CHAPTER 1 – INTRODUCTION

1.1 General

Over hundreds of years, concrete has become the material of choice for constructing residential and commercial buildings, infrastructural facilities such as highways, dams and bridges, canals, ports and other important facilities. The popularity of concrete owes to its economy, ability to be cast into any shape, ability to be fabricated practically anywhere and last but not the least, its inherent durability. Since the development of concrete, durability of concrete always remained a major concern for the Engineers. To produce durable concrete a large amount of compaction is required by the skilled labor. However, the gradual reduction in the number of skilled workers in Japan's construction industry has led to a similar reduction in the quality of construction work. One solution for the achievement of durable concrete structures was the development of self compacting concrete.

1.2 Self Compacting Concrete

Self-compacting concrete (SCC) is a flowing concrete mixture that is able to consolidate under its own weight. ACI 237 defines SCC as "highly flowable, non-segregating concrete that can spread into place, fill the form work, and encapsulate the reinforcement without any mechanical consolidation". The highly fluid nature of SCC makes it suitable for placing in congested reinforcement, filling forms completely and producing a void free mass with little or no mechanical vibration. Another advantage of SCC is that the time required to place large sections is considerably reduced. High quality of concrete surface finish is achieved with a better final appearance regardless the skill of the workers using SCC. The disadvantage of using SCC is its relative higher cost compared with ordinary concrete but the in place cost of concrete will actually reduce due to reduced construction time, reduced manpower and elimination of rubbing and patching cost. Applications of SCC include bridge construction, multistory buildings, dams, roads, tunnels, architectural buildings etc

To compact ordinary concrete vibrator is required due to which differential settlement and hence differential durability can result. To cater this problem, Prof.Okamura and his team developed powder type flowing concrete called self-compacting concrete. The main requirements of this concrete are very high flow and very high segregation resistance. SCC has been classified into three different classes, powder type, viscosity type and combination type depending upon the behavior on which it resists segregation. In powder type, a lower w/p ratio or higher powder content (cement as well as secondary raw materials) guarantees adequate segregation resistance while the same goal is achieved by viscosity enhancement agent in the viscosity agent type. Combination type of SCC uses both powder and viscosity modifying agent content in moderate quantity.

1.3 Mechanism for Achieving Self-Compactability

Self-compactability of SCC not only means to achieve the high deformability but also resistance to segregation is important because SCC flows through confined zone of reinforcing bars. Self-compactability is achieved by limiting the coarse aggregate content because most of the energy required for flowing is consumed in internal friction between large size aggregate particles resulting in blocking. To avoid blocking and to achieve high deformability high viscous paste is required which is done by using the super plasticizer and keeping the water powder ratio to minimum. Despite the lower coarse aggregate content, the shrinkage and creep are not increased because of the lower water/powder content.

SCC is normally characterized by the three properties named passing ability which is the ability of concrete to pass through congested reinforcement, filling ability which is the ability of concrete to fill all voids and the formwork in which it is being casted and segregation which means that concrete remains homogenous and do not segregate.

1.4 Components of Self Compacting Concrete

Ingredients used in SCC other than of normal concrete are mineral and chemical admixtures. Use of these mineral and chemical admixtures in self compacting concrete not only reduces the water demand and improves rheological properties but also improves the durability and other properties of SCC both in fresh and hardened state. Addition of SP ensures high deformation without bleeding and segregation at low mixing water contents. Addition of super plasticizer also improves the packing density to some extent. In modern concrete due to low w/c ratio all grains of cement do not get fully hydrated so a part of cement may be replaced partially by secondary raw materials also called mineral admixtures. The use of mineral admixtures not only improve the packing density but also responsible for increase in pozzolanic activity. Aggregates to be used in SCC should be non gap graded and their moisture content must be known and controlled.

The response of mortar and concrete system depends to a larger degree on the response of self compacting paste (SCP) system, because research work by different scientists proved that mechanical properties, volume stability and durability of mortars and concretes depends on the durability of their paste systems. In the present study the response of self compacting paste system has been study using powders cement (OPC – ASTM type 1), lime stone powder, marble powder and ground granulated blast furnace slag. Self compacting mortar (SCM) systems are special category of self compacting paste (SCP) systems used for repair and some special replacement purposes. Therefore, this study is further extended to see the response of these secondary raw materials in self compacting mortar (SCM) system.

1.5 Research Focus and Objectives

With the civil and structural engineering background, and working as an employee in the design office it was felt that structural engineers are concerned with the compressive strength and slump of concrete only while giving no importance to certain important properties like creep, shrinkage, rehology and micro structural development. Also knowledge about building materials and especially about incorporating secondary raw materials in concrete is at elementary stage in Pakistan. But now the time has come to incorporate new ideas in construction industry of Pakistan, to make structures durable, economical and environment friendly.

In the present study of self compacting paste (SCP) and self compacting mortar (SCM) systems the SRM’s used consisted of lime stone powder (LSP), marble powder (MP) and ground granulated blast furnace slag (GGBFS).

The research focuses on the study of SCP and SCM systems using secondary raw materials to assess the possibility of LSP, MP and GGBFS in such systems with a view to recommend the use of these materials as partial replacement of cement in developing countries like Pakistan where these secondary raw materials are available in abundance and cheap, to provide information to engineers about the field of modern concrete engineering, for energy saving in cement industry required for the production of cement and to address the related environmental aspects in carbon dioxide emission reduction.

The objectives of the present study on SCP and SCM systems were:

- To study the effect of shape, size, surface morphology and porosity on the properties of such systems.
- To study the properties of fresh concrete including its flow behavior, segregation resistance, deformability and initial and final setting.
- To study hydration kinetics of the systems using calorimetry.
- To study the volume stability by linear shrinkage measurements of these systems..
- To study the strength characteristics.
- To study the micro structure of secondary raw materials particles as well as the hydration products of these systems containing these secondary raw materials using scanning electron microscopy, mercury intrusion porosimetry and X – ray Diffraction analysis.

CHAPTER 2 – LITERATURE ON SCCS

2.1 Historical Development

Self compacting concrete was developed in order to overcome the problems associated with cast-in-place concrete. Another reason was, to make durable concrete structures; sufficient compaction by skilled workers is required. However, the gradual reduction in the number of skilled workers in Japan's construction industry has led to a similar reduction in the quality of construction work. One solution for the achievement of durable concrete structures independent of the quality of construction work is the employment of self-compacting concrete, which can be compacted into every corner of a formwork, purely by means of its own weight and without the need for vibrating compaction [1].The concept of self compacting concrete was proposed in 1886 by Professor Hajime Okamura, but the prototype was first developed in 1988 in Japan, by Professor Ozawa at the University of Tokyo [2]. SCC was also found to offer economic, social and environmental benefits over traditional vibrated concrete construction.SCC offers a rapid rate of concrete placement, with faster construction time, reduced noise and ease of flow around dense and congested reinforcement. The deformability and segregation resistance offers a high level of homogeneity, minimal voids, uniform strength, better surface finish and durability. Research and development work into SCC in Europe began in Sweden in 1990s and now nearly all countries in Europe conduct some form of research and development into material [3]. Due to its versatile nature and wide range of applications, the use of self compacting concrete spread throughout the world very rapidly; however, in Pakistan the research on self compacting concrete is still in elementary stage and its application and use in construction is very limited due to non availability of chemical and mineral admixtures at cheap rates and unclear understanding of basic concepts underlying the manufacture of self compacting concrete.

2.2 Secondary Raw Materials

Mineral admixtures, known as secondary raw materials are essential components of self compacting concrete nowadays because in self compacting concrete all cement particles do not get hydrated, therefore secondary raw materials (SRMs) like lime stone, marble powder, ground granulated blast furnace slag, fly ash, silica fume etc are used to replace part of cement in order to economize, to make environment friendly concrete and to get the same properties of SCC as mentioned above. Secondary raw materials are pozzolanic or inert powders which usually replace a part of cement and are used to improve the properties of concrete both in fresh and hardened which may include the control of early heat evolution, reduction in shrinkage, better packing, optimization of flow, enhancement of strength, improvement of microstructure, economy and the durability of cement based systems. In the literature secondary raw materials have been mentioned in a variety of ways like supplementary cementitious materials, fillers and powders depending upon the properties they exhibit. These are less energy intensive materials, mainly industrial by products, requiring little or no preprocessing. They 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 [4].

2.3 Pozzolan

As per ASTM C 125 [5], Pozzolan may be 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”.

