strength in the case of Marble powder but longer mixing time reduced the strengths of pastes using Silica Fume. This occurred because of the early hydration products caused by the release of $OH^-$ ions and alkalis into pore fluids which increases the evolution of heat. This early hydration is disrupted by prolonged mixing which causes a strength decrement in Silica Fume pastes.

# CHAPTER 3

# EXPERIMENTAL PROGRAM

## 3.1 General:

This study aims to study the effect of variable mixing time on the properties of self-consolidating paste systems (SCPS) using Supplementary Cementitious Materials (SCMs) in variable quantities as replacement of cement. The overall study has been divided into three main phases which are as following:

- Investigation of physical and chemical properties of materials to be used in the study
- Investigation of the properties of different blends of cement with SCMs
- Investigation of properties of formulations for different mixing times

This chapter contains the details from procurement of material to investigation different properties and different tests conducted on the established formulations.

A well-planned schematic experimental program was established to ensure the consistency of the procedures and optimization of the obtained results. The experimental program was conducted keeping all the external elements constant so that only the property under investigation can be studied. This results in credible and accurate data collection.

## 3.2 Materials Used:

The description of all the materials used in the experimentation is as following:

### 3.2.1 Cement:

The basic component of Self-Compacting Paste (SCP) is cement. The cement used in this study is Pak-CEM Ordinary Portland Cement (Grade 53). The cement was procured directly from the company and it was ensured that the bags of cement were fresh. 4 bags of cement were procured from the same production batch to ensure the consistency of chemical composition. The bags were positioned in a secure place and the cement was emptied from the bags into air-tight containers so that no moisture reaches the cement. The main chemical composition and physical properties of the cement used were found out using XRF and Particle Size Characterization and are as following:

**Table 1- Properties of Cement**

| **Sample Name** | **CEM-53** |
|---|---|
| $SiO_2$ | 19.19% |
| $Al_2O_3$ | 4.97% |
| CaO | 65.00% |
| Loss on Ignition (LOI) | 3.84% |
| Particle Size $D_{50}$(mm) | 22.4 |
| Specific Surface Area($m_2$/kg) | 544.1 |

### 3.2.2 Fly Ash (FA):

Fly Ash used in our study was EFA-Fuller® HP of class F, and it was imported from Germany. Fly Ash is the by-product of combustion of pulverized coal in furnaces of thermal-power generation plants and consists mainly of silicates, aluminates, carbon oxides and iron oxides. It was stored in an air-tight container in the laboratory. The main chemical composition and physical properties of the FA used were found out using XRF and Particle Size Characterization, and are as following:

**Table 2-Properties of Fly Ash**

| Sample Name | Fly Ash |
|---|---|
| $SiO_2$ | 59.06% |
| $Al_2O_3$ | 27.58% |
| CaO | 1.66% |
| $Fe_2O_3$ | 5.14% |
| Loss on Ignition (LOI) | 1.38% |
| Particle Size $D_{50}$($\mu$m) | 11 |
| Specific Surface Area($m_2$/kg) | 3865 |

### 3.2.3 Marble Powder (MP):

The marble powder used has been purchased from local market of Islamabad. It is a by-product of the marble manufacturing industry formed in polishing and shaping of marble slabs. White marble was purchased to ensure its purity and it was later stored in the laboratory in air-tight containers. The main chemical composition and other properties of the MP used were found out using XRF and Particle Size Characterization are as following:

**Table 3- Properties of Marble Powder**

| Sample Name | Marble Powder |
|---|---|
| $SiO_2$ | 8.32% |
| $Al_2O_3$ | 0.05% |
| CaO | 55.64% |
| Loss on Ignition (LOI) | 43.27% |
| Particle Size $D_{50}$(mm) | 5.34 |
| Specific Surface Area($m_2$/kg) | 2282 |

### 3.2.4 Limestone Powder (LSP):

Limestone used in this study is finely ground Margalla crush.Limestone was procured from local market, washed and dried, after which it was milled to reduce its size and then passed through ASTM #350 sieve. The powder that passed the said sieve was collected and stored in an air-tight container in the laboratory. The main chemical composition and other properties of the LSP used were found out using XRF and Particle Size Characterization are as following:

**Table 4- Properties of Limestone Powder**

| Sample Name | **Limestone Powder** |
|---|---|
| $SiO_2$ | 3.00% |
| $Al_2O_3$ | 0.69% |
| CaO | 52.67% |
| Loss on Ignition (LOI) | 42.24% |
| Particle Size $D_{50}$(mm) | 10.3 |
| Specific Surface Area($m_2$/kg) | 1126 |

### 3.2.5 Superplasticizer (SP):

Melflux 2651-F Super Plasticizer (SP) was used in this research project, which is a third generation, spray dried powder of a modified polycarboxilic ester.Melflux 2651-F is manufactured at Germany by BASF and exported in 1 Kg air-tight jars. The properties of Melflux 2651-F are as following:

**Table 5- Properties of Super-Plasticizers**

| | |
|---|---|
| Physical Shape | Powder |
| Color | Yellow to Brown |
| Drying Loss | Max 2.0% |
| Bulk Density | 300-600 kg/m3 |
| Recommended Dosage | 0.05-1.00% of cementitious mass |
| pH value at 20°C | 6.5-8.5 |

### 3.2.6 Water:

Tap water from Structure Laboratory was stored in the container so that to achieve uniformity in the temperature. The water temperature used throughout the experimental program was maintained at 17±1°C to minimize the variations in results because of this external factor.

## 3.3 Analysis of Material:

### 3.3.1 Particle Size Distribution:

The purpose of this test was to determine the physical properties of dry powders of OPC and SRMs. This test shows us the distribution of particle sizes of said dry powders. A small quantity of a powder is mixed with a dispersing agent which in this case was ethanol. The suspension was placed in the apparatus which gave a graphical as well as a quantitative analysis of particle size and its distribution. The test was performed in Institute of Space Technology, Islamabad.

It is known that smaller particle size of powder ensures greater surface area causing fast hydration and hence greater strength early on. At the same time well-graded powders ensure better packing and high density.

### 3.3.2 XRF:

The chemical composition of OPC and SRMs was determined using XRF which basically consists of bombarding the material with high energy X-rays. This causes the elements to emit secondary X-rays which define the characteristics of elements and hence used for identification.

The XRF was carried out at Geoscience Advance Research, Geological Survey of Pakistan.

## 3.4 Formulations:

As the literature suggests blends of Secondary Raw Materials effect the fresh and hardened state properties of paste systems. These blends have particles of varying sizes giving a filler effect, producing less porous paste along with increasing strength and durability.

The formulations that are considered in this study include are 15, 30 and 45 percent replacement of cement individually with FA, LSP and MP. One control replacement is also kept with no replacement of cement, just plain cement paste.

| | |
|---|---|
| CI-00-WD | Pure OPC |
| CI-FA15-WD | 15% OPC replaced with FA |
| CI-FA30-WD | 30% OPC replaced with FA |
| CI-FA45-WD | 45% OPC replaced with FA |
| CI-MP15-WD | 15% OPC replaced with MP |
| CI-MP30-WD | 30% OPC replaced with MP |
| CI-MP45-WD | 45% OPC replaced with MP |
| CI-LSP15-WD | 15% OPC replaced with LSP |
| CI-LSP30-WD | 30% OPC replaced with LSP |
| CI-LSP45-WD | 45% OPC replaced with LSP |

Later on the formulations that provide the better results in terms of strength are undertaken to study the effect of varying mixing time.

## 3.5 Mixing Regime

As mentioned the purpose of our research is to study the impact of varying mixing time on the properties of blends of cement and SRMs. Initially the mixing time is kept at 3 minutes for each formulation. After this mixing time was changed to 5 and 10 minutes for replacement of cement with each SRM at a percentage replacement which provided the most desirable results in terms of strength.

Both ASTM standards C305 and C1738 have defined practices for mixing of cement paste [49-50]. EN 196-1 represents the British Standard of mixing of cement paste [51]. EN 196 and ASTM C305 have similar characteristics as they implement the usage of a Hobart mixer with low shearing rates (140-285rpm). ASTM C305 states that after placing the paddle and bowl in mixing position in the mixer and introduce the materials into the bowl. Start the mixer for 30 seconds at low speed after which the mixer is stopped so that any material stuck to the side of the bowl can be scraped down. Then start the mixer again at same speed for another 30 seconds after which mixer speed is increased for the last 2 minutes of mixing. Same procedure is followed for 5 and 10 minutes mixing variations instead mixing at high speed is done for 4 and 9 minutes respectively.

## 3.6 Testing Procedures:

### 3.6.1 Determination of Standard Water Demand:

The Water Demand (WD) of the paste to achieve standard consistency is determined. It refers to the minimum amount of water required for the complete hydration of cement. This demand is found using the Vicat Apparatus. Standard consistency is achieved when the 10mm dia plunger penetrates the paste in the 40mm tall mold such that it rests (5 ± 2) mm from the base plate.

