INFLUENCE OF FLY ASH AND LIMESTONE POWDER ON THE PROPERTIES OF SELF-COMPACTING PASTE SYSTEMS UNDER VARIABLE MIXING WATER TEMPERATURES



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This is to certify that the

Final Year Project, titled

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ABSTRACT

ACI 237R – 07 defines Self-Compacting Concrete (SCC) as "a highly flowable, non-segregating concrete that can spread into place, fills the formwork, and encapsulates the reinforcement without any mechanical consolidation". The salient characteristics of SCC include high deformation and high resistance to bleeding and segregation, the two opposite properties that are to be met with. Applications of SCC includes placements that have congested and heavy reinforcements such as pile foundations, raft foundations, bridge piers, tunnel linings, skyscrapers, aircraft runways, pre-stressed concrete sections and transportation structures etc. SCC is known for their uniform compaction and hence uniform durability.

The aim of this research was to know the response of SCPs using partial replacement of Cement by Fly Ash (FA) and Limestone Powder (LSP) under the influence of variable mixing water temperature. The parameters investigated were Water Demand (WD), Super Plasticizer Demand (SPD), Initial & Final Setting Times, Flow Times, Compression and Flexure Strengths of prisms having dimensions of 4x4x16 cm at 1, 3, 7, 28 and Calorimetry.

Test results showed an overall increase in WD (w.r.t % W/C, cement mass) as percentage replacement of SRMs increased because of small particle size of SRMs, which increases the total powder surface area. SPD (% cement mass) also increased for the target flow of 30 ± 1 cm when the replacement percentage of OPC by SRMs was increased. Formulations were cast, cured and tested in SSD condition as per EN 196-1 standards. The early strength of SCP formulations containing FA decreased as compared to that of pure OPC and LSP. However, 28 days strengths of formulations containing FA are appreciably high. It can be explained due to the pozzolanic behavior of FA. LSP gave higher early strengths than OPC and FA. 20% replacements of OPC by FA and LSP have shown highest compressive strengths among all FA and LSP formulations. Therefore, FA20 and LSP20 were selected for studying the response of variable mixing water temperatures. To match the average climatic conditions of Pakistan, control temperature of 20°C was selected. A lower temperature of 10°C and a higher temperature of 30°C were selected. SP demand (% cement mass) tends to decrease with increase in temperature. Generally, temperature of 30°C showed more compressive strengths.

The overall outcome of this study is the affirmation of the positive outcomes of SRM replacement in terms of strength, flowability and segregation-resistance. Cement production could be minimized due to SRM replacements and as a result, CO_2 emissions would reduce. Subsequently, we end up with a product having more strength, workability, segregation resistance, flowability than conventional concrete that can be used on large scale placements, reducing both labor cost as well as section dimensions.

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LIST OF ABBREVIATIONS

SCCS	Self-Compacting Cementitious System
SCC	Self- Compacting Concrete
SCPS	Self-Compacting Paste System
SCMS	Self-Compacting Mortar System
FA	Fly Ash
LSP	Limestone Powder
ACI	American Concrete Institute
ASTM	American Society for Testing and Materials
WD	Water Demand
w/c	Water to Cement Ratio
СН	Calcium Hydroxide
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
SP	Super Plasticizer
SRM	Secondary Raw Materials
OPC	Ordinary Portland Cement
PSD	Particle Size Distribution
BET	Brunauer-Emmett-Teller
SAA	Surface Area Analysis
ND	Not Determined
C_3S	Tri Calcium Silicate
C_2S	Di Calcium Silicate

CHAPTER - 1

INTRODUCTION

1.1 General:

The word concrete came from the Latin word "concretus", which means compact or condensed. Concrete is a composite material made by mixing binder, aggregate, water and mineral and/or chemical admixtures. It is the most widely used construction material all over the world because of its durability, economy and its ability to be cast in any desired shape. Concreting process, using conventional concrete, requires heavy compaction by skilled labor. If compaction is not done properly, it may reduce the strength of concrete. Therefore, now a days, conventional concrete is being rapidly replaced by SCC throughout the world as less skilled-labor is required for its placement because of its high flowability.

1.2 Self Compacting Concrete:

Self-Compacting Concrete (SCC) or Self Consolidating Concrete, is a type of concrete that is highly deformable but, at the same time, it is highly resistant to segregation. ACI committee 237R-07 defines SCC as: "A highly flowable, non-segregating concrete that can spreads into place, fills the formwork, and encapsulates the reinforcement without any mechanical consolidation"

The need of this type of concrete was proposed by Okamura in 1986 in Japan because of the durability problems of concrete structures. Then studies for developing such concrete were carried out by Maekawa and Ozawa at University of Tokyo. So, SCC was first developed in Japan in 1988.

In recent years, SCC is replacing conventional concrete rapidly because of its many advantages and wider applications.

Some advantages of SCC over conventional concrete include:

- High flowability
- Resistant to segregation
- Requires less labor
- No vibration is required during placement into forms

- More efficient and faster placement of concrete
- Less heat generated per unit weight due to low cement content.

SCC finds its application in many areas of construction industry. Some important applications of SCC are:

- Situations in which mechanical vibration is not possible or is uneconomical
- Tunnels
- Pre-stressed concrete
- Concreting in heavily reinforced members
- Columns of high-rise buildings
- Long span modern bridges

1.3 Secondary Raw Materials:

Secondary Raw Materials (SRMs) are also known as Supplementary Cementitious Materials (SCMs), Powders or Fillers depending upon their role in fresh and hardened state. These are mainly industrial by-products, requiring little or no pyroprocessing. They help in the advancement of hydration process. They contribute to the properties of fresh and hardened concrete through pozzolanic action. They include Fly Ash (FA), Limestone Powder (LSP), Rice Husk Ash (RHA), Bagasse Ash (BA) etc. We, however, used LSP and FA in our research.

The production of Portland Cement requires upto 3% of global energy. Also, 5% of total Carbon dioxide (CO₂) emissions in atmosphere by human activities are due to the cement industry, alone. It is known to us that for producing one ton of cement, almost one ton of CO₂ is released into the atmosphere. Because of these environmental concerns, the cement industry is under pressure to produce low heat and CO₂ into the atmosphere. To reduce clinker content in cement in order to reduce these environmental impacts, industrial wastes and naturally available environment friendly materials can be used in concrete.

Mostly, SRMs are inorganic materials and are pozzolanic. According to ASTM C 125, pozzolanic materials are defined as:

A siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the

presence of moisture, chemically react with calcium hydroxide (CH) produced by cement hydration at ordinary temperatures to form compounds possessing cementitious properties.

The particle sizes of SRMs are much smaller than Ordinary Portland Cement used in concrete. The small particles of SRMs fill the void spaces left in concrete by cement, thereby increasing the density of concrete, and thus increases the concrete strength.

1.4 Research Objectives:

The objective of research was to study the responses of SRMs in Self-Compacting Paste Systems (SCPS). The SRMs used in the research are FA and LSP. The main focus was on selecting the optimum formulation and then observing the effect of variable mixing water temperatures on these formulations

CHAPTER - 2

LITERATURE REVIEW

2.1 Introduction:

Self-compacting concrete (SCC) is blessing for construction industry. The focus of this study would be on self-compacting paste systems (SCPSs) and secondary raw materials (SRMs) as a suitable cement content replacement for producing such type of cementitious systems. Self-compacting paste system (SCP) is the main driving force behind self-compacting concrete (SCC).