2.4 Mechanism of Pozzolanic Reaction

Ordinary Portland cement when mixed with water forms calcium silicate hydrate (CSH) gel along with calcium hydroxide and ettringite. For the production of calcium hydroxide adequate amount of water and space should be available. However, when a pozzolan is present, its silica component reacts with liberated calcium hydroxide in hydrated cement paste in the presence of water to forms another form of calcium silicate hydrate. The reaction is generally slow, resulting in a slow rate of heat liberation and strength development. As the reaction consumes calcium hydroxide, thus reducing the weaker crystals, it has an important bearing on the durability of concretes especially in an acidic environment. Moreover, pore size distribution studies of such systems have shown that the reaction products are very efficient in filling up the large capillary pore, thus improving the strength and impermeability of the system [6]. In addition to reactive silica, pozzolans also contributes reactive alumina, which in presence of calcium hydroxide present in the system, forms cementitious products such as tetra calcium aluminate hydrate (of the form C_4AH_x, in which x varies from 9 to 13) , tricalcium aluminate hydrate (C_3AH_6), dicalcium aluminate silicate hydrate (C_2ASH_8), calcium carboaluminate ($C_3A.CaCO_3.H_{12}O$), high sulfoaluminate ettringite ($C_3A.3CaSO_3.32H_{12}O$) and low sulfoaluminate ($C_3A.CaSO_3.12H_{12}O$) [7, 8, 9].So it is the reaction between calcium hydroxide produced during hydration and the pozzolanic minor components added in the formulation to reduce the amount of cement. The reduction in the amount of cement will depend on the reactivity of pozzolanic material. These minor pozzolanic materials may be ground granulated blast furnace slag, flyash, marble powder, silica fume etc

2.5 Superplasticizers

Superplasticizers (SP) are chemical admixtures that increase the workability of the concrete at low mixing water content and thus are beneficial for the durability and strength of concrete because lower the water content for a given powder, higher will be the strength. A significant achievable concrete strength after 1980 was possible mainly due to the invention of superplasticizer simultaneously in Japan and in Germany. Superplacticizers are generally added at the time of mixing and they influence the properties of both fresh and hardened concrete. There are different groups of chemical substances influencing workability of cement pastes, mortars and concretes. These include lignosulfonates (LS), Sulphonated naphthalene and melamine formaldehyde condensates (SNF/SMF) and polycarboxylate ethers (PCE) [10].

2.6 Mechanism of Action of Supeplasticizers

There are four major clinker phases of cement namely C_2S, C_3S, C_3A and C_4AF. In a fresh cement paste without SP, C_2S and C_3S have a negative zeta-potential and C_3A and C_4AF have a positive zeta-potential. When SP is added along with mixing water , the SP is attacked in substantial amount to C_3A-Gypsum mixture leaving only small amounts for the dispersion of silicate phases. By late addition the SP is absorbed to a lesser extent on already wet powder particles, may be due to faster C_3A reaction with initial water leaving enough SP in the solution to promote dispersion of silicate phases and to lower the viscosity of the system [10].

2.7 Production of SRMs

2.7.1 Ground Granulated Blast Furnace Slag (GGBFS)

Ground Granulated Blast Furnace Slag (GGBFS) is a by-product from the blast furnaces used to make iron. The molten slag comprises of silicates and alumina, combined with some oxides from the limestone. The process of granulating the slag comprises of cooling of molten slag through high pressure water jets. The granulated slag is further processed by drying and then grinding in a rotating kiln to get a very fine powder, which is GGBFS. The use of GGBFS as a partial cement replacement not only saves the energy but also reduces emission of carbon dioxide and conserves natural resources. GGBFS is a glassy material and its colour varies from off-white to white depending on the moisture content, chemistry and efficiency of granulation. In the present study the GGBFS used was white in colour and when it was used it showed higher SP demand as compared with Cem1 (42.5R) alone and lesser shrinkage. GGBFS specific gravity is generally less than cement. GGBFS is made up of both glassy and crystalline phases but only glassy phase is responsible for its cementitious properties. ASTMC 989 [11] is the standard for evaluating the cementitious properties of the slag and according to that standard the factors that determine the cementitious properties of slag are chemical composition of slag, alkali concentration of the reactive system, glass content of slag, fineness of both slag and cement and temperature variations during the early phases of hydration. Advantages of slag as partial replacement of cement are improved workability, enhanced durability, low heat of hydration, high resistance to sulphate attack and enhanced architectural appearance.

2.7.2 Lime Stone Powder (LSP)

The use of supplementary cementitious can significantly improve the fresh and hardened properties of concrete. The use of SRM,s in concrete bring a lot of benefits like reduce water demand, better rehological properties, reduced shrinkage etc. The SRM,s do so because of their lower water requirement to wet their surfaces and the fact that they do not hydrate themselves but improve the hydration of cement rather indirectly. To verify these points investigation was done with help of different instruments using LSP (Lafarge). The LSP used was half white in colour. A part of CEM1 42.5R was replaced with LSP Lafarge. Results showed that LSP showed highest SP demand to meet the target flow. The MIP and SEM was also done for the solid powder to find out why LSP needs highest SP demand as compared with other SRM,s. The main effect of LSP is on physical nature by better packing of cement granular skeleton and a larger dispersion of cement grains.

2.7.3 Marble Powder (MP)

As stated earlier that Self compacting concrete mixtures contain higher cement content and low w/c ratio, in addition high workability is achieved by using chemical admixtures. In such mixtures all particles of cements do not get hydrated so a part of cement can be replaced by SRM,s , so in this way expensive particles of cement can be replaced by nonreactive economic particles of filler like marble powder. The marble powder used in this study was pure white in colour and was obtained from a mine in Germany. The idea of using marble powder in this study was to compare the results of marble powder with lime stone powder as both these SRM,s acts like a filler in concrete. The results showed that marble powder showed less SP demand as compared with LSP and GGBFS. But the setting time of marble powder was less as compared with LSP and GGBFS.

2.8 Rheology

Rheology is the science of the deformation and flow of matter. The hard, strong and durable cement-based product required by the user is only achieved following a period of plasticity and pumping, spreading, moulding and compaction all depend on rheology. The simplest analysis involving solid-like behavior is that of the Bingham model

$$\square\square = \square o + \square\gamma \qquad (1)$$

where the material is an elastic solid at shear stress □□ < □o , the yield stress, but flows at higher stresses, (□ is the plastic viscosity, the shear rate). The yield stress is a consequence of the interparticle forces, but these links are often broken irreversibly by shear and the measured shear stress is found to depend on time and previous shear history as well as on shear rate [12]. Rheological behavior of concrete can be described by two parameters i.e. yield stress and plastic viscosity. Slump test of concrete is related to yield stress. The concrete will flow only when yield stress of concrete is exceeded and will stop when the stress is below the yield stress.

2.9 Shrinkage

Volume stability of cement based system is the change in volume of final hydrated products compared with initial volume of constituent materials of the mix. Mostly the change in volume is shrinkage of the cementitious system, however in few rare cases it may be the expansion especially during the early hours of concrete placement if measured by linear technique. In general, shrinkage is caused by consumption / loss of water which includes the water consumed during hydration process and pozzolanic reaction, water suction by secondary raw materials and the external loss to the environment i.e. water evaporation. The expansion occurs mainly due to the growth of expansive species like calcium hydroxide and ettringite and may also be due to re-absorption of bleed water in the system.

Shrinkage is basically the sum of various parallel and over lapping simultaneously operating mechanisms which includes plastic shrinkage, chemical shrinkage, autogenous shrinkage and drying shrinkage. Out of all these, the rate of autogenous shrinkage is highest up till an age of 1 day and is quite significant for self compacting cementitious system using low w/c ratio. The measurement technique of shrinkage can be divided into two broad categories which are volumetric method and linear method. A careful analysis shows that both gives almost same results and choice of technique and interpretation of results require competence. The volumetric method gives shrinkage measurement as per its true definition of volume change whereas, its disadvantage includes sucking in of any entrapped air, thus falsely showing an increased shrinkage as well as bleeding resulting in loss of contact of sample with plastic condom membrane. With linear method, exact linear change in volume per unit length can be calculated; however significant shrinkage is registered after the onset of hardening only [13]. In the present study German classical “Schwindrinne” meaning shrinkage channel apparatus measuring 4x6x25 cm was used at 20±°C. The technique used in the present study measured total shrinkage during first 24 hours.

2.10 Calorimetry

The heat of hydration of concrete influence the workability, setting behavior, strength gain rates and pore structure development. The heat of hydration not effects the early age but also affects the long term performance of concrete. Calorimetry is a technique use to measure heat of hydration of concrete. Using Calorimetry the effect of w/c ratio, S.P content and addition of different mineral admixtures as a partial replacement of cement on the heat evolved from the system can be investigated. In the present study calorimetry is used to study the effect of LSP, MP and GGBFS on the heat released and reaction kinetics. The water used for calorimetry investigation should be 20oC.72 hours calorimetric investigation have been done on the samples to know the reaction kinetics of LSP, MP and GGBFS in both paste and mortar systems.