### 3.6.2 Super-Plasticizer Demand:

Super-plasticizer must be added to the cement paste is amounts such that a target flow is achieved without segregation of phases. To calculate the SP demand, the formulations were mixed at their water demand and the SP required to achieve a target flow of (30±1) cm was determined. A Hagerman's Mini-slump cone (top dia 6 cm, bottom dia 10 cm and height 7 cm) was placed over a glass surface with markings at 25cm and 30cm to carry out the experiment.

Figure 1-Hobart Mixer

Figure 2- Hagerman Cone Flow Apparatus

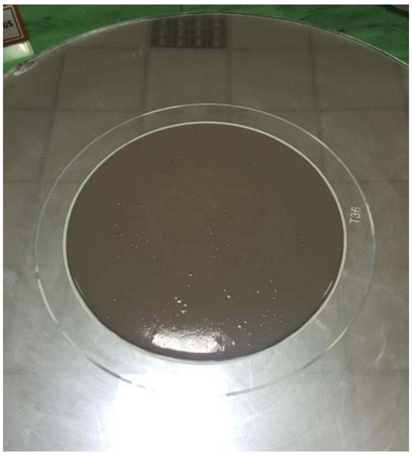

Figure 3- Observation of Spread

### 3.6.3 Flow Times:

The flow times T25 and T30 are recorded for each formulation. These are times taken to achieve the flow of 25 cm and 30 cm using Hagerman's cone of 6 x 7 x 10 $cm^3$ dimensions. The formulations are mixed at water demand and SP demand and the times are recorded using a least count of 0.01 seconds. Flow times essentially show the speed of flow and demonstrate the rate of deformation. The Hagerman's mini-slump flow cone was used for these tests.

### 3.6.4 Setting Times:

The initial and final setting times for all the formulations were determined using the Vicat apparatus. The initial setting time is elapsed when the 1mm diaVicat needle protrudes the paste such that it rests at a distance (6±1) mm from the base plate. The final setting time is achieved when the outer ring of the 3mm diaVicat needle fails to make an imprint onto the surface of the hardened paste.

**Figure 4- Vicat Needle Apparatus**

**Figure 5- Vicat Needles for Final and Initial Setting Time**

### 3.6.5 Casting and Curing:

Rectangular moulds (40x40x160mm) were used for casting. The British Standard EN-196 was used to cast our samples. Each mould was properly oiled and greased prior to pouring to ensure a perfect seal and easy removal of the samples. The samples were de-moulded after 24 hours and placed in the curing tank until the testing date.

Figure 6- SCP Mould

Figure 7- Hardened SCP in Mould

### 3.6.6 Water Absorption:

The samples were weighed immediately after de-moulding and after removal from the curing tank prior to the strength tests. The difference in their weight signified the amount of water absorbed which was used to roughly estimate the porosity of the sample. Water absorption was recorded for 7 and 28 day samples after achieving saturated surface dry condition.

### 3.6.7 Strength Testing:

The samples were tested for flexural and compressive strength 1, 7 and 28 days after mixing. 1 day strength was found immediately after de-molding whereas further strength tests were carried out after the samples were cured for the desired times and a saturated surface dry condition was achieved. A loading rate of 0.02 kN/sec was used for flexure while a rate of 0.2 kN/sec was employed for compression. The dual chamber was used to test the flexural strength which resulted in the splitting of the samples that allowed each half to be separately tested for compression afterwards.

**Figure 8- Compression Testing Machine**

### 3.6.8 Calorimetry:

Hydration of cement is a highly exothermic process. The semi-adiabatic calorimeter F-Cal 8000 was used to collect data for temperature change over two days. Each paste weighed 500g and was mixed and left inside the calorimeter cylinders for 2 days after which the logged data was extracted to plot the calorimetric curves.

Figure 9-F-Cal 8000

### 3.6.9 Variable Mixing Times:

The mixing times were increased for the replacement level of each SCM exhibiting the greatest strength to 5 and 10 minutes. Strength tests and calorimetry tests were carried out for the variable mixing time to study the effects of increasing the time for mixing.

# CHAPTER 4

# RESULTS

## 4.1 General:

Formulations with different replacement levels of OPC with Fly Ash, Limestone Powder and Marble Powder were studied using the experimental programme explained in Chapter 3. After determining the 28 day compression strengths of the initial formulations, the formulations for each SCM with the highest strength were studied with varying mixing times of 5 minutes and 10 minutes. The results of these studies are presented in this chapter.

## 4.2 Self-Compacting Pastes with SCM replacements:

The initial formulations studied to find the optimum replacement percentage are shown below. Self-Compacting Concrete Systems usually incorporate large proportions of SCMs to reduce the water demand due to filler effect [a], thus, the replacement levels as high as 45% were used.

Each formulation went through many trials and verifications in order to produce the results presented in this chapter. The testing is done at the mixing water temperature of 17 ± 1 °C. The lab temperature and relative humidity were constantly monitored and noted throughout the experimental procedures.

**Table 6-Formulation Replacement Levels**

| **Formulations** | **% OPC** | **% SCM** |
|---|---|---|
| **CI-00-WD** | 100 | 0 |
| **CI-FA15-WD** | 85 | 15 |
| **CI-FA30-WD** | 70 | 30 |
| **CI-FA45-WD** | 55 | 45 |
| **CI-MP15-WD** | 85 | 15 |
| **CI-MP30-WD** | 70 | 30 |
| **CI-MP45-WD** | 55 | 45 |

| | | |
|---|---|---|
| **CI-LSP15-WD** | 85 | 15 |
| **CI-LSP30-WD** | 70 | 30 |
| **C1-LSP45-WD** | 55 | 45 |

### 4.2.1 Water Demands:

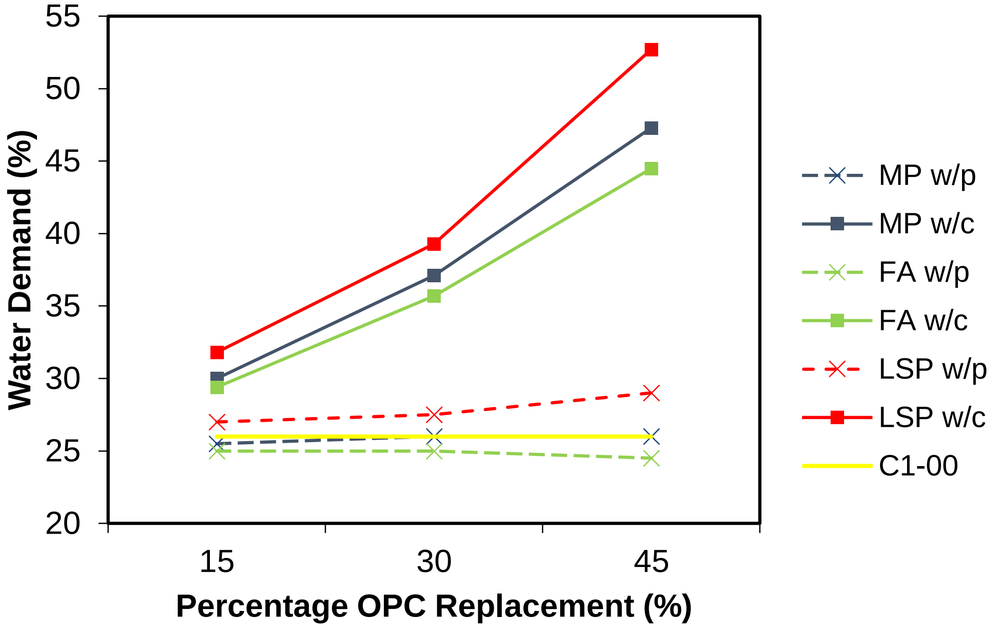

**Figure 10- Water Demand of Formulations**

Water is required for the hydration of cement and with cement replaced by SCMs, lesser water is required in the system due to the filler effect of SCMs. Water demands of all the formulations were measured with Standard Vicat Apparatus using EN-196-3. The water demand for cement paste without any SCM replacement (C1-00-WD) was found out to be 26%. The water demands with respect to paste were the same. Fly Ash showed a decrease in water/paste demand while the water/paste demand for LSP was higher than that of cement.

Water-to-cement (W/C) ratios were greater than the water/paste ratios due to the dilution theory. We can also see that with the increase in the replacement levels of SCMs, the W/C ratios increased. The highest W/C ratios were seen for LSP and the lowest were seen for FA.