2.2 Brief History:

Pouring concrete in heavily reinforced mesh is a nightmare. It is difficult to ensure that the formwork gets completely filled with concrete and is fully compacted without voids or honeycombs. Resorting to methods of manual compaction or vibration is not a suitable option in all cases. This issue led the creation of self-compacting concrete (SCC). Self-compacting concrete (SCC) describes a concrete with the ability to compact itself only by means of its own weight without the requirement of mechanical vibration [2]. Placement of self-compacting concrete does not require vibration and can pass around obstructions while filling every nook and corner due to its high fluidity. It does all this without the risks like concrete ingredients or mortar separating out and formation of entrapped air or rock pockets. The introduction of the self-compacting concrete (SCC) is associated with the drive towards better quality of concrete pursued in Japan in late 1980's, where the lack of uniform and complete compaction had been identified as the primary factor responsible for poor performance of concrete structures [3]. Professor Hajime Okamura gave the concept of such type of concrete, this was pursued by Professor Ozawa at university of Tokyo who developed the first prototype in 1988. Professor Hajime Okamura studied the details of this concrete and named it "High Performance Concrete" [4].

An ACI committee "ACI 237R–07 Self Consolidating Concrete" was formed to further do research on this new system. Europe started to work on this new type of concrete while Sweden was the first country to study the properties of SCC and work on it. Also self-compacting concrete (SCC) has been successfully used in France, Denmark, Netherlands and UK [5].

ACI committee "ACI 237" was formed to research and standardize the properties of Self-compacting concrete (SCC) and to develop a suitable definition of SCC. This committee submitted its findings in April 2007.

2.3 Self-Compacting Concrete:

According to ACI committee "ACI 237 R-07" SCC is defined as a highly flowable, non-segregating concrete that can spreads into place, fills the formwork, and encapsulates the reinforcement without any mechanical consolidation [3]. This committee also further divided self-compacting cementitious systems (SCCS) into three categories:

1. Self-Compacting Paste Systems (SCPS) or Single Component Systems.

2. Self-Compacting Mortar Systems (SCMS) or Double Component Systems.

3. Self-Compacting Concrete Systems (SCCS) or Triple Component Systems.

2.4 Mechanism:

2.4.1 Ordinary Portland Cement (OPC):

OPC is produced by burning finely ground raw material which mainly consists of limestone, smaller degree of clay, marl and shale, at about 1450°C in a rotary kiln. Material that is obtained after burning these materials is called Clinker. Clinkers are then cooled down rapidly, blended with Gypsum (CaSO₄) and finally ground to fine powder [6].

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

- ≻ CaO (60-70%),
- \succ SiO₂ (18-22%),
- $hightarrow Al_2O_3 (4-6\%)$
- \blacktriangleright Fe₂O₃ (2-4%)

Remaining 5 % includes MgO, Mn₂O₃, SO₃, K₂O, Na₂O, and TiO₂ [7].

The typical composition of main compounds that these oxides form are;

\triangleright	Alite	3CaO.SiO ₂	C_3S	55-65%
	Belite	2CaO.SiO ₂	C_2S	15-25%
	Aluminate	3CaO.Al ₂ O ₃	C ₃ A	8-14%

2.4.2 Self-Compacting Concrete:

A self-compacting concrete must:

- ▶ Have a fluidity that allows self consolidation without external energy.
- > Remain homogenous in a form during and after the placing process and
- Flow easily through reinforcement

To achieve these objectives Okamura design process focused on three aspects [8]:

- Reduction of the aggregate content in order to reduce the friction, or the frequency of collisions between them increasing the overall concrete fluidity
- > Increasing the paste content to further increase fluidity
- Managing the paste viscosity to reduce the risk of aggregate blocking when the concrete flows through obstacles.

The self-compaction of SCC is mainly governed by yield stress, while the viscosity will affect the homogeneity and the ability to flow through reinforcement [9]. Self-compatibility requires high deformability of paste or mortar and segregation resistance between coarse aggregate and mortar. Okamura and Ozawa achieved this by:

- Limited aggregate content
- Low water-powder ratio
- Use of super plasticizer

Limiting coarse aggregate content increases the relative distance between aggregates which in return decreases the frequency of collision and contact between aggregates. This lowers internal stresses when concrete is deformed. Super plasticizers help in reducing the paste's viscosity enabling it to decrease localized stresses due to deformation on the arrival of coarse aggregate.

2.4.3 Self-Compacting Paste (SCP):

These are primary agents behind the transport of aggregates. Properties of Selfcompacting concrete and Self-compacting mortars depend on Self-compacting paste systems.

2.5 Secondary Raw Materials (SRMs):

2.5.1 Definition:

Cement, with its high carbon footprint and high utilization of energy in its production phase, is by no standards an environment friendly material. Various efforts are being made to lessen this effect of concrete on environment and so use of secondary raw materials with cement is rapidly increasing in the world.

Secondary raw materials are not as energy intensive and are mostly industrial by-products which are easily available. SRMs replace part of cement in the mix which reduce the cost as cement is the most expensive component of concrete system. These also inherent or latent cementitious properties.

2.5.2 Effects of SRMs on Properties of Mix:

SRMs reduce the cement content in the system that reduces shrinkage and heat of hydration, hence decreasing shrinkage cracking. This study would employ fly ash and limestone powder as SRMs. The use of these SRMs assists SCC decreased level of permeability, higher particle packing and in achieving high flow-ability of system which results in overall higher durability and higher compressive strength. In the light of literature on the studies carried out in the past, the use of SRMs have benefited the workability while decreasing the cement content in the system. Studies show that use of SRMs results in better packing of the system [10, 11].

2.5.3 Fly Ash:

Fly ash is an inorganic non-combustible by product obtained from combustion of pulverized coal. It is collected by mechanical separators. [12] The fly ash consists of spherical glassy particles. Its particle diameter varies between 1 to 150 microns. It mainly consists of silica, alumina and iron oxides. The composition of fly ash varies with type of fuel burnt and load on the boiler. It is extensively used in construction industry [13]. Use of fly ash as an SRM results in workability and long-term strengths due to their spherical morphology which allows them to reduce inter particle friction. Use of fly ash also increases durability by providing decreased chloride diffusion, reduction in calcium hydroxide, control of the alkali-silica reduction and better sulfate resistance. Fly ash is also an additional source of calcium.

In the European standard, EN-197-1 Fly ash is classified into two major classes:

1) Siliceous 2) Calcareous, based on the presence of different oxides content. Siliceous FA contains less than 10% of calcium oxide (CaO) while Calcareous FA contains more than 10% of CaO.

ASTM C 618-89 classifies the fly ash used as admixtures to cement or concrete. The classifications are:

- Class F: If total amount of SiO₂, Al₂O₃ and Fe₂O₃ is more than 70%, then it belongs to Class F and indirectly to Siliceous Fly ash.
- Class C: If total amount of SiO₂, Al₂O₃ and Fe₂O₃ is less than 70% but higher than 50%, it belongs to Class C and in directly to calcareous Fly Ash.