2.11 Scanning Electron Microscopy (SEM)

Scanning electron microscope is an excellent multipurpose used for studying the microstructure, interfacial transition zone (ITZ), present of various phases and their interconnectivity. SEM was used in this study to have a closer look at the surface morphology, microstructure and hydration products of selected specimens. Application of scanning electron microscopy enhances our ability to characterize cement and concrete microstructure, evaluate the influence of secondary raw materials, estimate the concrete durability and indirectly predict the service life [13, 14]. In the present study FEI XL30 environmental scanning electron microscope with field emission gun (ESEM FEG) was used to study the microstructure.

2.12 Mercury Intrusion Prosimetry (MIP)

MIP is used to get an idea about the porosity of powders or of cementitious material samples. In a standard procedure, a small specimen is first dried to empty the pores of any existing fluid. It is then weighed, transferred to chamber and the chamber is evacuated. Sample is subsequently surrounded by mercury and pressure on mercury is gradually increased. As the pressure increases, mercury is forced into the pores on surface of the sample. If the pore system is continuous and extends to surface, mercury penetrates the smallest pore necks with increase in pressure (penetrates the bulk sample volume). If the pore system is not continuous, mercury may penetrate the sample volume only by breaking through pore walls. Through tracking pressures and intruded volume during the experiment, it is possible to get a measure of the connecting pore neck diameter of a continuous system or a break through pressure in a discontinuous system. The pore width corresponding to the highest rate of mercury intrusion per change in pressure is known as “threshold”, “critical” or “percolation” pore width [15]. After achieving this pressure, mercury has been shown to penetrate interior of the sample. Using the technique, one also obtains the measure of total porosity in the sample as that corresponding to volume of mercury intruded at the maximum experimental pressure divided by the bulk volume of the un-intruded sample.

2.13 X-Ray Diffraction (XRD)

X – Ray Diffraction is a unique and powerful scientific tool basically applied for detection and quantification of crystalline materials. It also yields fundamental data when applied to amorphous solids and liquids. The term amorphous solid is for those substances that show no crystalline nature and the term solid is synonymous to crystalline. Most of the minerals occur in crystalline form. The phenomenon of x – ray diffraction includes a scattering process in which x – rays are scattered by electrons of the material without any change in wavelength. The resulting diffraction pattern is a fundamental physical property of each individual substance which not only gives speedy identification but also the complete elucidation of micro structure. For cement based systems both qualitative and quantitative XRD analyses are performed. While quantitative analysis is more precise, it is certainly time consuming, more expansive and demands expertise. Therefore, qualitative analysis is preferred. XRD analysis is also used to follow the process of hydration by determining the amount of un-reacted clinker minerals and calcium sulfate and / or by determining the amount of formed hydrates as function of time. For determining the amount of un-reacted cement constituents, quantitative XRD appears to be more suitable and widely used method [16].

CHAPTER 3 – EXPERIMENTAL PROGRAM

3.1 General (SCP Systems)

The secondary raw materials used for this included lime stone powder (LSP), marble powder (MP) and ground granulated blast furnace slag (GGBFS). The experimental program comprised of carrying out necessary tests pertaining to self compacting paste (SCP) systems. The experimental program started by first determining the particle characterization by using Beckmann Coulter LS 230 Laser Granulometer. Scanning electron microscopy (SEM) by FEI XL 30 Environmental Scanning Electron Microscope with field emission gun (ESEM FEG) was done to get the shape and surface morphology of secondary raw materials used in the present study. The chemical composition of secondary raw materials and cements was then determined and the densities were also obtained for these powders. The characterization of secondary raw material particles was also done using X –Ray Diffraction. All secondary raw materials in self compacting paste formulation for the present study were used in replacement mode. The water demand along with setting times was determined for the paste formulations using Vicat apparatus. Super plasticizer demand of the self compacting paste formulations was also determined. The flow level of 30 ± 1 cm was achieved by using PCE (Polycarboxylate ether) based super-plasticizer. Low w/p ratio was used to achieve the segregation resistance. The flow and flow times were noted for each formulation using Hagerman's mini-slump cone and V funnel apparatus. To determine the effect of these SRM,s as replacement of cement on hydration kinetics calorimetry investigation was done. Shrinkage measurements were also performed to check the early volume stability of these systems. To check the effect of these SRM,s on age vs strength relationship, strength testing was done. Microstructural study of hydrated sampled at specified ages were also carried out by scanning electron microscopy, mercury intrusion porosimetry and X –Ray Diffraction analysis.

3.2 Materials

The properties and tests conducted on the materials are listed below:

3.2.1 Cement

An ordinary Portland cement (OPC) CEM 1 42.5 R (Germany), conforming to ASTM C150 [17], was used in the experimental program carried out at TU Freiberg, Germany. The cement was stored in controlled environment accordance with requirements of research to keep it moisture free. The results by EDAX of CEM 1 are given in Table 3.1

Table 3.1: Chemical Composition of CEM1 42.5 R

Constituents	Percent by Weight sample
SiO_2	16.46
Al_2O_3	4.18
Fe_2O_3	3.51
MgO	1.23
CaO	66.56
Na_2O	-
K_2O	1.65
SO_3	6.41
Avg Particle Size (D_{50}) µm	14.77
Density(g/cm^3)	3.181

3.2.2 Lime Stone Powder (LSP)

The LSP used in the present study was white in color. Lime stone powder used in this study had 80.01% CaO. The EDAX analysis results are given in Table 3.2.

Table 3.2 Chemical Composition of LSP

Properties/ Oxide (% age)	%age
SiO2	10.68
Al2O3	4.17
CaO	80.01
Fe2O3	2.41
P2O5	-
TiO2	-
MgO	1.43

K2O	0.68
SO3	0.41
Na2O	-
Particle size d50 (µm)	7.353
Density(g/cm3)	2.784

3.2.3 Ground Granulated Blast Furnace Slag (GGBFS)

The chemical composition depends on the raw materials and the type of pig iron produced. The GGBFS used in the present study was off-white in colour. The chemical composition is of extreme importance and determines the physical-chemical characteristics of the GGBFS. The XRF analysis (Annexure D) results are given in Table 3.3.

Table 3.3 Chemical Composition of GGBFS

Properties/ Oxide (% age)	%age
SiO_2	34.30
TiO_2	0.94
Al_2O_3	10.07
Fe_2O_3	0.43
MgO	6.92
CaO	42.04
Na_2O	0.41
K_2O	0.82
SO_3	3.83
Particle size D50 (µm)	8.603
Densities(g/cm^3)	2.930

3.2.4 Marble Powder (MP)

The MP used in the present study was pure white in color. The EDAX analysis results are given in Table 3.2.

Table 3.4 Chemical Composition of MP

Properties/ Oxide (% age)	**%age**
SiO_2	2.22
TiO_2	-
Al_2O_3	0.50
Fe_2O_3	0.12
MgO	1.78
CaO	95.23
Na_2O	-
K_2O	0.15
SO_3	-
Particle size D50 (µm)	4.275
Densities(g/cm^3)	2.816

3.3 Mixing Regime and Mix Proportions of SCP Formulations

A fixed mixing procedure was adopted and used throughout the practical work. For maximum superplasticizer efficiency and full dispersion of the powder, a fixed mixing procedure was adopted and used throughout the practical work. Mixing and testing was carried out in a controlled environment of 20 °C and 60% relative humidity Hobart Mixer of 5 L capacity was used for the mixing. Before starting mixing in Hobart mixer cement, secondary raw material and powder super plasticizer were first manually mixed in closed plastic container in dry state. After dry mixing for 180 seconds mixed materials were then fed into the bowl of mixer containing requisite mixing water. After that slow mixing (145 rpm) was carried out for 30 seconds and then interior of bowl was cleaned. Then again slow mixing was done for 30 seconds and finally, the fast mixing (285 rpm) was carried out for 120 seconds of fast. The mix proportions of various self compacting formulations used are given in Table 1 of Annexure A.

3.4 Water Demand and Setting Times of SCP Formulations

As per the European Guidelines for Self Compacting Concrete [18], the calculation of a system’s water demand (WD) is often the first step required for self compacting cementitious system. Sum of water demand of powders as well as the aggregate phase is the WD of the system. The water demand of powder component can be determined by taking cement and other selected SRM,s in the desired proportions by mass and testing with Vicat apparatus, whereas for aggregate phase water demand can be found by procedures outlined in ASTM C127 and 128 standards [19, 20]. For the production of a durable self compacting concrete mix, it is important that the water content should be equal to the water demand of the system.The water demand and setting times of various self compacting paste systems were determined by Vicat apparatus at 20±1°C.

Fig 3.1: Vicat Apparatus

3.5 Flow Measurement of SCP Formulations

The quantity of third generation powder type PCE (poly carboxyl ate ether) based Melflux 2651 super plasticizer needed to obtain target spread of 30±1 cm was calculated with Hagerman's mini slump cone. The slump cone had an upper diameter equal to 70 mm, a lower diameter equal to 100 mm with a height of 60 mm. All formulations had mixing water equal to water demand of the system. T_{25} cm (time taken by the paste to travel 25 cm) and T_{30} cm was measured (time taken by the paste to travel 30 cm) along with total spread.