### 4.2.2 Super-plasticizer Demands:

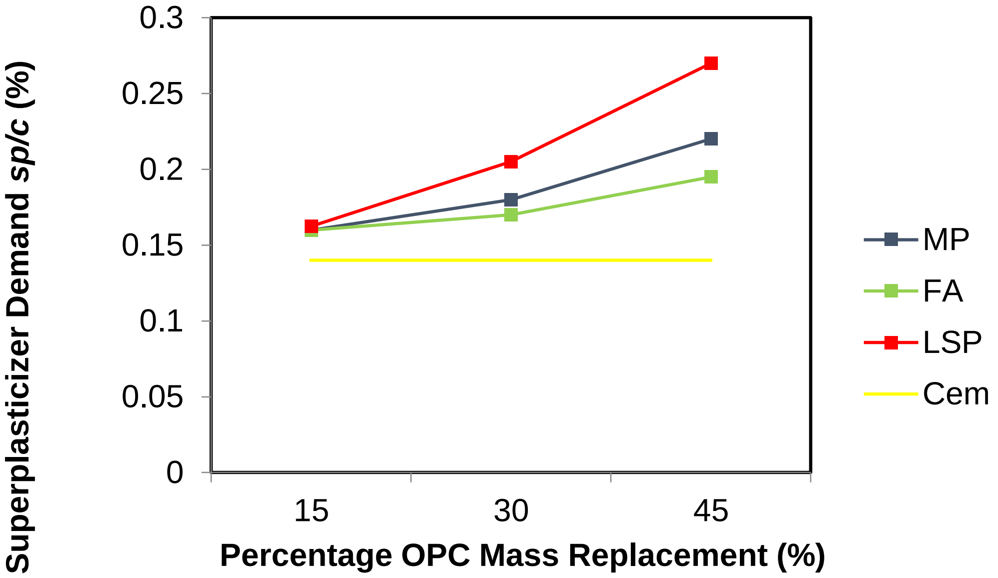

**Figure 11- Super-Plasticizer Demands of Formulations**

The Hagerman's mini slump cone was used to find superplasticiser demand for a target flow of 30±1 cm. Percentage of SP demands w.r.t cement weight are shown above. The SP demand for cement was tested to be 0.14%. In comparison to cement, all the SCMs showed higher SP demands, and these demands increased with the increase in % replacement. This can be attributed to their finer particles which resist the flow. LSP had the highest and FA had the lowest SP demand at any given replacement, owing to the difference in their particle shape and sizes.

### 4.2.3 Flow times:

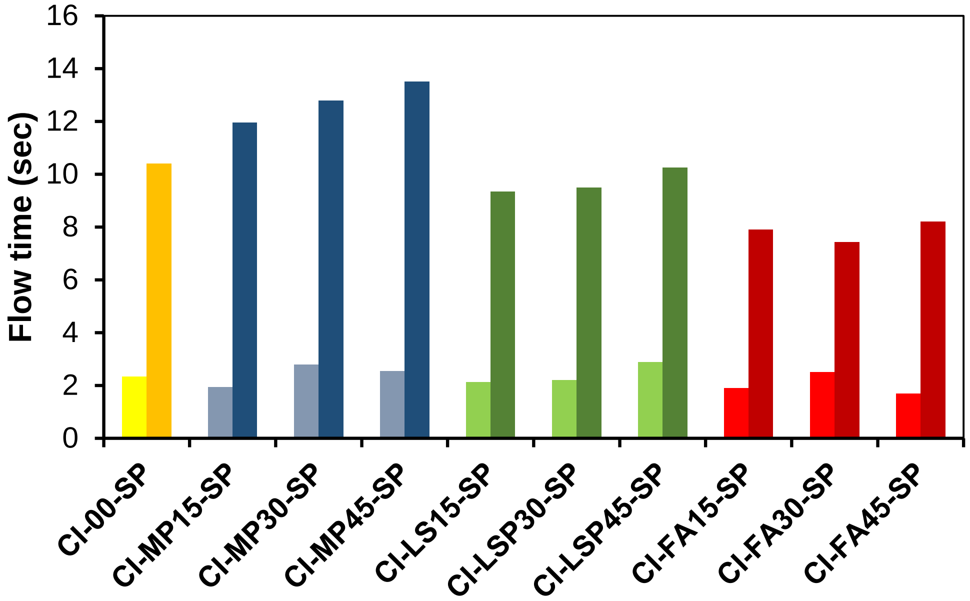

Figure 12- Flow Times OF Formulations

The times to achieve the flow diameters of 25cm and 30cm for each formulation are shown in the graph above. For each SCM, with the increase in % replacement, the flow times generally increase due to increased resistance to flow. MP has the highest flow time due to increased resistance to flow owing to its angular nature. FA shows least resistance to flow due to its spherical shape.

### 4.2.4 Setting Times:

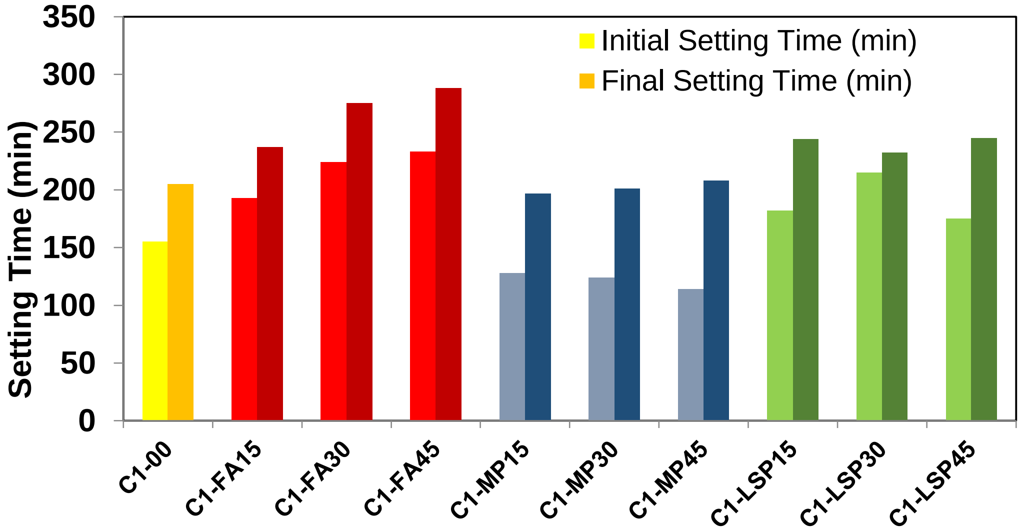

Figure 13- Setting Times of Formulations

Hydration process results in the conversion of fluid suspension of water and cement to a porous solid, resulting in setting of the mix. The hydration process starts at once with the addition of water, but cement and SCMs have different hydration speeds, which results in a variety of setting times. Setting Times were measured according to EN-196-3 and the initial and final setting times of the formulations are tabulated in the graph above. LSP and FA generally act as retarders and delay the setting process. On the other hand, MP accelerates the process of setting.

### 4.2.5 Water Absorption:

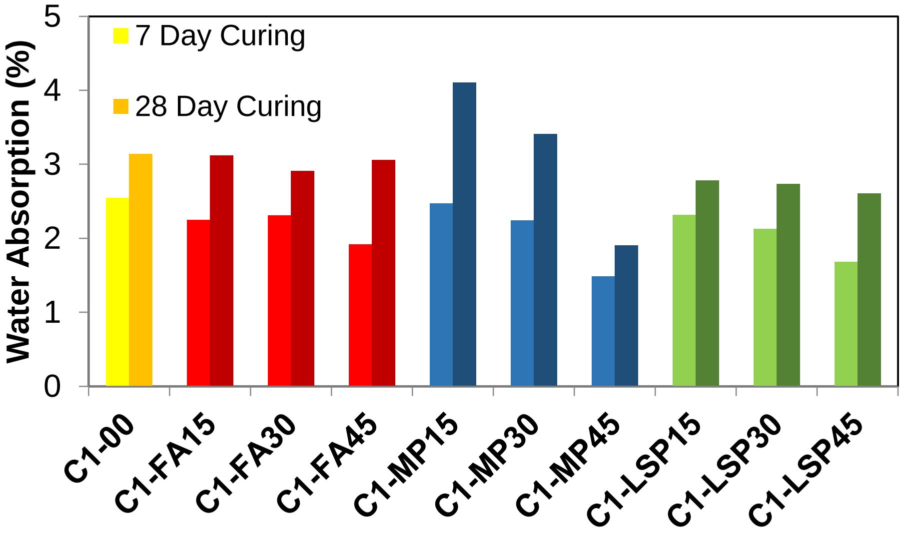

**Figure 14- Water Absorption Trends for Formulations**

Water absorption for each formulation was measured by weighing the casted prisms before and after the curing and calculating the increase in weight by water absorption as a percentage to the initial weight. Water absorption is a measure of porosity and thus the durability of the mix. Increase in the replacement levels of all the formulations decrease the water absorption to some extent, owing to their filler effect. MP has the highest porosity in its 15% replacement, which decreases to the lowest at 45% replacement. Water absorptions of MP and LSP are similar to that of plain cement.