Higher fly ash content in cementitious system will result in higher effective w/c ratio for a given w/c ratio, retard the setting time, reduce early shrinkage and improve the long term strengths as a result of pozzolanic reactions [14].

2.5.4 Lime Stone Powder:

Limestone is a sedimentary rock primarily of calcium carbonate, obtained from calcareous remains of marine or fresh water organisms. It is acceptable to replace 5% of cement with limestone powder as it does not affect the properties of cement paste. Most of the regulations allow it like Europe (EN-196) and America (ASTM C150). As in cement production about 0.8-0.9 ton of CO₂ is produced during the production of 1 ton cement, that CO₂ is causing green-house effect and affecting the climate very badly. From different experiments it is concluded that 5-10 % of replacement of limestone powder would not affect compressive strength to higher extent.

Limestone filler improves the hydration rate and increases the strength of cement compounds at early ages. It improves the workability and permeability but reduces initial and final setting times. It causes high early shrinkage and reduces the long term strength as compare to control mix due to continuous pores or higher total porosity. [15, 16]

2.5.5 Blend of Limestone Powder and Fly-Ash:

The chemical effect of LSP is limited in the presence of OPC due to lesser content of alumina about 5-10 %. But when OPC is replaced by FA and LSP then higher content of aluminates about 30% due to FA [17], increases the effect of LSP as it alters the products of AFm and AFt phases [18]. Due to the presence of CaCO₃ instead of calcium monosulpahte hydrate, hemicarbo-aluminate hydrate forms which controls the stabilization of ettringites and volume control [19], as water with higher ettringites would cause increase in volume [20]. LSP improves the early strength while Fly-ash improves the later strength.

2.6 Superplasticizers:

2.6.1 High Range Water Reducers / Superplasticizers

Chemical admixtures are used where well-dispersed particle suspension is required. Super plasticizer is essential for the creation of SCC as it increases workability without the need of adding more water or the side effect of excessive retardation. The main job of a superplasticizer is to impart a high degree of flowability and deformability.

When water reducing admixtures are used in concrete mixtures, some increase in compressive strength can be anticipated and that increase can be observed in as early as one day if excessive retardation does not occur. This is possible due to the reduction of water cement ratio and aiding in development of uniform pore structure that reduces permeability of concrete and results in improved durability.

The charged polymers of SP adsorbed on cement particles. The adsorption of charged polymers on cement particles create particle to particle repulsive forces, which overcome the attractive forces. This repulsive force is called Zeta Potential. The cement particles are deflocculated and entrapped water is released [21].

ASTM C494 enlists the requirements of SP and classifies them as different types. SPs are organic products and fall into three categories depending on their ingredients:

- Sulfonated melamine-formaldehyde condensate;
- Sulfonated naphthalene-formaldehyde condensate; and
- Polyether-polycarboxylates.

2.6.2 Melflux (2651F):

Melflux 2651F by BASF Germany is a poly-carboxylate ether (PCE) type of superplasticizer which is optimized for plasticization and water reduction of cementitious construction material. It's a high performance third generation superplasticizer which has anti-bleeding and segregation properties which makes it more effective [22].

Physical shape	Powder
Appearance	Slightly to intensely pastel colored.
Drying loss	Max. 2.0%
Bulk density	350 – 550 kg/m ³
Dosage recommendation	0.05 - 1.00% of cement weight.
pH value at 20 °C,	6.5 - 8.5

Table 2.6.2 Properties of Melflux

2.7 Experimental Techniques:

2.7.1 Calorimetry of Cement:

The hydration process of cement is an exothermic reaction which is measured in milliwatt (mW). It consists of small plates with thermopiles, when two sides of plates are exposed to different temperatures then that difference causes the flow of heat from higher temperature to lower temperature side, that flow of heat is measured by sensors. Isothermal calorimetry is a versatile tool for studying the hydration of cement paste.

- The curve between heat flow and time represents the hydration process of cement.
- The effect of an admixture could be seen in the form of change in hydration curve.

The hydration process of cement takes place in 5 different stages that are;

- ➤ (I) Rapid initial process
- ➤ (II) Dormant Period
- ➤ (III) Acceleration Period
- ➤ (IV) Retardation Period
- ➤ (V) Long-term reactions

Heat of hydration of cement is very important because it affects the workability, strength development rates, setting times, early and long term performances of cement concrete. The first peak in hydration process is due to reaction of tri-calcium aluminates (C₃A), main product that is formed in this process is AFt. After the first phase rate of heat of hydration decreases to minimum within 2-3 hours, this phase is called dormant period. Then second highest value of heat of hydration occurs due to pozzolanic reactions and mass precipitation of hydration products mainly of calcium silicate hydrate (C-S-H) gel. Again there is reduction in heat of hydration and smaller peaks are formed due to presence of super plasticizers. Rizwan et al [23] stated "Superplasticizer's presence in the cementitious systems delays the heap peaks produced during Calorimetry of cement process".



Figure 2.7.1 Typical Calorimetric Curve

Heat of hydration depends of cement type, its content and w/c ratio.

2.7.2 X-Ray Diffraction:

X-ray diffraction is a useful technique used to detect and quantify the crystalline material. It can also provide results about amorphous materials. The working procedure is when x-ray is diffracted by atoms or molecules in many directions, by measuring the angles and intensities of these diffracted rays. 3-D picture of the density of electrons within crystals can be produced. In this way, it provides comprehensive information about the crystalline structure of a molecule or atom. Quantitative and qualitative analysis both can be used, quantitative analysis gives more accurate results but it requires more time, expertise and is very expensive. So mostly qualitative analysis is used [24].

Moreover, X-ray diffraction is more useful to find the amount of unreacted cementitious constituents. It can also be done by determining the amount of formed hydrates as a function of time.

2.7.3 X-Ray Fluorescence:

It is a technique in which material is excited by bombarding the high energy rays like x-rays or gamma rays. As a result, material emits characteristic x-rays. When high energy rays collide with the material, they cause ionization of atom by expelling one or more of its electrons as energy of bombarding rays is higher than ionization energy. Due to removal of electrons, electronic structure of atom becomes unstable. To fill the hole, electrons from higher orbits fall into lower orbits to fill the hole as electron moves from higher energy shell to lower energy shell, so material emits radiations which have energy characteristics of the atom.

X-Ray Fluorescence gives the chemical analysis of a sample and provides the quantities of chemical compounds present in the sample. XRF spectrometer is also used for chemical analysis. It provides different advantages like ease of sample preparation, ease of calibration and suitability for determining a range of elements occurring in cement [25].

2.7.4 BET Surface Area:

Brunauer–Emmett–Teller (BET) theory explains the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. Developed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1983 it is the basics behind the working of the procedure of BET Surface Area measurement. In the BET technique, an adsorption isotherm is measured by plotting the volume of gas adsorbed versus the pressure, P, of the gas. Pressure is represented as P/P₀, where P₀ is the saturation pressure of the adsorptive gas. The total surface area of a powder can be calculated using the Langmuir theory and the BET generalization.

The calculation of surface area is based on an extension of the Langmuir theory to a multi-molecular layer adsorption.