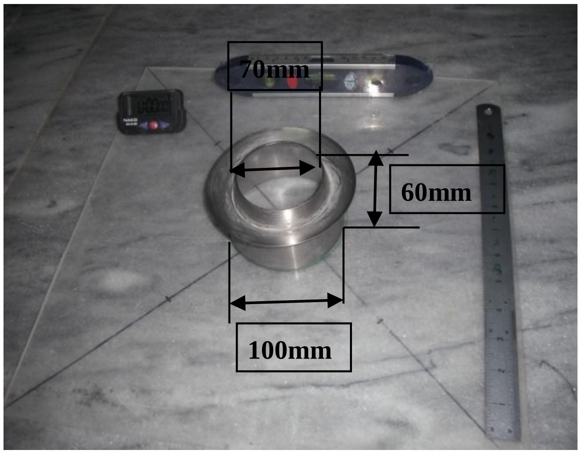

Fig 3.2 (a): Mini-Cone Flow Apparatus

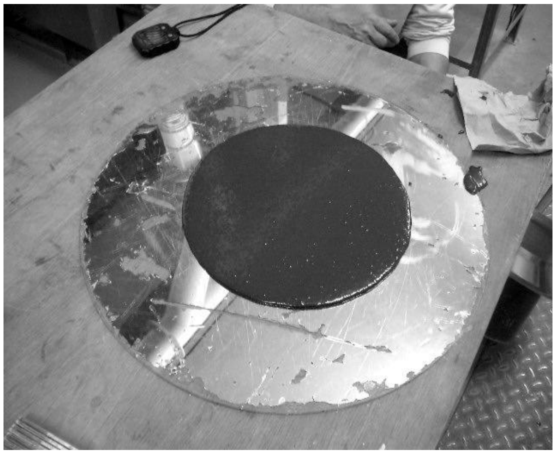

Fig 3.2 (b): Flow Spread After Removal of Cone (Rizwan 2006)

For each formulation at their particular water contents, the superplasticizer content required to give the target flow was determined by trials. The mixing was done by using Hobart Toni Technik mixer. The dry constituents of the formulations along with superplassticizer were first maually mixed in a plastic bag and then were fed into the Hobart mixer containing required a It has been mentioned in the literature[6] that total flow spread is a function of yield of the amount of mixing water. The mixing regime adopted was slow mixing (145 rpm) for 30 seconds and then interior of the bowl was cleaned. After that fast mixing (285rpm)was done for 150 seconds. The V-funnel flow time is the time required for a SCCS to pass a narrow opening and gives an indication of the filling ability of SCC provided that blocking and/or segregation do not take place; the flow time of the V-funnel test also gives an indication about the plastic viscosity of the system..

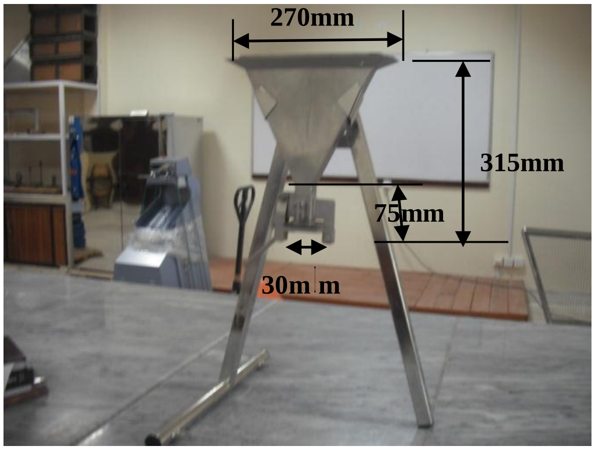

Fig 3.3: V Funnel Apparatus

The V-funnel test was done to get an idea about the viscosity of the sample by recording the time from opening the gate until the first light can be seen from the top. V funnel time was measured for all the formulations. V-funnel, as shown in Fig 3.4, made of steel, with a flat, horizontal top and placed on vertical supports, and with a momentary releasable, watertight opening gate. The funnel consisted of a rectangular cross section with top dimension as 270 x 30 mm and bottom square opening of 30 x 30 mm. The total height of funnel was 315 mm with a 75 mm long straight bottom square or rectangular section with a gate at bottom. Before doing the V funnel test, the funnel is filled with water to clean the ineer surfaces. For the test measurement, the V funnel is completely filled with self compacting paste, then the gate at bottom is opened.

Time taken between opening the lower gate and emergence of light from the gate while viewing the apparatus from the top is called funnel time.

3.6 Calorimetry of SCP Formulations

72 hours conduction calorimetry was done on the cement pastes with super plasticizer and with as well as without secondary raw materials using Calmetrix F-Cal 8000 instrument. F-Cal measures the temperature using eight 3”x6” cylinders. The temperature curve provides a fingerprint of the chemical reactions in the sample that can be analyzed to infer specific reactions during early stages of hydration, usually 24 to 36 hours after mixing. The samples were taken from the dry mixes of formulations prepared for other tests e.g. strength / shrinkage tests etc. Almost 530 grams of the mixed sample was put in the each cylinder of the Calorimeter. Concrete cylinders must be clean on the outside before inserting them into the calorimeter. Calorimetry was done for both the paste and mortar formulations to get an idea about the heat of hydration of these systems.

3.7 Early Shrinkage of SCP Formulations

In cement based composites, the cement paste is the source of shrinkage while other components are inert and may well control shrinkage deformation [21,22].For the measurement of shrinkage, a modified version of German shrinkage channel apparatus, measuring 4x 6x 25 cm interfaced with the computer was used for non-zeroed, linear early shrinkage measurements at 20 ± 1 ^{o}C with a relative humidity of 60 ± 5%. Fig 3.4 shows details of the apparatus.

Fig 3.4: German modified shrinkage channel apparatus

The samples were tested in uncovered condition thus approximating the field conditions. The measurements started ten minutes after the water addition to the constituents of self-compacting cementitious systems and these measurements lasted for the first 24 hours only. The frontal end of the apparatus is fixed while the rear end is flexible and is therefore, capable of a recording of 0.31 microns displacement due to shrinkage or expansion of cement based systems. The computer software recorded the shrinkage readings automatically with one minute interval. At the end of 24 hours, the shrinkage strains were picked up and imported into Excel sheets. The details of the measuring device can be seen in literature [10].

3.8 Casting, Curing and Strength Response Evaluation of SCP Formulations

Prisms for flexural and compressive strength measurement having 4 x 4 x 16cms dimensions were cast for different self compacting paste formulations. The samples were cured in sealed plastic bags for initial 24 hours at 90% relative humidity and 20±1°C. These were then tested for flexural and compression strength as per EN 196-1:1994 at the age of 1, 3, 7 and 28 days. . For flexural strength, the average of 3 samples broken in flexure was noted. For compressive strength, average of 6 samples was taken as strength of the sample.

3.9 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was done using FEI XL 30 Environmental Scanning Electron Microscope. The specimens of powdered secondary raw materials as well as the self compacting paste samples were studied at specified ages after stopping hydration with Iso-Propanol and Acetone. The purpose was to study the microstructure, morphology and the hydration products at various ages. In addition to the SEM images, qualitative chemical composition and X – ray micro analysis by Energy Dispersive X – ray Spectroscopy (EDAX) was also obtained for each sample.

3.10 Mercury Intrusion Porosimetry (MIP)

Maintaining lower water contents (as in HPC) whilst achieving an acceptable level of workability, results in higher strength for a given cement content as well as in lower permeability and lower shrinkage [37].The pore size distribution study was performed using Pascal 440 mercury intrusion porosimeter. The samples were prepared from the previously cast prisms for flexure and compression tests. These prisms after subjected to compression were broken to a size of 5mm by chisel and hammer. The hydration process was stopped by dipping the samples in a mixture of Iso-Propanol and Acetone. After drying the samples, these were subjected to a controlled incremental pressure till 400 MPa. All the measurement of pressure, volume of mercury intruded into sample and radii of pores etc were recorded by Pascal 440 Porosimeter. The contact angle between mercy and the pore wall was 140^o and mercury surface tension was 480 dyne / cm.

3.11 Marking and designation of Samples

A typical formulation used in the experimental program may be written as; C + 10 LSP, 1D where the first letter donates cement, followed by a numeral which indicates mass of secondary raw material in percent mass of cement. The next letters denote secondary raw material type, followed by the age of sample in days. The designation does not specify water and superplasticizer content.

3.12 General (SCM Systems)

In mortar system, aggregate component is also present along with paste component but the requirement of self compaction in terms of deformability, passing ability and segregation remains the same. High deformability and passing ability in SCM system is achieved by the use of powerful superplasticizer while segregation resistance is achieved by the use of low water powder ratio. SRM,s are also used in the formulations of SCM systems to reduce water demand, to increase packing and to reduce shrinkage.