### 4.2.6 Flexure Strengths:

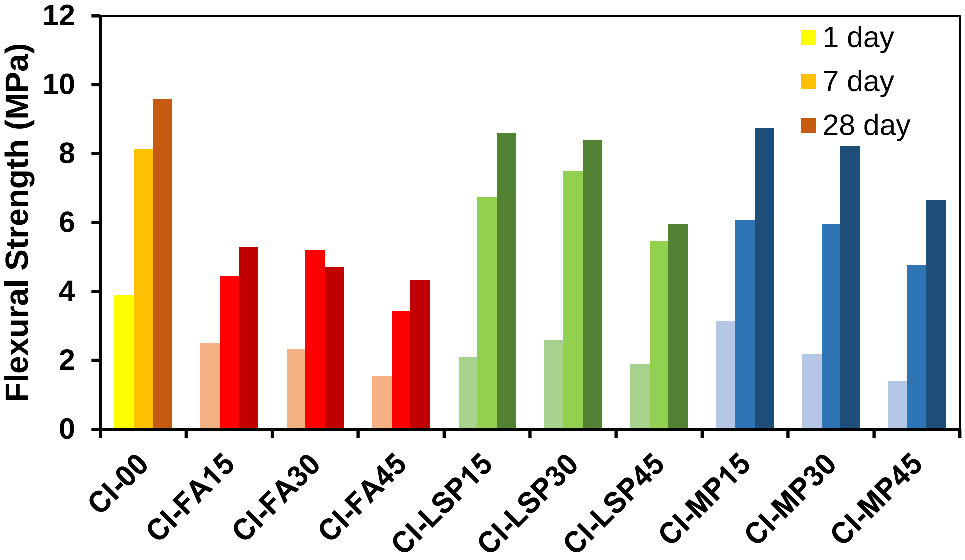

Figure 15- Flexure Strengths of Formulations

Flexure strength is a measure of the tension taken by the cement paste.

Addition of SCMs generally reduces the flexure strength, therefore plain cement showed the highest flexure strength. We can also see from the results above that with the increase in the replacement of OPC with SCMs, flexure strengths decrease for all 1, 7 and 28 days progressively.

### 4.2.7 Compression Strengths:

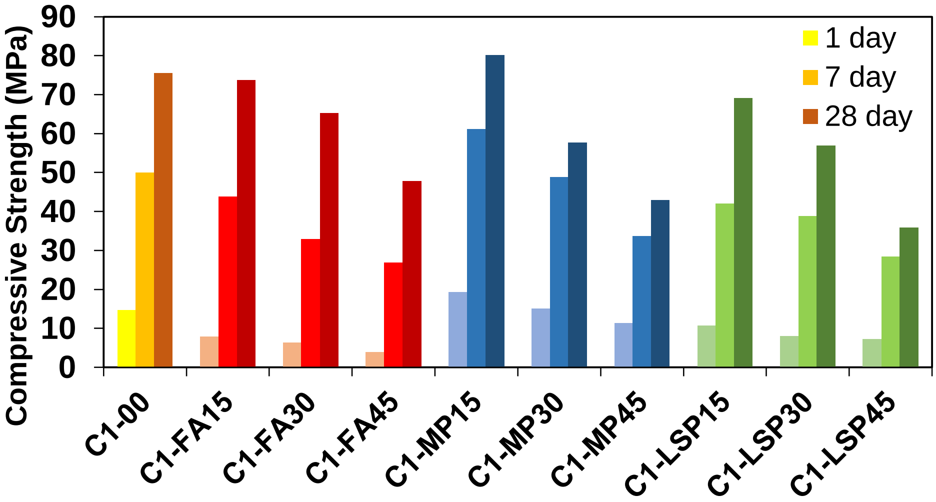

Figure 16- Compression Strength of Formulations

Compressive strength depends upon the hydration activity of cement and the SCMs. The general trend that is visible from the figure above is that with the increase in the replacement level, the compressive strengths reduce due to the dilution theory. FA and LSP have compressive strengths lower than that of MP at any replacement level.

15% replacements of all the SCMs yielded highest compression strength and the study with varying mixing times will be carried out on these formulations.

### 4.2.8 Calorimetry:

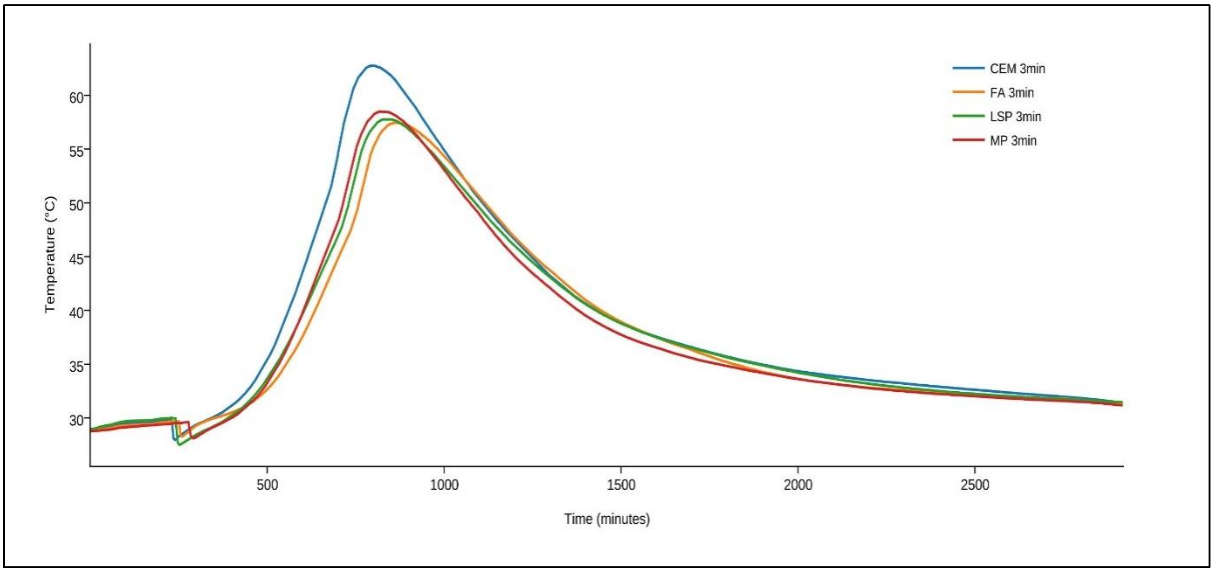

**Figure 17- Calorimetry Curves for Formulations**

Calorimetry was performed on F-Cal 8000 and software used for data logging was CalCommander. SCMs modify the hydration kinetics of the mix according to their size, shape and chemical composition. Pure cement has the highest and the earliest peak compared to all the other SCMs, which can be explained by dilution theory. Of all the SCMs, MP has the highest and earliest peak because of its role in the hydration kinetics.

## 4.3 Self-Compacting Paste Systems with Varying Mixing Times:

Effects of varying mixing times on different properties of Self-compacting Paste System were studied using the formulations for each SCM which yielded the highest compressive strengths in the initial stage. The formulations are:

C1-MP15-WD, C1-LSP15-WD, C1-FA15-WD and C1-00-WD (as the control formulation). The mixing times were increased from 3 minutes to 5 minutes and 10 minutes. The tests were carried out keeping water demand, superplasticizer demand and all other parameters same as before while changing mixing times.

### 4.3.1 Water Absorption:

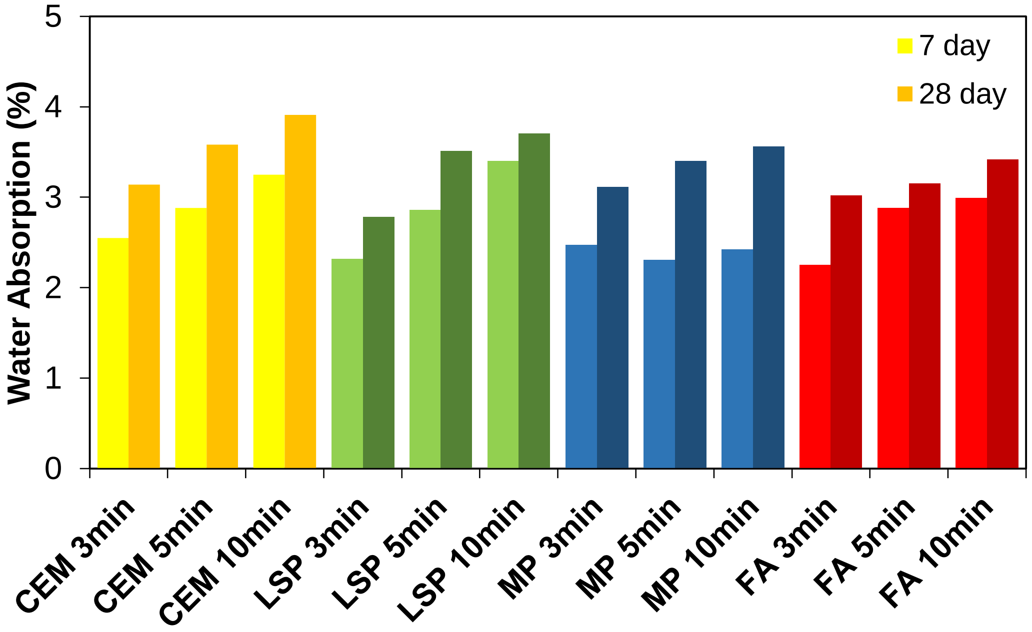

**Figure 18- Trends of Water Absorption with Varying Mixing Times**

Water absorption is a measure of porosity of the microstructure. We can see that with the increase in mixing time, water absorption increased for all the formulations due to greater entrainment. Cement has the highest water absorption at any mixing time. This can be explained due to the filler effect of the SCMs.