Equation:

$$V_a = \frac{V_m CP}{(P_0 - P)[1 + (C - 1)\frac{P}{P_0}]}$$

Where

- ➤ V_a is the quantity of gas adsorbed at pressure P (measured value),
- \succ V_m is the quantity of gas adsorbed for the entire surface to be covered,
- ➢ C is a constant,
- \triangleright P₀ the saturation pressure of the gas, and
- \blacktriangleright P is the gas pressure of the measurement.

Rearranging the above equation gives:

$$Y = \frac{P}{V_a(P_0 - P)}$$
$$a = \frac{1}{V_m C}$$
$$b = \frac{C - 1}{V_m C}$$

Thus, the values of V_m and C can be obtained from the linear plot. From the value V_m , it is possible to calculate the surface area if the area occupied by a single adsorbed molecule is known.

2.7.5 Particle Size Distribution (PSD):

Particle size distribution (PSD) is a technique used to measure the size of the particles present in a sample and their relative distribution according to their size. PSD can be important indicator of a materials physical and chemical properties. Accurate and precise PSD results help in computational modeling of hydration phase of cement and in predicting its performance.

ASTM C115 is the standard method currently in use. It states that the distribution of particle sizes or particle size distribution (PSD) is a fundamental characteristic of cement powder. This method uses Wagner turbidimeter to determine the fineness of cement as represented by a calculated measure of specific surface, expressed as square centimeters of total surface area per gram, or square meters of total surface area per kilogram, of cement. It has a limitation of lower size detection limit of 7.5 μ m [26].

CHAPTER - 3

EXPERIMENTAL PROGRAM

3.1 General:

The experimental program was designed such that optimization of the obtained results was achieved and consistency in the procedures of experiments conducted was ensured. All this was done so that the results obtained were credible and valid. This chapter will contain details pertaining to the procurement, handling and usage of all the materials used to conduct this research. All materials were stored at average room temperature in the laboratory and were kept in air tight jars to avoid contact with moisture and other impurities that could disturb its existing properties. Overall lab temperature throughout the course of our research varied from 17-26 °C due to seasonal variation.

The overall study pertains the determination of material properties (physical & chemical), to evaluate the response of SRMs replacement in SCP and finally to ascertain the response to variable mixing water temperature.

The study was conducted while making sure that all external elements were maintained and a single variable was kept under observation, for instance, mixing water temperature.

3.2 Materials Used:

3.2.1 Cement:

The major part of the paste system is the cement. An Ordinary Portland Cement (OPC) Grade 43, following EN 196-1, was procured directly from plant of Lafarge Cement Factory, a well-established name in this field in Pakistan. 8 bags of Lafarge Stallion were obtained from a single batch of production to ensure that even minor changes in their properties wouldn't be detected. The bags were placed at an elevated place to avoid the bags being damaged and accidentally ingress of water. The bags were opened one at a time and emptied into a water proof, air tight jar.

3.2.2 Fly Ash:

It is dark grey, fine grained pozzolanic binder that contains calcium oxide, silicates & ferric oxides. Fly Ash was directly obtained from a German company BauMineral Kraftwerkstoffe by the name of EFA-Fuller® HP of class F. Main use of fly ash was to reduce cement content, maximize water/cement ratio, improve workability, reduction of reduce sulfate attack and to use with aggregates that are sensitive to alkalis. It was stored in air tight containers to avoid moisture affecting its properties.

Characteristic Values			
Loss on ignition: Category A	\leq 5% by mass		
Fineness > 45 μm	20 ± 10 % by mass		
Bulk Density (DIN EN 459 part 2)*	1.20 t/m³		
Particle density	$2.32 \pm 0.20 \text{ t/m}^3$		

TADIE J.2.2 FIODELLIES OF FA

3.2.3 Limestone Powder:

Limestone was procured from Taxila, Rawalpindi District. It is the byproduct of the local stone crushing plants. It was collected in bags and brought to our laboratory where it was first washed, dried and later milled using Los Angles Abrasion Machine and passed through BS-410 # 350 which has mesh size of 45um. It was then stored in air tight jars.

Oxides	OPC (%)	Fly Ash (%)	Limestone Powder (%)
Al ₂ O ₃	ND	ND	ND
SiO2	49.81	62.14	22.09
CaO	43.33	10.26	74.21
Fe2O3	5.61	22.44	2.23

Table 3.2.3 General Composition of OPC, FA and LSP

3.2.4 Super Plasticizer:

Melflux 2651-F Super Plasticizer (SP) was used for our project. It is a third generation, spray dried powder of a modified polycarboxilic ether. It is used as a high performance SP to achieve flow, produce plasticibility and decrease the amount of water needed to acquire flow of (30 ± 1) cm.

3.2.5 Water:

Normal tap water of the laboratory was used and stored in a big jar to ensure regularity of temperature and other properties. Source was kept same throughout the project to ensure consistency in results. It was cooled and heated as required.

3.3 Physical Analysis of Materials:

3.3.1 Particle Size Distribution (PSD):

The PSD analysis was carried out on Cement and the SRMs. The overall purpose of conducting this test is to ascertain the distribution of the various particle sizes. The analysis was done by Horiba Size Analyzer, using ethanol as the dispersing agent. The test was conducted by School of Chemical and Materials Engineering (SCME), NUST.

3.3.2 Brunauer–Emmett–Teller (BET):

To find the specific area of the materials, BET surface analysis was done. This helps us to determine the surface area of the materials. Greater the surface area of a material, smaller would be its particle size thus we can get an idea of the size of particles as well. The experiment was carried out in Surface Engineering Lab of SCME, NUST.

3.3.3 Scanning Electron Microscopy (SEM):

SEM is a special type of electron microscope that uses a focused beam of electrons to produce an image of a sample. It is an effective method to analyze the shape and size of particles of the materials used.

3.4 Chemical Analysis of Materials:

3.4.1X-Ray Fluorescence (XRF):

XRF is the emission of fluorescent X-rays after excitation of a material using high-energy X-rays or gamma rays. The emissions are then compared with the characteristic emissions of known elements and hence the chemical composition of the material is known. XRF was conducted on Cement as well as on the SRMs. The test was conducted in IESE, NUST.

3.4.2X-Ray Diffraction (XRD):

X-Ray Diffraction or X-Ray Crystallography is a method used to find out the molecular and atomic structure of a crystal by diffraction of X-Rays into different specific directions. This helps to identify the molecular and atomic structures. XRD was performed on Cement and SRMs at XRD Lab SCME, NUST.

3.5 Formulations:

The formulations were based on the amount of Cement to be replaced with the SRMs. The replacements started from 0-40%. A control mix with no replacement was also used to serve as a benchmark to compare our results. The list of formulations goes as follows:

CI-00, CI-FA10, CI-FA20, CI-FA30, CI-FA40, CI-LSP10, CI-LSP20, CI-LSP30, CI-LSP40

For ease of understanding:

CI-00 is mixture containing no replacement of cement (control mixture)

CI-FA20 is the formulation containing 20% replacement of Cement with Fly Ash

CI-LSP30 is the formulation containing 30% replacement of Cement with Limestone Powder

3.6 Testing Procedures:

3.6.1 Water Demand (WD):

Determining the water demand is usually the first step. It is the least quantity of water needed for the cement's complete hydration. Different specimens of varying water percentages were prepared in the Hobart mixer and tested using the Vicat Apparatus until the 10 mm plunger managed to achieve a height of (5 ± 2) mm from the base plate. The percentage that produces this specific result is called the water demand of the cement.