3.13 Materials

Material used in SCM system include CEM1 42.5 R Cement and three SRM,s, viz, lime stone powder (LSP), marble powder (MP) and ground granulated blast furnace slag (GGBFS). The chemical composition and other physical properties of these powders are same as explained in section 3.2. Sand used was naturally occurring locally available Roba sand 0-2 mm size with fineness modulus (FM) of 2.39. SP used was PCE type Melflux 2510 L with 45.7 % solid content.

3.14 Composition of Mortars

The composition used for mortar system study was 1:1:2 mix proportion (cement: SRM: sand). The w/c ratio used in the study was 40% water powder ratio. Low water powder ratio was used to ensure adequate safety against segregation. All the formulations were tested in a control laboratory environment of 20^oC and 60% relative humidity.

3.15 Mixing Regime of SCM Formulations

For self compacting mortar systems incorporating various powders to get a target flow of 31±2 cm following mixing regime was adopted. First dry mixing including cement SRM and sand was done in a plastic bag for 60 seconds. Then measured amount of SP was fed into requisite amount of water and mixed thoroughly in a plastic jar. After that dry mix was fed into Hobart mixer of 5L capacity and then mixture of water and SP was fed into Hobart mixer. Then slow mixing was done for 30 seconds, after that inner wall of the mixer were cleaned. Then again slow mixing was done for 30 seconds followed by fast mixing for additional 120 seconds.

3.16 Flow Measurement of SCM Formulations

Literature suggests that the indices of deformability and segregation resistance are mini slump cone spread and V-Funnel time [1, 23]. According to some other authors the relationships between slump spread and yield stress and those between V-funnel time and plastic viscosity are very closely related [24]. Using Hagerman mini cone T25 cm was measured for all formulations because T25 cm in seconds seems to be a better flow index for the comparative flow response of SRM,s in SCM systems [10]. To get an idea about the plastic viscosity of the system V-funnel test was also performed for all the formulations using the same procedure as explained in section 3.5.

3.17 Shrinkage of SCM Formulations

Shrinkage apparatus was explained in detail in section 3.7. Same apparatus was used to measure the shrinkage of self compacting mortar system. Sum of plastic, chemical and drying shrinkage is the total shrinkage of the system. In literature complex instruments and conditions were used to measure a particular type of shrinkage that can never be applied on site. Engineers are only interested in total amount of early shrinkage of SCC system due to their low w/c and w/p ratio. Therefore, in this research total early shrinkages produced by different simultaneously occurring mechanisms was studied for SCM system using different SRM,s.

3.18 Calorimetry of SCM Formulations

To measure the heat of hydration of SCM system the calorimetry investigation was done using the same procedure and equipment as explained in section 3.6.

3.19 Strength of SCM Formulations

The casting, curing and strength testing's done according to EN196-1 of 1994. The casted specimens had dimensions 4x4x16 $cm^{3.}$ For flexure the average of three specimen of a particular formulation at a particular age and for compression the average of six samples was taken as the mean strength.

CHAPTER 4 – RESULTS

4.1 Particle Characterization by Scanning Electron Microscopy

Secondary raw materials particle shape, size and morphology are quite important parameters for understanding their role in flow, strength, shrinkage and microstructure of self compacting paste systems. The scanning electron microscopic pictures of secondary raw material particles used in the study are shown in Fig 4.1.

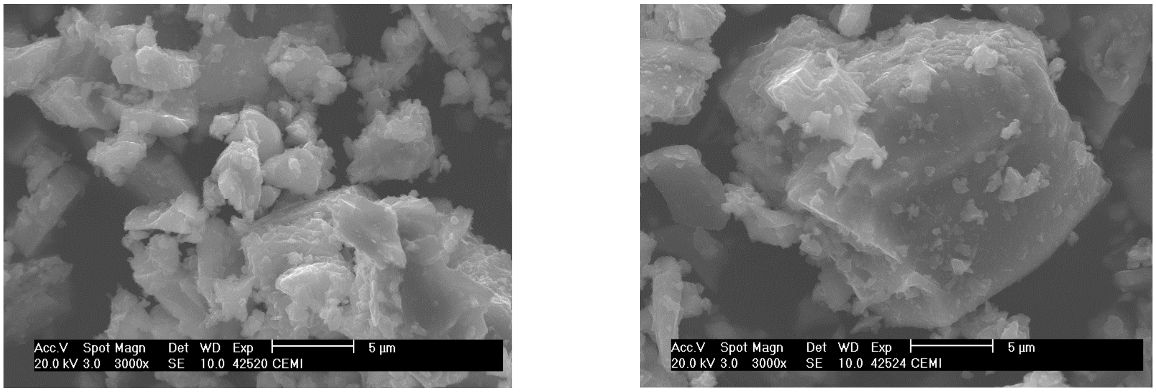

Fig 4.1 (a): SEM Characterization of "CEM1 42.5R" Particles

The particles of CEM1 42.5R are rough and angular as can be seen in Fig 4.1(a)

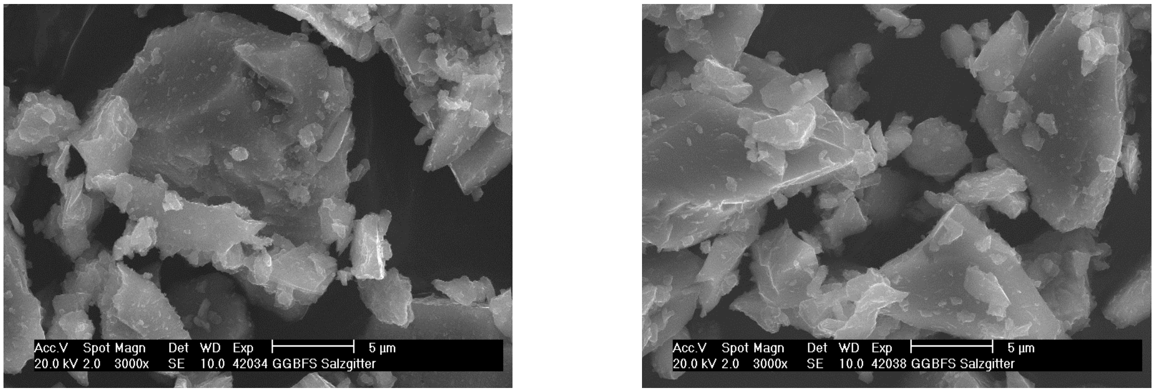

Fig 4.1 (b): SEM Characterization of "Ground Granulated Blast Furnace Slag" Particles

The particles of GGBFS are broken, elongated and flaky with smoother surface. The surface of these particles seems comparatively less porous.

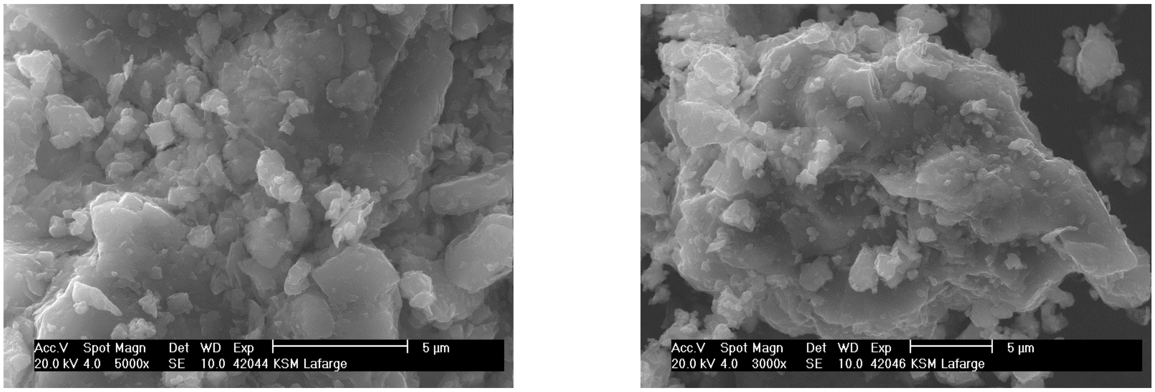

Fig 4.1 (c): SEM Characterization of "Lime Stone Powder" Particles

The particles of LSP are broken, angular and flaky with rough surface as can be seen in Fig 4.1(c).