### 4.3.2 Flexure Strengths:

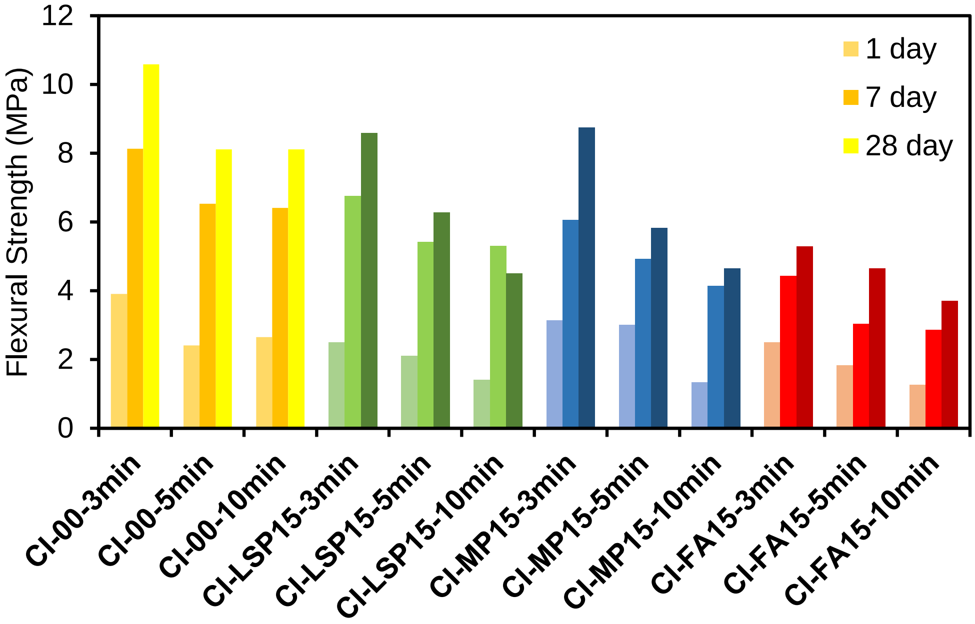

Figure 19- Trends of Flexure Strength with Varying Mixing Times

The increase in mixing time resulted in a decrease in the flexure strength, and this trend is visible for every formulation. Cement yields highest flexure strengths compared to all the SCMs at any mixing time and FA yields the lowest flexure strengths.

### 4.3.3 Compression Strengths:

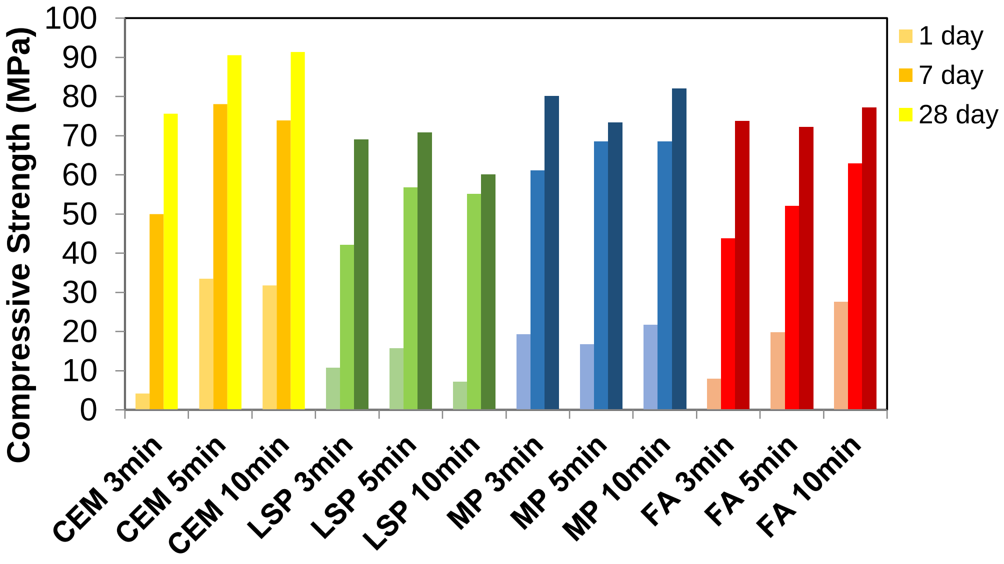

Figure 20- Trends of Compressive Strength with Varying Mixing Times

Compression strength depends upon the hydration kinetics of the mix. From the figure above we can evaluate that increasing the mixing time has a positive effect on the all the compression strengths (1, 7 and 28 day) progressively. This may be the result of increased interaction between the particles due to enhanced mixing, resulting in a faster hydration process.