3.6.2 Super Plasticizer Demand:

Self-Consolidating Paste system is known for its flowability and no segregation of phases. In order to achieve these desirable properties, the right amount of Super Plasticizer needs to be determined. The formulations were mixed with the percentages found from the water demand and SP's quantity was kept as a variable. Trials were performed until (30 ± 1) cm flow was achieved using the Hagerman's Mini-Slump flow cone.

3.6.3 Flow Times:

 T_{25} and T_{30} are the times which are recorded in order to attain the desirable flow of 30cm. After finding the water demand and the super plasticizer demand, batches for all the formulations were tested again using the Hagerman's Mini-Slump flow cone.

3.6.4 Setting Times:

Vicat Apparatus was used to estimate the Initial & Final Setting times for all the formulations. After the estimation of the water demands of all the formulations, the setting times were noted. To monitor the effect of SP on the paste system, these setting times were found out both with and without SP.

3.6.5 Casting:

The mould size of 40x40x160 mm was used according to European Standards EN 196-1 to cast our samples. Special care was taken to ensure that the moulds were properly oiled so that on removal, the samples would easily come off. Also the moulds were properly greased to ensure that no leakage was there after pouring the paste in them. The moulds were kept at a safe place to ensure that they remained undisturbed and plastic sheet was used to cover them to ensure no foreign particle disturbed the samples. The samples would be removed exactly after 24 hours from casting to be placed in the curing tank.

3.6.6 Strength Testing:

The samples were tested for 1, 3, 7 & 28 days for flexure and compressive strengths. The 1 day strength was noted just after it was de-moulded. For the remaining day strengths, the samples were placed in the curing tanks and just before performing

the test, the samples were brought to Saturated Surface dry condition to achieve accuracy in the results. Loading rate of 0.02 kN/sec for flexure and 0.2 kN/sec for compression was applied onto the specimen. The sample was placed in the Dual Strength Chamber and tested with a flexural arrangement which breaks the sample in two halves after giving the flexural strength. The compression arrangement is then used for those two broken halves to find their compressive strengths.

3.6.7 Water Absorption:

The same samples that are casted for the mentioned day strengths are used to find the water absorption. The samples are weighed after SSD condition is achieved to have an estimate the porosity of the samples. 1, 3, 7 & 28 day samples are used to conduct water absorption test on each one of them.

3.6.8 Calorimetry:

Hydration of cement phases is an exothermic reaction (one that releases heat). The rate of reaction can directly be associated with the amount of heat released at a particular time. Using this concept, calorimeter F-Cal 8000 is used to record the rising temperature against time. Two-day data is obtained for all formulations after the mixes are prepared and poured into the cylinders. The calorimeter plots the curves which are exported after manipulation to create the desired look.

3.6.9 Variation of Mixing Water Temperature:

Water temperature needs to be altered to achieve 10°C, 20°C and 30°C. Normal water in the lab was around 15-25 °C. So in order to cool it down, regular ice was used and to heat it, hot water from dispenser was used. Water temperature was weighed and the temperature noted just before it was used for mixing. Water temperature is adjusted by pouring it in the Hobart mixer and then adding and extracting hot and cold water until the desired temperature is achieved.

CHAPTER -- 4

RESULTS

4.1 General

At the first stage of our study, all formulations are tested at (20 ± 1) °C and the formulation giving the highest 28 day strength is then tested at (30 ± 1) °C and (10 \pm 1) °C to depict the hot and cold water temperatures in Pakistan, respectively. This variation of temperature will lead to a better understanding of the blends of Fly Ash & Limestone Powder.

4.1.1 Particle Size Distribution:



Figure 4.1 PSD Curve

The graph shows the percentage of sizes in the powders used in our study.

4.1.2 Water Demand:





The graph above shows the trend for the water demand achieved for the formulations. The water demand increases for increase in the replacement of OPC with both Fly Ash and Limestone Powder. Also water demand for Fly Ash seems to be more than that of Limestone Powder.



4.1.3 Super-Plasticizer Demand:

Figure 4.1.3 SP Demand of SCP system

The graph above shows the percentage by mass of Super Plasticizer needed to achieve the target flow of (30 ± 1) cm. The SP demand is increasing as the SRM replacement

increases. The increase is more visible for Limestone Powder than that of Fly Ash. This can be accounted for the shape and particle size of Limestone Powder.



4.1.4 Flow Times:

Figure 4.1.4 Flow Times of Formulations at WD and SPD

The above graph shows the T-25 and T-30 times, taken at 25cm and 30cm respectively, whilst achieving the target flow of (30 ± 1) cm using the Hagerman's Mini Slump Cone. There seems to be no trend to be followed by the formulations' results.

4.1.5 Setting Times:



Figure 4.1.5 Initial and Final Setting Times of Formulations

The graph above shows the variation in the initial and final setting times of all the formulations. These were obtained using the Vicat Apparatus. The trend above shows that initial and final setting times decrease for Limestone Powder and increase for Fly Ash replacements.



4.1.6 Strength Tests:

Figure 4.1.6 (a) Flexural Strength of SCPSs



Figure 4.1.6 (b) Compressive Strength of SCPSs

The prisms having dimensions of 40x40x160cm were tested as per standard EN196-1. The tests were conducted for strengths at 1, 3, 7, and 28 days. It can be interpreted from the results that both for flexure and compression, strengths tend to increase for each formulation as testing day increases. The results showed that early strength of formulations containing FA decreased as compared to pure OPC. However, 28 days strengths of formulations containing FA are appreciable. It can be explained due to the pozzolanic behavior of FA. On the other hand, LSP formulations have shown somewhat higher early strength than FA formulations. The highest peak is observed at 20% replacement for both Fly Ash and Limestone Powder.

4.1.7 Calorimetry:



Figure 4.1.7 Calorimetry Curves of SCPSs

Calorimetry was conducted for all formulations to generate the response of hydration kinetics due to changes in SRM replacement. Data for 1 day was recorded to produce the above curves as output.

4.2 Self Compacting Pastes at Variable Mixing Water Temperature

After having found out the strengths of both flexure and compression, it was decided to test the best formulations to study their response to change in mixing water temperature. For this purpose, formulations of both Fly Ash and Limestone Powder at 20% replacement (FA20 and LSP20) were chosen since they were giving the highest Compression Strengths. All the tests conducted above are repeated for these two formulations and the Control Mix at the temperature 10° and 30° and the results were compared with the control temperature of 20° .

4.2.1 Water Demand:





Water Demands were calculated at different temperatures for the formulations that gave the highest Compressive Strengths (FA20 and LSP20). The results show that for all formulations, there seems to be increase in Water Demand for both the increase and decrease of temperature with respect to control temperature i.e 20°C.