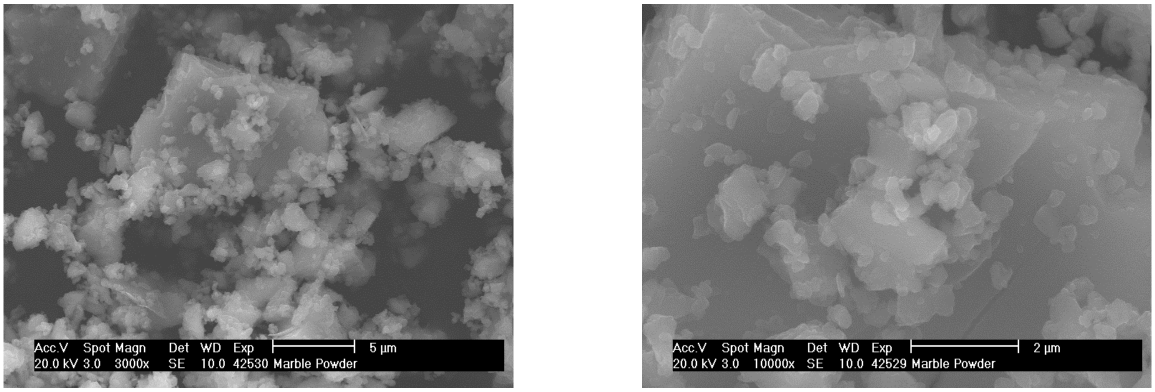

Fig 4.1 (d): SEM Characterization of "Marble Powder" Particles

The particles of MP are small, with moderate rough and porous surface as can be seen in Fig 4.1(d).

4.2 Tests on Self Compacting Paste (SCP) Systems.

4.2.1 Water Demand, Super Plasticizer Demand and Setting Times

The SRM's particle shape, size and morphology have a direct bearing on its water demand. The details of water demands and setting times of neat cement and various SRM's with 10 and 15% replacement mode are shown in fig 4.2 and fig 4.3. The change in the setting time of formulations varies according to the individual characteristics of each SRM used.

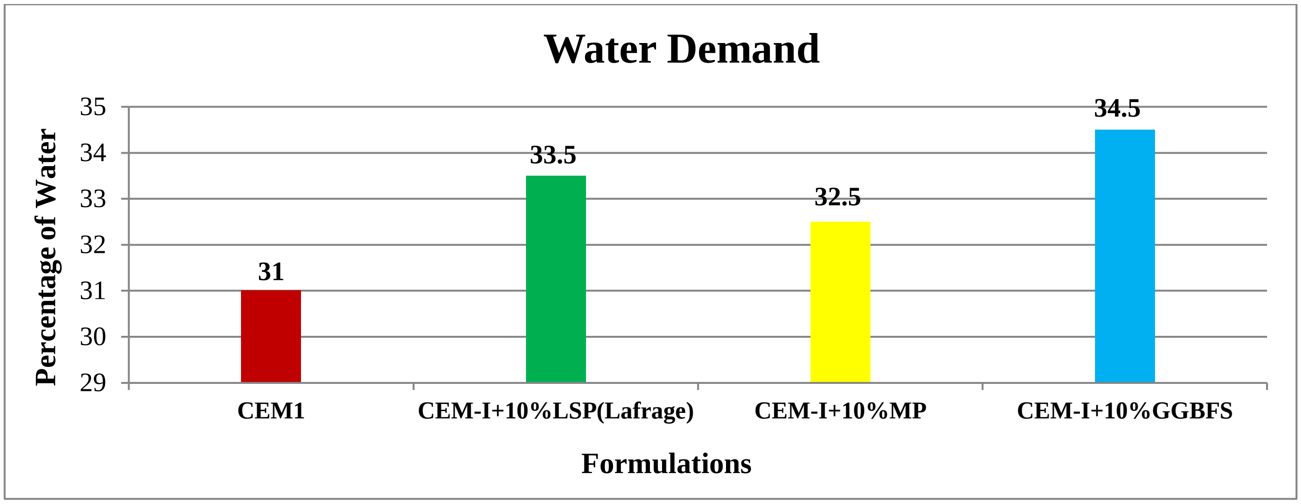

Fig 4.2: Water Demand of Cement and SCP formulations

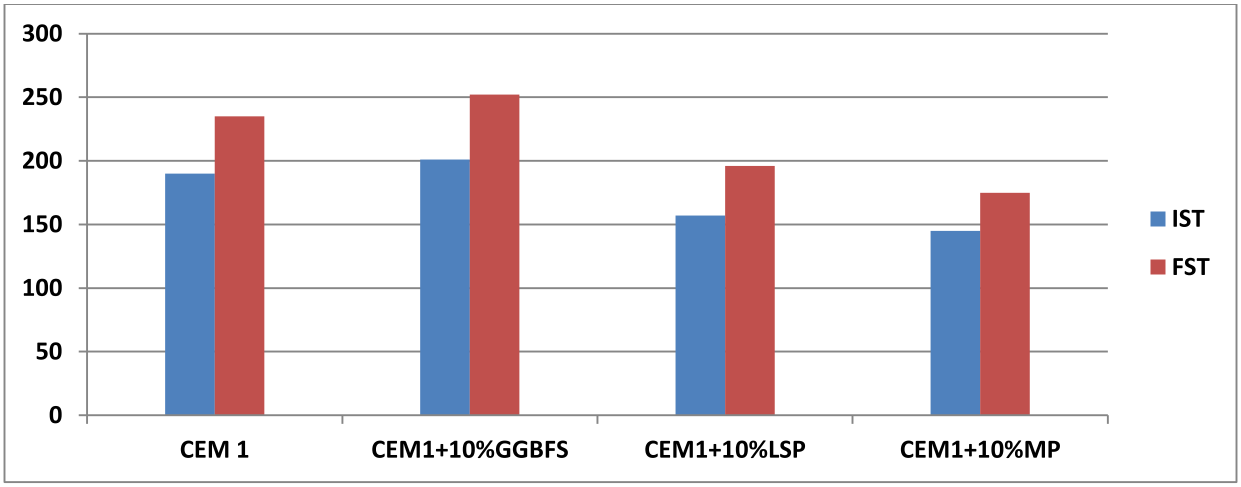

Fig 4.3: IST and FST of SCP formulations at respective WD's

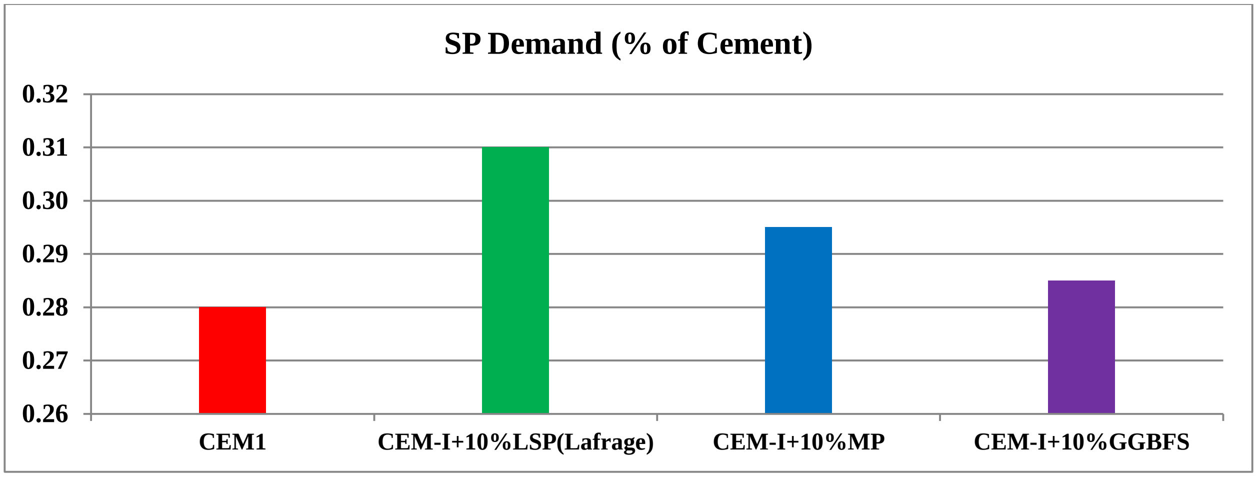

Fig 4.4: Superplasticizer Demand for target flow

Fig.4.4 shows the SP quantity required for 30 cm spread for different formulations using different types of SRM,s. One thing can be noticed that even a small SRM content (10% of cement mass) is added and SP requirement to give the target flow increased. This increased SP content has effect on certain properties like flow retention, strength, pore structure and shrinkage.

4.2.2 Flow of SCP Formulations

The timings were determined for flow of SCP systems to a 25cm and 30cm spread using glass sheet after lifting Hagerman's mini slump cone. Fig (4.5) graphically show the timings of different formulations for 25 cm. Fig (4.6) graphically show the timings of different formulations for 30 cm .T 25cm and T 25cm times were noted for a target flow of 30±1 cm, achieved by a using superplasticizer Melflux 2651 powder and mixing water equal to the demand of the system. Fig (4.7) shows the mean diameter of the flows after the flow has been stopped for each formulation.