### 4.3.4 Calorimetry:

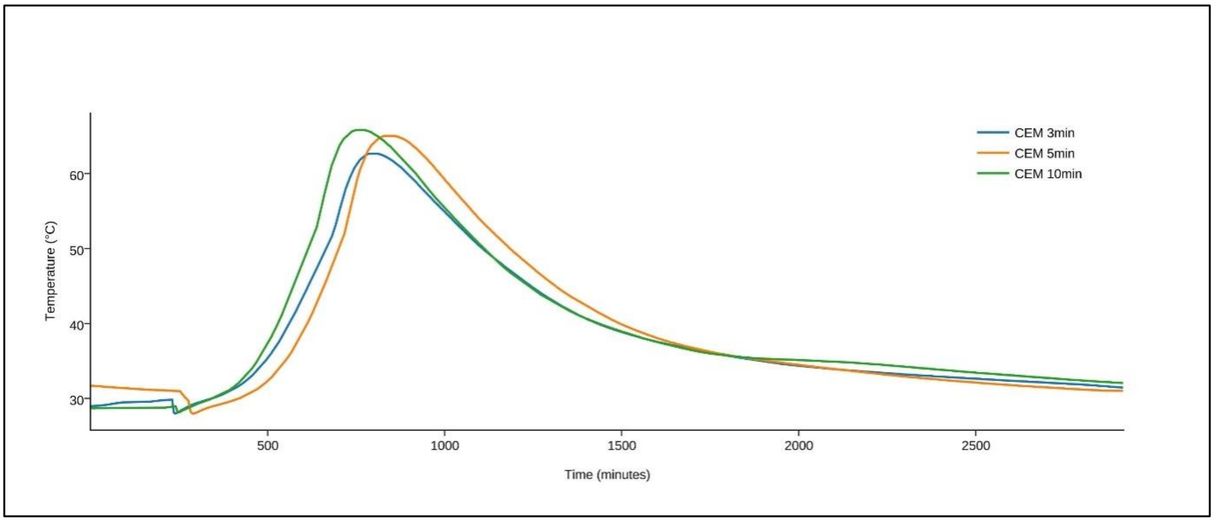

Figure 21- Calorimetry Curves for Cement with Varying Mixing Times

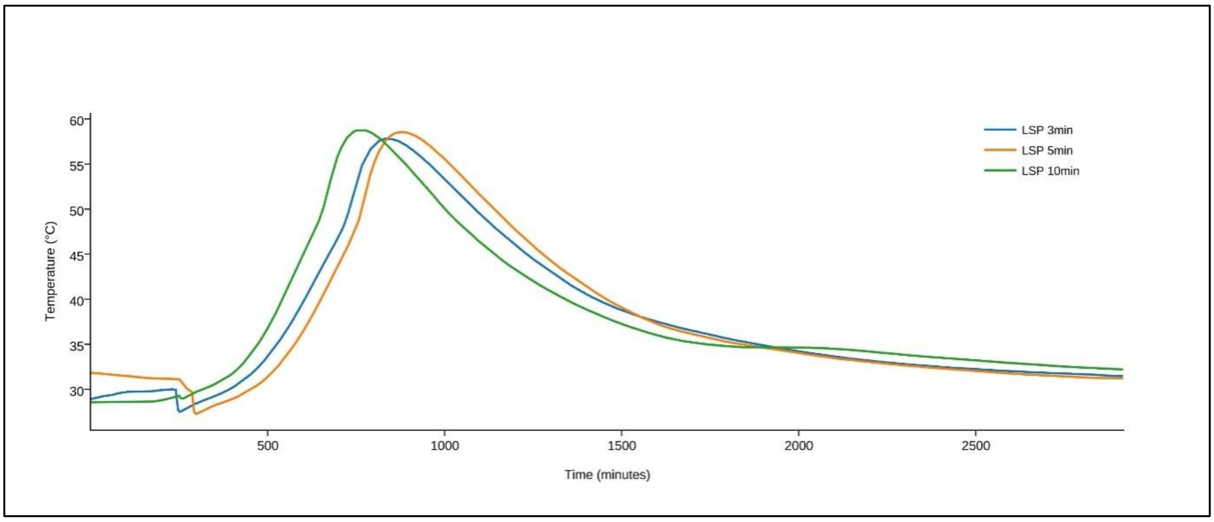

Figure 22- Calorimetry Curves for Limestone Powder with Varying Mixing Times

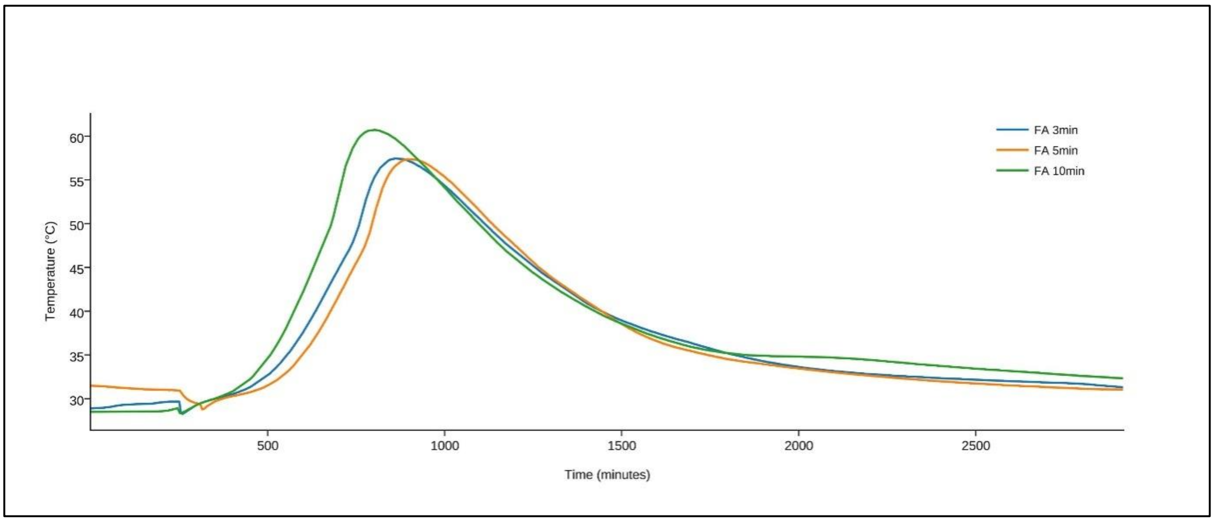

Figure 23- Calorimetry Curves for Fly Ash with Varying Mixing Times

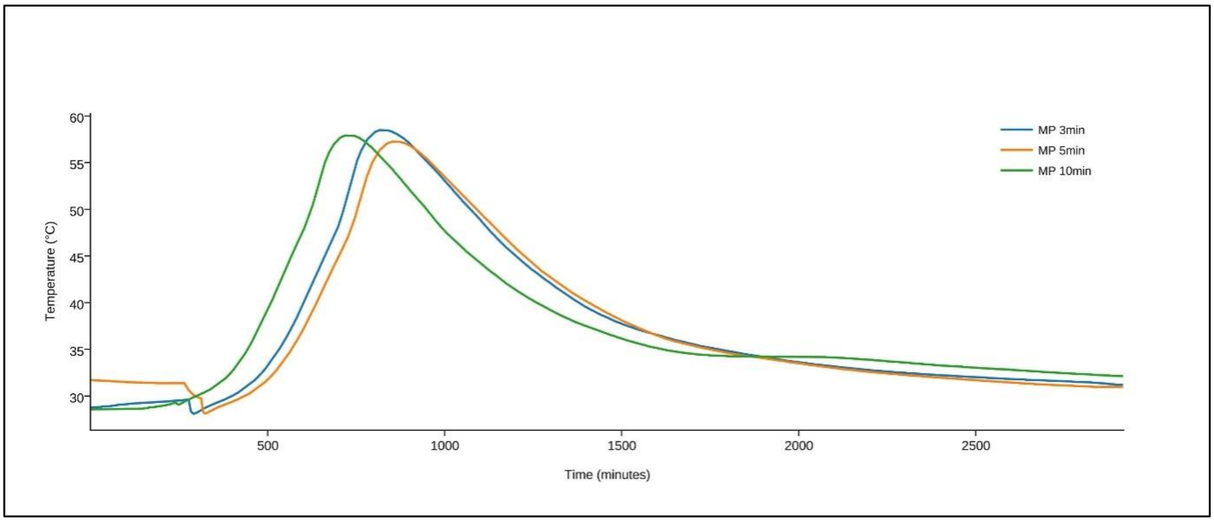

Figure 24- Calorimetry Curves for Marble Powder with Varying Mixing Times

The results of calorimetry for our four formulations at 3, 5 and 10 minutes mixing times can be compared from the series of figures above. 10 minutes mixing generally resulted in highest and earliest hydration for all the formulations.

# CHAPTER 5

# DISCUSSION

This chapter focuses on the explanations of results obtained and tabulated in the previous chapter. The addition of SCMs to the Self-Compacting Paste Systems alter the properties of the system in many ways and this chapter deals with those variation in results and the characteristics of SCMs that lead to such variation.

Self-compacting paste is partially replaced with the SCMs (Fly Ash, Marble Powder and Limestone Powder) at different mixing times. SCMs have physical and chemical influence on the properties of the mix because of their shape, size, and chemical composition. SCMs alter the hydration kinetics mainly through the dilution theory, the filler effect, by providing nucleation sites and by addition of $Ca^+$ ions in the hydration mix.

The SCMs stated before at different replacement levels and mixing times are discussed below with respect to water demand, superplasticizer demand, setting times, strength, water absorption, and calorimetry.

## 5.1 Water Demands:

Water demands were calculated in the terms of both water/paste ratios and water/cement ratios. The general trend that SCMs show for water/paste ratios is that with the partial replacement of OPC with SCMs in the paste, water/paste ratio decreases because of the filler nature of SCMs. SCMs are very fine particles which fill the pores between the cement particles and improve the packing of the mix, thus reducing the water demand. This trend is followed by Fly Ash whose spherical particles reduce the internal friction due to the ball-bearing effect and the fineness of its particles results in better packing of the cement mix, thus reducing the water demand for FA.

The water reducing rate increases with the level of FA replacement. The Fly Ash actually function as a kind of mineral water reducers and we can observe from the results that increasing the FA replacement further reduces the water/paste ratio. MP and LSP are both angular particles thus their water/paste ratio is greater than that of FA at any given replacement. Due to small size of MP it has a greater filler effect, but due to greater size of LSP the filler effect is lesser and thus it has a greater water demand as compared to both MP and FA.

Water/cement ratios are higher compared to water/paste ratios at any point because of the dilution effect. The dilution effect is a consequence of the replacement of cement by SCMs and results in an increase in the water/cement ratio as at any given water/paste ratio, greater amount of water is available for the cement in the system.

## 5.2 Super-Plasticizer Demand:

SCMs have finer particle sizes, this increases the surface area, causing higher viscosity and resistance to flow. Presence of SCMs densify the microstructure, decreasing the deformability and resist the spread of the paste system. Therefore, the target flow is achieved with greater amount of superplasticizer when quantity of SCMs in the system is increased.

Results show that FA has the least SP demand of all the SCMs at any given replacement level due to the ball-bearing effect caused by its spherical nature which reduces the resistance to flow. On the other hand, MP and LSP show very high SP demands due to their angular microstructures. LSP has the highest SP demand which can be justified because of its immense angular nature and large particle size compared to MP, minimizing the lubricant effect.

## 5.3 Setting Times:

When cement particles dissolve in water, there is a growth of ionic concentration of mainly $Ca^+$ ion, which leads to formation of Hydration products in the solution. After reaching a specific concentration, these hydration compound precipitate out. Densification of these products cause setting of cement.

Different SCMs have different effects on the setting times because of their diverse behaviour in the hydration kinetics. FA act as a retarder and delays the setting time of the cement mix. FA particles absorb calcium ions on their surface, which inhibits calcium ions concentration build-up in the paste during early hydration, resulting in the prolonged setting time. Increase in the replacement of FA further delays the setting time.

LSP acts as retarder mainly because of the dilution theory as LSP plays no major role in the hydration kinetics of the cement mix except in the very early stage. Replacement of OPC with LSP reduces the amount of cement in the mix, diluting the cement concentration, which delays the built-up of hydration particles, and prolongs the mechanism of setting.

MP shows a very different behaviour than the other two SCMs as it acts as an accelerator. This is mainly because MP has a very high calcium content. MP provide Ca+ ions to the solution which speeds up the setting time by increasing nucleation and growth of hydration products. Increasing the replacement level further doesn’t have a pronounced effect on the setting.

## 5.4 Water Absorption:

Water absorption is a measure of porosity of the paste system. SCMs are known to reduce the water absorption owing to their filler effect. They improve the internal packing of the system and thus increase the durability. Results of water absorption in the previous chapter displayed this trend when the presence of LSP and FA reduced the water absorption. Increasing the replacement levels further reduce the water absorption for all the SCMs because of the improved filler effect, leading to better internal packing.

When the effect of varying mixing times was observed on the porosity of the cement mix, the results we obtained showed that increase in the time of mixing resulted in an increase in water absorption. This can be justified by the fact that when the mixing time is increased, air-entrainment increases due to excessive shearing, which results in greater quantity of pores which can absorb water and therefore, the porosity is reduced.