4.2.2 Super Plasticizer Demand:





The Super Plasticizer Demands were calculated at 10°C, 20°C and 30°C and the resulting graph is displayed above. The results show that increase in temperature seems to reduce the amount of SP needed to achieve the target flow of (30 ± 1) cm.



4.2.3 Flow Times:

Figure 4.2.3 (a) T₂₅ of SCPSs at variable mixing water temperatures



Figure 4.2.3 (b) T₃₀ of SCPSs at variable mixing water temperatures

Flow times were calculated using the Hagerman's Mini Slump Cone for the paste to cross the 25cm and 30cm marks respectively. The above graphs show no trend being followed for both T_{25} and T_{30} . It may be because of human error while using stop watch.



4.2.4 Setting Times:

Figure 4.2.4 (a) IST of SCPSs at variable mixing water temperature



Figure 4.2.4 (b) FST of SCPSs at variable mixing water temperature

The initial and final setting times were found out using the Vicat Apparatus. The graphs above are then generated to evaluate the response to mixing water temperature variation. The above graphs show that with increase in temperature, both IST and FST of SCPSs decrease. These results can be explained using the calorimetry curves of above SCPSs. As mixing water temperature increases, rate of hydration also increases, thereby reducing the setting times of SCPSs.

4.2.5 Strength Tests (Compression):



Figure 4.2.5 (a) Compressive Strength of CI-00 at variable mixing water temperatures



Figure 4.2.5 (b) Compressive Strength of FA-20 at variable mixing water temperatures



Figure 4.2.5 (c) Compressive Strength of LSP-20 at variable mixing water temperatures 4.2.6 Strength Tests (Flexure):



Figure 4.2.6 (a) Flexural Strength of CI-00 at variable mixing water temperatures



Figure 4.2.6 (b) Flexural Strength of FA-20 at variable mixing water temperatures





In order to determine the response of variable mixing water temperature to strength of prisms, the formulations were tested for 1, 3, 7 and 28 day strengths for mixing water temperature of 10° and 30° . The graphs above display the effect on strength by water temperature for each SRM formulation as well as for the control mix.

4.2.7 Calorimetry:



Figure 4.2.7 (a) Calorimetry Curves of CI, FA20 and LSP20 at 10 °C



Figure 4.2.7 (b) Calorimetry Curves of CI, FA20 and LSP20 at 30 °C



Figure 4.2.7 (c) Calorimetry Curves of FA20 at 10 °C, 20 °C and 30 °C



Figure 4.2.7 (d) Calorimetry Curves of LSP20 at 10 °C, 20 °C and 30 °C

The figures of calorimetry above shows that peak of CI-00 is observed first, then for LSP20 and lastly for FA20. Upon further observation it can also be noticed that peak for CI-00 is maximum, smaller for FA20 and least for LSP20. This is true for both 10°C and 30°C.

The lower two graphs show the comparison of hydration for both SRMs at 10°C, 20°C and 30°C. For both FA and LSP, peaks are arriving earlier for higher temperatures and also the maximum peaks are also observed at higher temperatures and decreases subsequently for decreasing temperatures.

CHAPTER - 5

DISCUSSIONS

5.1 Water Demand and Superplasticizer Demand:

Water demand and SP demand generally depend upon the shape and size of particles. Water demand increases as the particle size of material decreases. Finer the particle size, more will be the surface area, hence more water is required to lubricate the surface of the particles. Figure 4.1.1 shows that particle size of fly ash is smallest than cement and limestone powder, so water demand of FA is higher than both. Water demand of fly ash increases as the percentage replacement of cement with FA increases. (Figure 4.1.2)

Similarly, particle size of limestone powder is finer than control formulation. Hence more water is required to lubricate the particles. (Figure 4.1.2)

SP demands of SCPSs are shown in Figure 4.1.3. SP demand for LSP replacement is more than that of FA replacement. This is due to the internal porosity and irregular particle shape of LSP, which causes internal friction among the particles. Hence more SP is required to achieve the target flow for LSP than for FA.

5.2 Initial and Final Setting Times:

Usually initial and final setting times increase with the addition of Secondary Raw Materials. Literature shows that FA behaves as retarder. It increases the setting times. Fly Ash becomes active in the presence of CH that is formed as a byproduct in the hydration of C_3S , C_3A and C_4AF in early stages. FA40 shows the largest setting time as it contains the highest percentage of FA. (Figure 4.1.5)

But setting times reduce with the addition of limestone Powder as it contains very high amount of $CaCO_3$ which is an inert material, so it provide nucleation sites for the hydration reaction, thus the setting times decrease. LSP40 shows the smallest setting time as it contains highest percentage of LSP. (See Figure 4.1.5).

5.3 Strength of SCPSs:

Self-Compacting Cementitious Systems have finer particles which act like fillers, that results in higher packing density. When failure occurs, the cracks pass through the pores in the system. These cracks are filled by finer particles of SRMs due to which porosity of the system decreases. In this way, higher loads are required to fail the material. Ultimately, it causes increase in strength. Also the pozzolanic reactions of SRMs, like Fly Ash, result in increased strength. In pozzolanic reactions, SRMs react with CH, which causes reduction in strength, is replaced by C-S-H gel, and thus provide higher strengths.

When cement is replaced by Fly Ash, 1, 3 and 7 days strengths are reduced due to the slower rate of hydration as discusses earlier, but 28 days strength is slightly higher than control formulation. And FA20 is the optimum replacement, which gives highest 1, 3, 7 and 28 days strengths among all of the FA formulations. The increase in strength is due to the pozzolanic reactions and filler effect of Fly Ash. (Figure 4.1.6 (b))

In case of Limestone powder, 1 day strength is lower but 3 and 7 days strengths increase due to presence of higher amount of CaO, which accelerates the rate of hydration and helps to achieve high early strengths. But 28 days strength is lower than control mix, due to early shrinkage cracks. LSP20 is the optimum formulation among all LSP replacements which shows the highest compressive strengths. (Figure 4.1.6 (b))

5.4 Self-Compacting Pastes at Variable Mixing Water Temperature

5.4.1 Water Demand and Superplasticizers Demand:

Temperature is one of the major factors that affects water demand, SP demand and compressive strengths of SCPSs. At higher temperatures, rate of hydration is faster as compared to lower temperatures. At lower temperatures, rate of hydration decreases.

At 30°C, temperature is higher than the control (20°C) and because of higher temperature, rates of hydration and evaporation are high. This results in increased water demand. (Figure 4.2.1).

At 10°C, due to lower temperature, rate of hydration is low but because of flocculation, clods are formed and paste becomes thick, so this results in increased water demand. (Figure 4.2.1)

SP demand also changes with variation in temperature. At 30°C, temperature is higher than control and molecules of the products of hydration have high energy, so they increase the flow of paste systems. But as the temperature decreases, paste becomes thicker and it causes flocculation of particles and as a result, workability decreases. Therefore, at lower temperatures, SP demand increases. (Figure 4.2.2)

5.4.2 Strengths at Variable Mixing Water Temperatures:

Temperature is one of the main factors that changes the rate of hydration. Higher hydration rate causes high early strengths but there are problems of early shrinkage, which reduces the long term strengths.