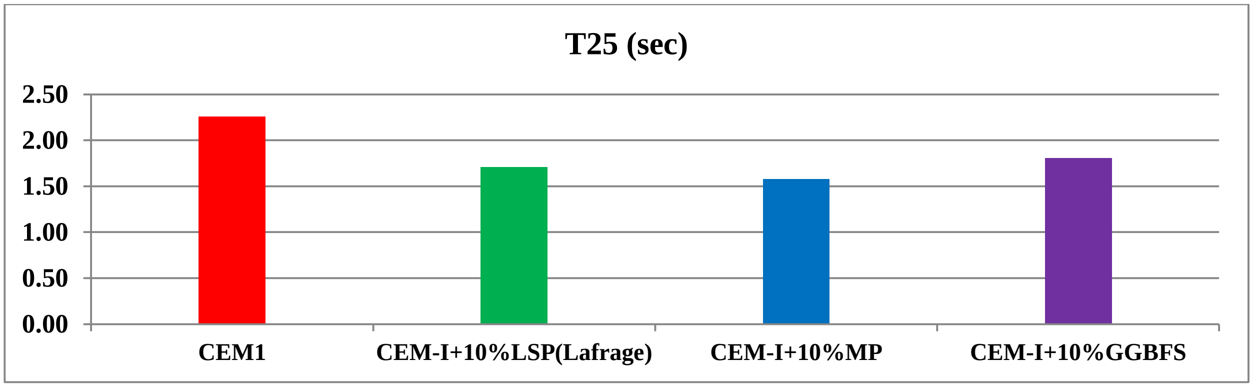

Fig 4.5: Variation of T25 timing

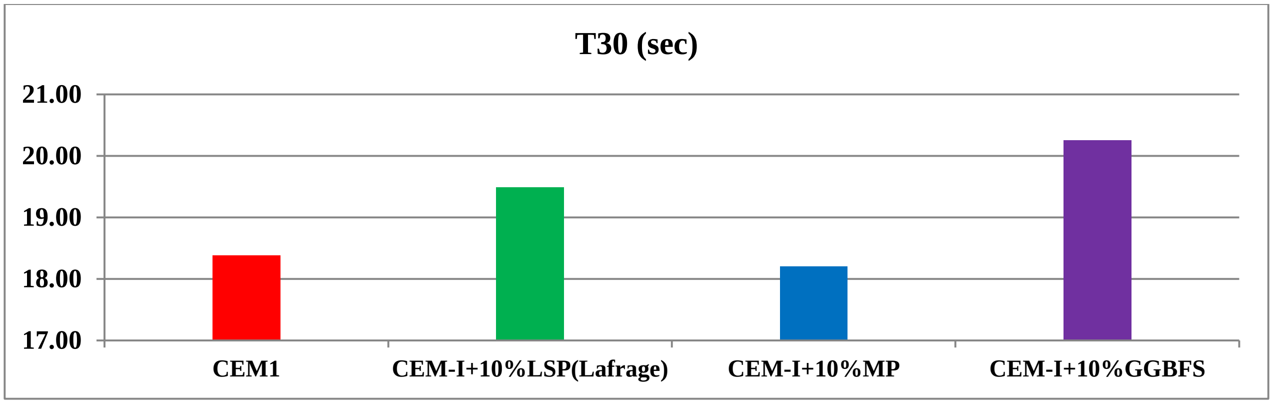

Fig 4.6: Variation of T30 timing

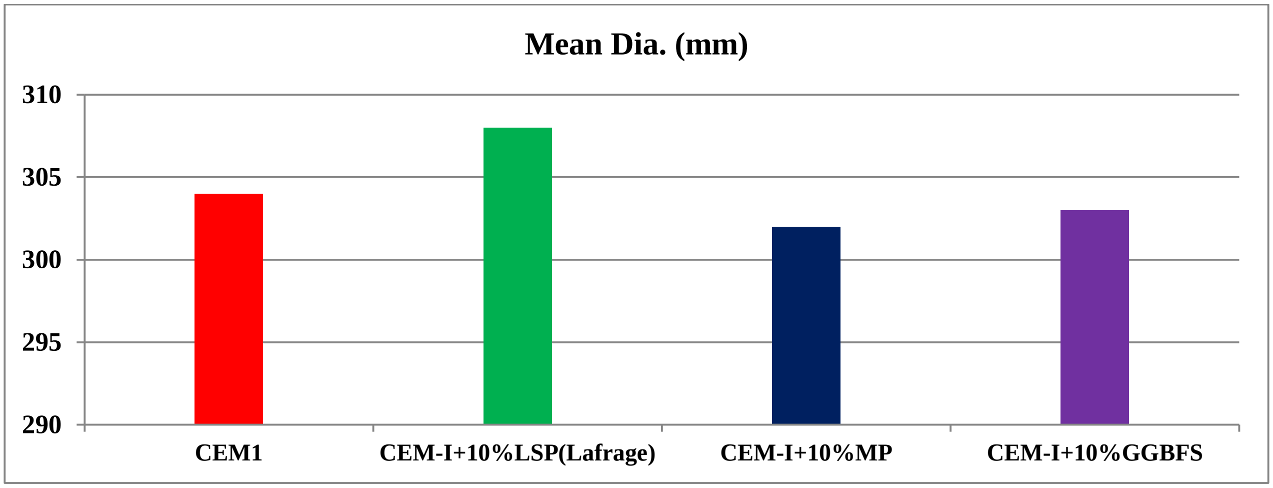

Fig 4.7: Variation of Mean Diameter (mm)

4.2.3 Calorimetry

The objective of the Calorimetry was to measure the heat liberated over time due to hydration reactions. Fig 4.8 shows the graphic representation of heat flow of self compacting paste systems using different SRM,s for duration of 72 hour. Calorimetry gives an idea about the effect of different SRM,s on the heat evolved from the system.

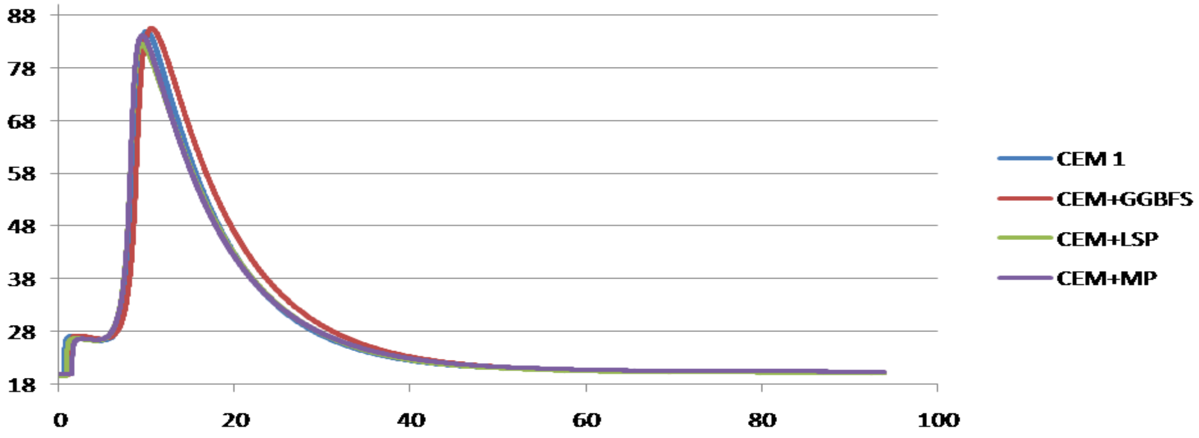

Fig 4.8: Heat of Hydration in ^{o}C vs. Time (hrs)

4.2.4 Heat of Hydration by Testo 177-T4

Another instrument that was used to measure heat of hydration was Testo 177-T4. When shrinkage samples were casted, the sensors of this instrument were immersed in the shrinkage channels to measure the heat of hydration of the formulations containing different SRM,s. Fig 4.9 shows the heat of hydration of different formulations

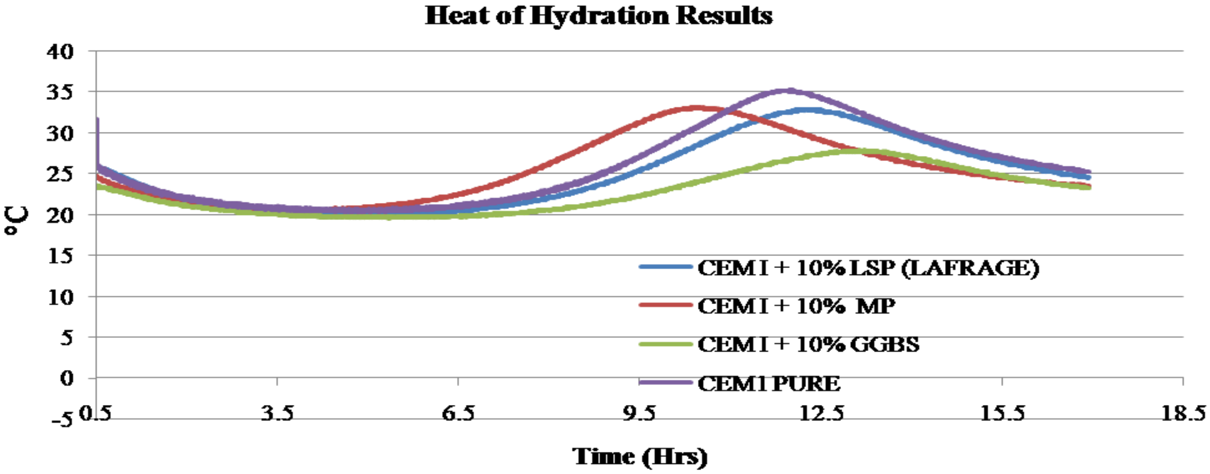

Fig 4.9: Heat of Hydration in ^{o}C vs. Time (hrs)

4.2.5 Early Shrinkage

Fig 4.10 shows the arrangement of early shrinkage measurement of self-compacting cementitious systems studied in this research. The shrinkage plots presented in figure show the effect of secondary raw material on the amount of early shrinkage of self-compacting paste systems.