## 5.5 Compression Strength:

Strength development is dependant on the hydration kinetics of the cement and the SCMs. SCMs that don't play a role in the hydration kinetics decrease the overall compressive strength of the paste due to the dilution theory, which has been explained earlier.

LSP and FA don't have a major role in hydration, as they mainly act as filler or provide nucleation sites for cement hydrate crystals and their replacements result in strengths lower than that of cement. Limestone particles can act as nucleation sites for reactions in the first stages of the hydration, however, at later stages, LSP acts only as inert filler and play no role in strength development of the hardened paste.

MP at lower replacement gives compression strength greater than that of cement as it plays a noticeable role in the hydration kinetics of the paste. MP is rich in calcium and it provides more Ca+ ions to the cement slurry thus providing greater quantity of hydration products(C-S-H and C-H) and ettringite. Additional surface area provided MP also provides sites for the nucleation and growth of hydration products that leads to further increase in strength. Decrease in the strength when the replacement level in increased can be justified by the dilution effect.

Increased mixing time shows a positive effect on the strength development for all the formulations. With the increase in mixing time, the inter-particle contact increases, which speeds up the hydration mechanism. More hydration products are formed faster, resulting in an enhanced strength development.

## 5.6 Calorimetry:

Calorimetry graphs provide an insight of hydration activity, setting times, and effect of admixtures added to cement. The addition of SCMs cause lower and delayed energy release as lesser hydration occurs in the system due to lower cement content. With increase in SCM replacements, the peaks of calorimetry occur late and are lower compared to that of cement, because of the dilution effect.

Increase in mixing times generally speed up the hydration reaction, resulting in high and faster evolution of heat. Therefore, the peak of energy release corresponding to 10 minute mixing in all the formulations is highest and earliest compared to other mixing times.

# CHAPTER 6

## CONCLUSION

After the literature review, detailed experimentation, data collection and the analysis of results, the study can be concluded by the following main points:

- The addition of SCMs to the cement mix increases the water/cement ratio and the superplasticizer demands.
- LSP and FA act as retarders while MP acts as an accelerator in the setting of the paste.
- LSP and FA reduce the porosity of the paste system when all the other conditions and parameters re constant.
- For each SCM, formulations with 15% replacement gave the highest strengths and these replacements (CI-00, CI-FA15, CI-MP15, and CI-LSP15) were used to study the effects of varying mixing times.
- As a general trend, increasing the mixing time increases the porosity of the cement mix.
- Extended mixing time resulted in retarded rheological properties of the paste.
- Increasing mixing time results in faster and increased hydration the cement mix.
- Higher mixing time also has a positive impact on the compressive strengths as the strengths increase gradually with increasing the mixing time.
- Highest strengths were achieved through CI-00 10 minute mixing and CI-MP15 10 minute mixing.

# ANNEXURE-A

## Physical and Chemical Characteristics of Materials

### Table 7 A-1 Physical Properties of Cementitious Materials

| Properties | CEM-53 | Fly Ash | Marble Powder | Limestone Powder |
|---|---|---|---|---|
| **Physical State** | Powder | Powder | Powder | Powder |
| **Particle Size (D50)** | 22.40 µm | 11.00 µm | 5.34 µm | 10.30 µm |
| **Colour** | Dark Grey | Grey | White | Light Grey |

### Table 8 A-2 Chemical Composition of Cementitious Materials

| Sample | CEM-53 | Fly Ash | Marble Powder | Limestone Powder |
|---|---|---|---|---|
| **$SiO_2$** | 19.19% | 59.06% | 8.32% | 3.00% |
| **$Al_2O_3$** | 4.97% | 27.58% | 0.05% | 0.69% |
| **CaO** | 65.00% | 1.66% | 55.64% | 52.67% |
| **$Fe_2O_3$** | 3.27% | 5.14% | 0.02% | 27.00% |
| **$TiO_2$** | 0.29% | 1.58% | 0.00% | 0.04% |
| **MnO** | 0.04% | 0.05% | 0.00% | 0.01% |
| **MgO** | 2.23% | 1.27% | 0.28% | 0.67% |
| **$K_2O$** | 0.51& | 1.59% | 0.01% | 0.10% |
| **$Na_2O$** | 0.58% | 0.54% | 0.30% | 0.30% |
| **$P_2O_5$** | 0.08% | 0.15% | 0.11% | 0.00% |
| **Loss on Ignition** | 3.84% | 1.38% | 43.27% | 42.24% |

# ANNEXURE-B

## Self-Compacting Paste Systems with Mixing Time of Three minutes

Table 9 B-1 Formulations

| Formulations | % OPC | % SCM |
|---|---|---|
| **CI-00** | 100 | 0 |
| **CI-FA15** | 85 | 15 |
| **CI-FA30** | 70 | 30 |
| **CI-FA45** | 55 | 45 |
| **CI-MP15** | 85 | 15 |
| **CI-MP30** | 70 | 30 |
| **CI-MP45** | 55 | 45 |
| **CI-LSP15** | 85 | 15 |
| **CI-LSP30** | 70 | 30 |
| **CI-LSP45** | 55 | 45 |

## Table 10 B-2 Water Demands

## Percentage of Cement and Powder Mass

| Percentage Replacement | MP w/p | MP w/c | FA w/p | FA w/c | LSP w/p | LSP w/c | CI-00 |
|---|---|---|---|---|---|---|---|
| **15** | 25.5 | 30.0 | 25.0 | 29.4 | 27.0 | 31.8 | 26.0 |
| **30** | 26.0 | 37.1 | 25.0 | 35.7 | 27.5 | 39.3 | 26.0 |
| **45** | 26.0 | 47.3 | 24.5 | 44.5 | 29.0 | 52.7 | 26.0 |

## Table 11 B-3 Super Plasticizer Demand

## Percentage Cement Mass

| Percentage Replacement | MP | FA | LSP | CEM-53 |
|---|---|---|---|---|
| **15** | 0.16 | 0.16 | 0.1625 | 0.14 |
| **30** | 0.18 | 0.17 | 0.205 | 0.14 |
| **45** | 0.22 | 0.195 | 0.27 | 0.14 |

Table 12 B-4 Flow Times

| Formulations | T25 (Seconds) | T30 (Seconds) |
|---|---|---|
| CI-00-SP | 2.34 | 10.4 |
| CI-MP15-SP | 1.94 | 11.96 |
| CI-MP30-SP | 2.8 | 12.8 |
| CI-MP45-SP | 2.54 | 13.51 |
| CI-LS15-SP | 2.12 | 9.34 |
| CI-LSP30-SP | 2.21 | 9.49 |
| CI-LSP45-SP | 2.9 | 10.25 |
| CI-FA15-SP | 1.9 | 7.9 |
| CI-FA30-SP | 2.51 | 7.43 |
| CI-FA45-SP | 1.69 | 8.21 |

## Table 13 B-5 Setting Times

| Formulation | Initial Setting Time (min) | Final Setting Time (min) |
|---|---|---|
| CI-00 | 155 | 205 |
| CI-FA15 | 193 | 237 |
| CI-FA30 | 224 | 275 |
| CI-FA45 | 233 | 288 |
| CI-MP15 | 128 | 197 |
| CI-MP30 | 124 | 201 |
| CI-MP45 | 114 | 208 |
| CI-LSP15 | 182 | 244 |
| CI-LSP30 | 215 | 232 |
| CI-LSP45 | 175 | 245 |

Table 14 B-6 Water Absorption

| Formulations | 7 Day Curing (%) | 28 Day Curing (%) |
|---|---|---|
| CI-00 | 2.55 | 3.14 |
| CI-FA15 | 2.25 | 3.12 |
| CI-FA30 | 2.31 | 2.91 |
| CI-FA45 | 1.92 | 3.06 |
| CI-MP15 | 2.47 | 4.11 |
| CI-MP30 | 2.24 | 3.41 |
| CI-MP45 | 1.49 | 1.91 |
| CI-LSP15 | 2.32 | 2.78 |
| CI-LSP30 | 2.13 | 2.74 |
| CI-LSP45 | 1.68 | 2.61 |

Table 15 B-7 Compressive Strengths

| Formulations | 1-Day (MPa) | 7-Day (MPa) | 28-Day (MPa) |
|---|---|---|---|
| **CI-00** | 14.7 | 50.0 | 75.6 |
| **CI-FA15** | 7.9 | 43.8 | 73.7 |
| **CI-FA30** | 6.3 | 32.9 | 65.2 |
| **CI-FA45** | 3.9 | 26.9 | 47.8 |
| **CI-MP15** | 19.3 | 61.2 | 80.1 |
| **CI-MP30** | 15.1 | 48.9 | 57.7 |
| **CI-MP45** | 11.3 | 33.7 | 43.0 |
| **CI-LSP15** | 10.7 | 42.1 | 69.1 |
| **CI-LSP30** | 8.0 | 38.9 | 56.9 |
| **CI-LSP45** | 7.3 | 28.4 | 35.9 |