Figure 4.2.5 (a), Figure 4.2.5 (b) and Figure 4.2.5 (c) shows that at 30°C, 1, 3, 7 and 28 days strengths are higher due to the high rate of hydration. As temperature decreases, early strengths reduces due to slower rates of hydrations.

Overall FA behaves as a retarder while LSP accelerates the rate of hydration, so early strengths of FA formulations are lower than that of LSP.

5.4.3 Setting Times:

At higher temperatures, SCPS set more quickly because of increased rate of hydration. So, as mixing water temperature increases, initial and final setting times of SCPS decrease and vice versa for decrease in mixing water temperature.

5.4.4 Strength of SCPS at variable mixing water temperatures:

At higher temperatures, SCPS show higher early strengths but strength at later ages decreased as compared to lower temperatures. This may be due to thermal cracking.

ANNEXURE - A:

Physical and Chemical Properties of Materials

Oxides	OPC	Fly Ash	Limestone Powder
Physical State	Powder	Powder	Powder
Particle Size (D ₅₀)	17.82 μm	7.20 μm	7.70 µm
Color	Dark grey	Light grey	Light grey

Table A-1 Physical Properties

Table A-2 Chemical Composition of Materials

Oxides	OPC	Fly Ash	Limestone Powder
Al ₂ O ₃	ND	ND	ND
SiO ₂	49.81	62.14	22.09
CaO	43.33	10.26	74.21
Fe ₂ O ₃	5.61	22.44	2.23
SrO	0.25	0.97	1.33
TiO ₂	0.35	1.73	-
ZnO	0.44	0.17	-
MnO	0.07	0.20	-
Cr ₂ O ₃	0.07	-	-
V ₂ O ₅	0.06	0.02	-
K ₂ O	-	1.75	-
ZrO ₂	-	0.21	-
Rb ₂ O ₃	-	0.06	-
Ga ₂ O ₃	-	0.05	-

ANNEXURE - B:

Self-Compacting Paste Systems with Mixing Water at Room Temperature

Formulations	% OPC	% Fly Ash	% Limestone Powder
CI-00	100	0	0
CI-FA10	90	10	0
CI-FA20	80	20	0
CI-FA30	70	30	0
CI-FA40	60	40	0
CI-LSP10	90	0	10
CI-LSP20	80	0	20
CI-LSP30	70	0	30
CI-LSP40	60	0	40

 Table B-1
 Formulations

 Table B-2
 Water Demands

Formulations	Mixing Water Temperature (°C)	Water Demand (% cement mass)
CI-00	20.6	29.00
CI-FA10	20.4	30
CI-FA20	20.6	33.25
CI-FA30	21.0	37
CI-FA40	20.4	45
CI-LSP10	19.9	30
CI-LSP20	20.3	32
CI-LSP30	20.9	35.25
CI-LSP40	19.6	39.25

Formulations	Mixing Water Temperature (°C)	SP Demand (% cement mass)
CI-00	20.7	0.100
CI-FA10	19.8	0.123
CI-FA20	19.9	0.132
CI-FA30	19.0	0.145
CI-FA40	19.3	0.152
CI-LSP10	20.7	0.123
CI-LSP20	21.0	0.137
CI-LSP30	20.6	0.153
CI-LSP40	19.9	0.167

 Table B-3
 Super Plasticizer Demands

Table B-4 Flow Times

Formulations	Flow (cm)	T-25 (sec)	T-30 (sec)
CI-00	20.7	2.50	11.68
CI-FA10	19.8	2.39	9.77
CI-FA20	19.9	2.25	6.37
CI-FA30	19.0	2.47	7.46
CI-FA40	19.3	1.56	5.33
CI-LSP10	20.7	2.10	8.91
CI-LSP20	21.0	2.11	11.22
CI-LSP30	20.6	2.27	8.38
CI-LSP40	19.9	2.45	10.38

Formulations	Initial Setting Time (min)	Final Setting Time (min)
CI-00	193	210
CI-FA10	205	246
CI-FA20	218	250
CI-FA30	229	255
CI-FA40	244	260
CI-LSP10	174	192
CI-LSP20	162	188
CI-LSP30	155	184
CI-LSP40	143	179

 Table B-5
 Setting Times

Formulations	1-Day (MPa)	3-Day (MPa)	7-Day (MPa)	28-Day (MPa)
CI-00	2.3	3.6	4.6	4.9
CI-FA10	2.1	2.7	2.9	4.5
CI-FA20	1.5	3.2	3.5	4.0
CI-FA30	1.4	3.1	3.6	3.7
CI-FA40	1.3	2.6	3.0	3.2
CI-LSP10	2.0	3.5	3.9	4.1
CI-LSP20	2.5	2.9	3.4	4.2
CI-LSP30	2.0	2.7	3.4	3.5
CI-LSP40	1.7	2.6	3.0	3.5

 Table B-6
 Flexural Strengths

 Table B-7
 Compressive Strengths

Formulations	1-Day (MPa)	3-Day (MPa)	7-Day (MPa)	28-Day (MPa)
CI-00	21.59	37.18	46.07	56.40
CI-FA10	16.47	23.82	31.78	55.78
CI-FA20	20.97	35.40	45.18	56.66
CI-FA30	18.67	32.54	36.79	55.34
CI-FA40	12.53	16.67	24.28	47.25
CI-LSP10	19.04	37.88	46.53	49.15
CI-LSP20	21.24	39.70	48.31	52.01
CI-LSP30	20.41	37.92	47.04	50.66
CI-LSP40	17.43	37.83	44.65	47.98

ANNEXURE - C:

Self-Compacting Paste Systems with Variable Mixing Water Temperature

Formulations	% OPC	% Fly Ash	% Limestone Powder
CI-00	100	0	0
CI-FA20	80	20	0
CI-LSP20	80	0	20

Table C-1 Temperature Variation Blend Formulations

Table C-2 Water Demands

Formulations	$T_W = (10 \pm 1) {}^{0}C$ Water Demand	$T_w = (20 \pm 1) {}^{0}C$ Water Demand	$T_W = (30 \pm 1) {}^{0}C$ Water Demand
CI-00	29.5	29	30
CI-FA20	34	33.25	35.5
CI-LSP20	33.5	32	34.5

Table C-3 Super Plasticizer Demands

Formulations	$T_{W} = (10 \pm 1) {}^{0}C$ SP Demand	$T_{W} = (20 \pm 1)^{0}C$ SP Demand	$T_{W} = (30 \pm 1) {}^{0}C$ SP Demand
CI-00	0.132	0.100	0.096
CI-FA20	.141	.132	.127
CI-LSP20	.137	.130	.126

Essential disease	$\mathbf{T}_{\mathbf{W}} = (1$	$0 \pm 1)^{0}C$	$T_W = (20)$	$0 \pm 1) {}^{0}C$	$T_{\rm W} = (3)$	$(0 \pm 1)^{0}$ C
Formulations	T25 (sec)	T30 (sec)	T25 (sec)	T30 (sec)	T25 (sec)	T30 (sec)
CI-00	2.45	7.68	2.37	11.68	3.59	5.79
CI-FA20	1.61	4.73	2.39	6.37	2.35	7.11
CI-LSP20	2.35	7.16	2.11	11.22	2.60	9.88