Table 16 B-8 Flexural Strengths

| **Formulations** | **1-Day (MPa)** | **7-Day (MPa)** | **28-Day (MPa)** |
|---|---|---|---|
| **CI-00** | 3.91 | 8.13 | 9.59 |
| **CI-FA15** | 2.50 | 4.44 | 5.28 |
| **CI-FA30** | 2.34 | 5.19 | 4.70 |
| **CI-FA45** | 1.56 | 3.44 | 4.34 |
| **CI-LSP15** | 2.10 | 6.75 | 8.59 |
| **CI-LSP30** | 2.59 | 7.50 | 8.40 |
| **CI-LSP45** | 1.88 | 5.47 | 5.94 |
| **CI-MP15** | 3.13 | 6.06 | 8.75 |
| **CI-MP30** | 2.19 | 5.97 | 8.22 |
| **CI-MP45** | 1.41 | 4.75 | 6.66 |

# ANNEXURE-C

## Self-Compacting Paste Systems with Varying Mixing Time

Table 17 C-1 Water Absorption

| Formulations | 7-Day Curing (%) | 28-Day Curing (%) |
|---|---|---|
| **CEM 3min** | 2.55 | 3.14 |
| **CEM 5min** | 2.88 | 3.58 |
| **CEM 10min** | 3.25 | 3.91 |
| **LSP 3min** | 2.32 | 2.78 |
| **LSP 5min** | 3.26 | 3.51 |
| **LSP 10min** | 1.76 | 3.4 |
| **MP 3min** | 2.47 | 4.11 |
| **MP 5min** | 2.31 | 2.96 |
| **MP 10min** | 2.42 | 3.36 |
| **FA 3min** | 2.25 | 3.02 |
| **FA 5min** | 2.88 | 3.15 |
| **FA 10min** | 2.59 | 2.82 |

Table 18 C-2 Compressive Strength

| Formulations | 1-Day (MPa) | 7- Day (MPa) | 28- Day (MPa) |
|---|---|---|---|
| **CEM 3min** | 4.17 | 50 | 75.6 |
| **CEM 5min** | 33.5 | 78.1 | 90.6 |
| **CEM 10min** | 31.8 | 73.9 | 91.4 |
| **LSP 3min** | 10.7 | 42.1 | 69.1 |
| **LSP 5min** | 15.7 | 56.8 | 70.8 |
| **LSP 10min** | 7.2 | 55.2 | 60.1 |
| **MP 3min** | 19.3 | 61.2 | 80.1 |
| **MP 5min** | 16.78 | 68.5 | 73.3 |
| **MP 10min** | 21.7 | 68.6 | 82.1 |
| **FA 3min** | 7.9 | 43.8 | 73.7 |
| **FA 5min** | 19.8 | 52 | 72.2 |
| **FA 10min** | 27.6 | 63 | 77.2 |

### Table 19 C-3 Flexural Strength

| Formulations | 1-Day (MPa) | 7-Day (MPa) | 28-Day (MPa) |
|---|---|---|---|
| CI-00-3min | 3.91 | 8.31 | 10.59 |
| CI-00-5min | 2.41 | 6.53 | 8.11 |
| CI-00-10min | 2.65 | 6.41 | 8.11 |
| CI-LSP15-3min | 2.50 | 6.75 | 8.59 |
| CI-LSP15-5min | 2.11 | 5.42 | 6.28 |
| CI-LSP15-10min | 1.41 | 5.30 | 4.50 |
| CI-MP15-3min | 3.13 | 6.06 | 8.75 |
| CI-MP15-5min | 3.00 | 4.92 | 5.83 |
| CI-MP15-10min | 1.33 | 4.14 | 4.64 |
| CI-FA15-3min | 2.50 | 4.44 | 5.28 |
| CI-FA15-5min | 1.82 | 3.03 | 4.65 |
| CI-FA15-10min | 1.26 | 2.86 | 3.70 |

# ANNEXURE-D

## Particle Size Analysis

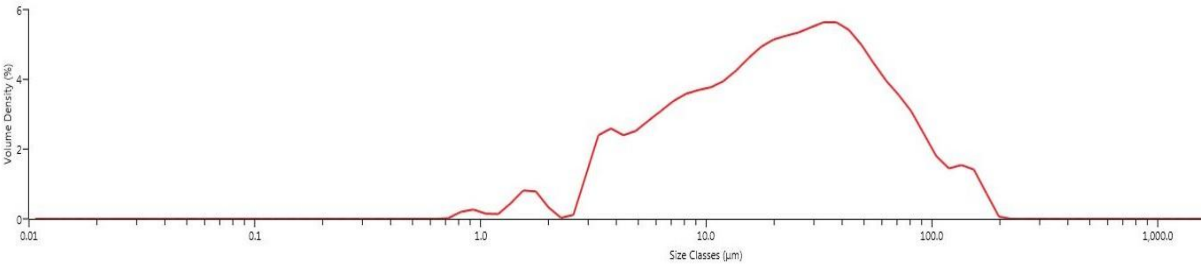

Figure 25- Particle Size Analysis of Cement

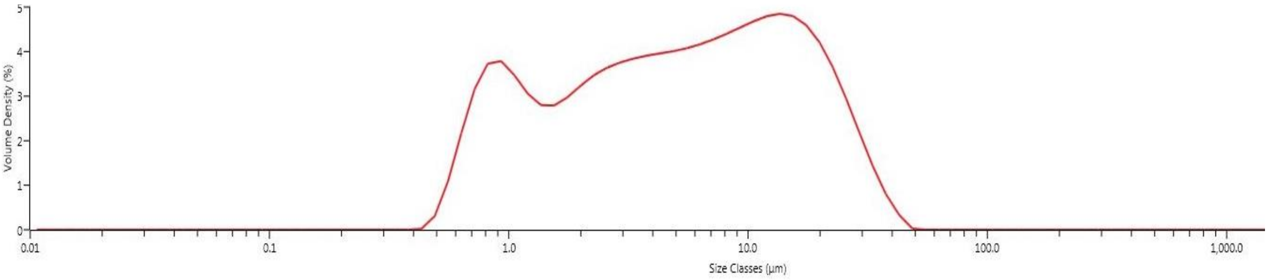

Figure 26-Particle Size Analysis of Marble Powder

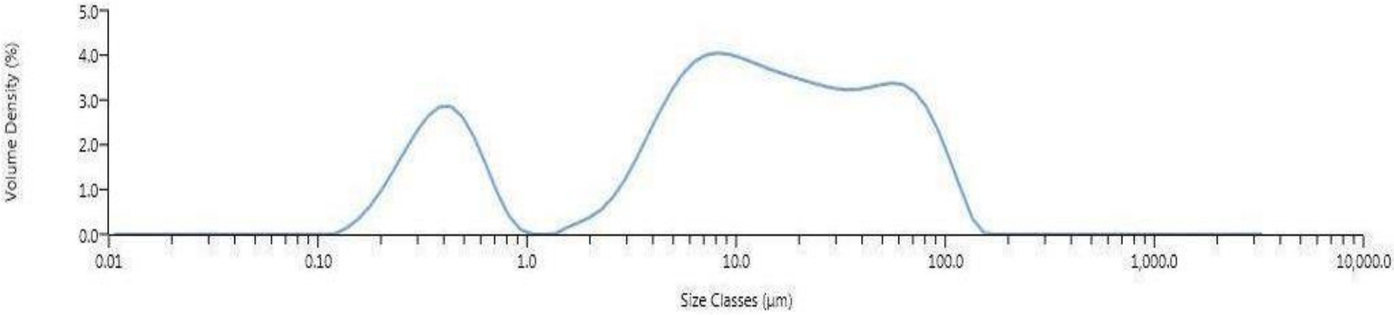

Figure 27-Particle Size Analysis of Fly Ash

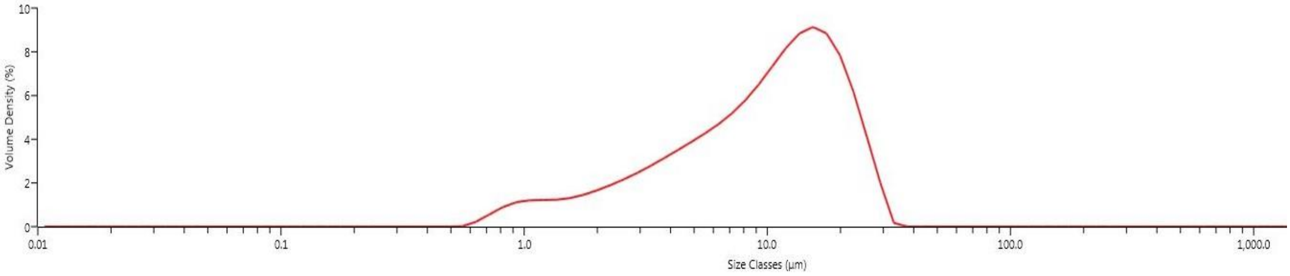

Figure 28-Particle Size Analysis of Limestone Powder

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