Table C-4 Flow Times

Table C-5 Setting Times

	$\mathbf{T}_{\mathbf{W}} = (10$	$(0 \pm 1)^{0}$ C	$T_W = (20)$	$0 \pm 1)$ ⁰ C	$T_{\rm W} = (30$	$(0 \pm 1)^{0}$ C
Formulations	IST (min)	FST (min)	IST (min)	FST (min)	IST (min)	FST (min)
CI-00	196	225	193	210	185	196
CI-FA20	224	264	218	250	194	247
CI-LSP20	167	191	162	188	149	152

Table C-6 Flexural Strengths for $T_W = (10 \pm 1) {}^{0}C$

Formulations	1-Day (MPa)	3-Day (MPa)	7-Day (MPa)	28-Day (MPa)
CI-00	2.11	3.23	6.19	11.25
CI-FA20	0.94	2.78	5.62	10.31
CI-LSP20	2.11	3.44	4.75	12.19

Formulations	1-Day (MPa)	3-Day (MPa)	7-Day (MPa)	28-Day (MPa)
CI-00	22.00	32.14	44.29	54.88
CI-FA20	14.00	27.54	36.30	53.71
CI-LSP20	15.25	34.67	46.70	51.54

Table C-7 Compressive Strengths for $T_W = (10 \pm 1)^{\circ}C$

Table C-8 Flexural Strengths for $T_W = (30 \pm 1)^{0}C$

Formulations	1-Day (MPa)	3-Day (MPa)	7-Day (MPa)	28-Day (MPa)
CI-00	2.87	3.81	5.60	13.13
CI-FA20	1.79	3.56	5.60	11.95
CI-LSP20	2.81	3.80	5.40	11.48

Table C-9 Compressive Strengths for $T_W = (30 \pm 1) {}^{0}C$

Formulations	1-Day (MPa)	3-Day (MPa)	7-Day (MPa)	28-Day (MPa)
CI-00	24.65	38.54	46.44	53.19
CI-FA20	15.91	30.97	37.05	52.76
CI-LSP20	19.23	39.28	48.91	50.55

ANNEXURE – D

PARTICLE SIZE ANALYSIS:



Lafarge Stallion CEM-I







Limestone Powder

X-RAY FLUORESCENCE (XRF):



50

X-RAY DIFFRACTION (XRD):



51

REFERENCES

[1] Self-Compacting Paste Systems using Secondary Raw Materials by S. A. Rizwan, Civil Engineering Department, University of Engineering and Technology, Lahore, Pakistan, and T. A. Bier, Technical University of Freiberg, Germany. (Presently National University of Science and Technology, Islamabad)

[2] Improving mechanical properties of Self compacting light weight concrete on mixture (SCLWC) with Fiberglass by Kashish Gupta, Prof. Sarita Singla. Civil Engineering, Punjab Engineering College (PEC).

[3] Okamura. H, Ouchi. M; "Self Compacting Concrete", Journal of Advanced Concrete Technology, Vol. 01, No. 05, 5-15 April 2003

[4] Neville, A. M.; "Properties of Concrete", 4th Edition, Publisher: Pearson Education,
 Inc. and Porling Kindersley Publishing, Inc, ISBN 81 – 7758 – 587 – 8.(7)

[5] Industrial concrete construction for a better economy and working environment – possibilities and obstacles with self-compacting concrete by Peter Simonsson and Mats Emborg Professor LTU Head R&D Betongindustri AB Luleå University of Technology.

[6] Blended cement with reduced CO2 emission - utilizing the fly ash-limestone synergy K. De Weerdt

[7] W. Kurdowski, Cement manufacture, in: J. Bensted, P. Barnes (Eds.) Structure and Performance of Cements, Spon Press, London, 2002, pp. 1-23.

[8] Okamura. H, Ouchi. M; "Self Compacting Concrete", Journal of Advanced Concrete Technology, Vol. 01, No. 05, 5-15 April 2003

[9] Rizwan S.A, Bier T.A. (2009), "Self-consolidating Mortars using various secondary Raw materials", ACI materials journal, 106 (1) p. 25-32.

[10] Uysal M., Yilmaz K., (2011) "Effect of Mineral Admixture on Properties of Self-Compacting Concrete", Cement Concrete Composites 33, p. 771-776.

[11] Rizwan, S.A, Bier, T.A, "Self-compacting paste systems containing secondary raw materials", fifth international conference on construction in the 21st century (CITC-V), may 20-22,2009, Istanbul, Turkey.

[12] Characterization of fly ash for their effective management and utilization a thesis submitted by rakesh kumar behera bachelor of technology in mining engineering [13]"High performance mortars and concrete using secondary raw materials" by Syed Ali Rizwan of Faculty of Maschinenbau, Verfahrens-und Enrgietechnik of the Technishen Universitat Bergakademie Freiberg

[14] Kurita M, Nomura T. Highly-flowable steel fiber-reinforced concrete containingfly ash. In: Malhotra VM, editor. Am Concr Inst SP 178, June 1998. p. 159–75

[15] Investigate causes & develop methods to minimize early-age deck cracking on michigan bridge decks december 2003 Center for Structural Durability by Wayne state university

[16] W. Kurdowski, Cement manufacture, in: J. Bensted, P. Barnes (Eds.) Structure and Performance of Cements, Spon Press, London, 2002, pp. 1-23.

[17] H.F.W. Taylor, Cement chemistry 2nd edition, Thomas Telford, London, 1997

[18] Blended cement with reduced CO2 emission - utilizing the fly ash-limestone synergy K. De Weerdt

[19] K. De Weerdt et al.," Synergy between fly ash and limestone powder in ternary Blends", Cement and Concrete Composites 33(2011) 30-38

[20] K. De Weerdt et al., "Hydration mechanisms of ternary Portland Cements containing limestone powder and fly ash", Cement and Concrete Research 41(2011) 279-291

[21] The influence of chemical admixtures on cement hydration and mixture properties of very high performance self-compacting concrete by Beata Łaz'niewska-Piekarczyk Silesian Technical University, Faculty of Civil Engineering, Department of Building Materials and Processes Engineering

[22] Construction Polymers Melflux® 2641 F technical data sheet.

[23] Rizwan, S. A.; Bier, T. A.; and Nizami, M. S., "High Performance Self Compacting Mortars containing Pozzolanic Powders", Proceedings of 8th International Symposium on Brittle Matrix Composites, BMC – 8, Warsaw, Poland, October 23-25, 2006, pp. 175-185.

[24] Ljiljana Marjanovic, Robert I. McCrindle, Barend M. Botha and J. Hermanus Potgieter; "Analysis of cement by inductively coupled plasma optical emission Spectrometry using slurry nebulization" J. Anal. At. Spectrom. 2000, 15, 983-985

[25] Rizwan, S. A. and Bier, T. A.; "Application of XRD, Calorimetry and Thermal Analysis Techniques in the Study of Hydration Kinetics of Cement Based Systems".

[26] Chiara F. Ferraris, Vincent A. Hackley, and Ana Ivelisse Avil'es ; "Measurement Of Particle Size Distribution in Portland Cement Powder: Analysis of ASTM Round Robin Studies" Cement, Concrete, and Aggregates, Dec. 2004, Vol. 26.