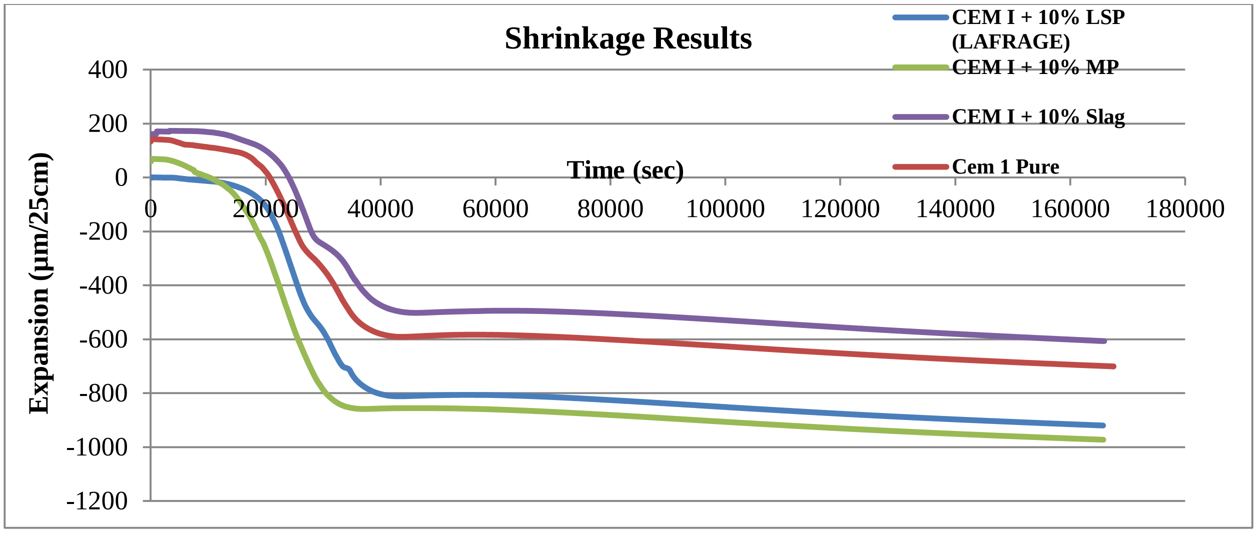

Fig 4.10 Volume Stability study of various SCP Systems

4.2.6 Strength of SCP Formulations

The specimens were tested for strength in SSD condition at the ages of 1,3,7 and 28 days and results. The development of flexural and compressive strength of specimen at specified age is shown in fig 4.11 and fig 4.12. As pozzolanic action takes some time to get started in some pozzolans therefore strength activity index of SCP formulations containing secondary raw materials is increasing with age.

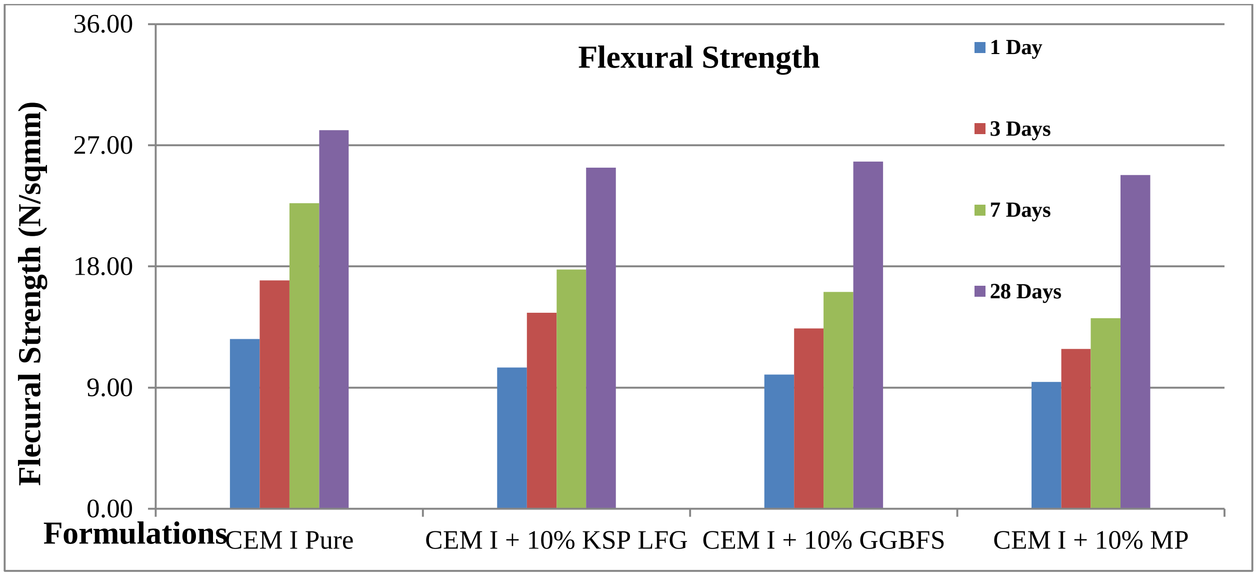

Fig 4.11 Flexural Strength of SCP Systems with various SRM,s

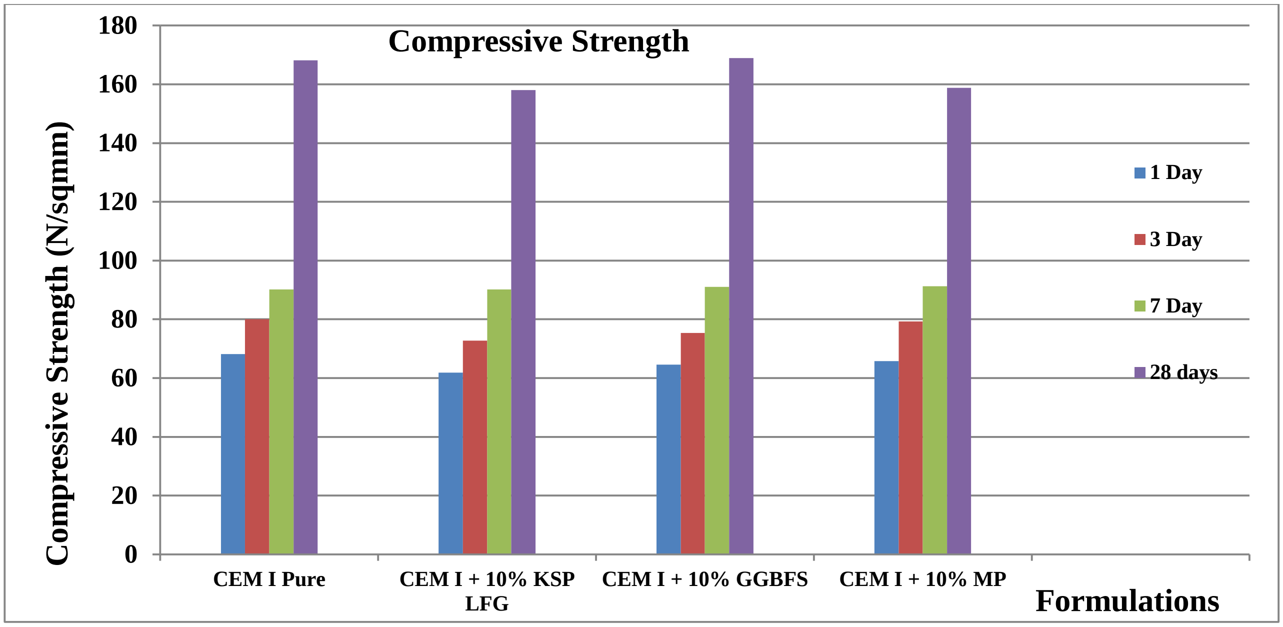

Fig 4.12 Compressive Strength of SCP Systems with various SRM,s

4.2.7 MIP of SCP Formulations

Fig.4.13 (a) shows the MIP results of CEM1 and Fig.4.13 (b) shows the MIP results of CEM 1 with 10% LSP. Fig.4.14 (a) shows the MIP results of CEM1 with 10 % GGBFS and Fig.4.14 (b) shows the MIP results of CEM 1 with 10% MP.

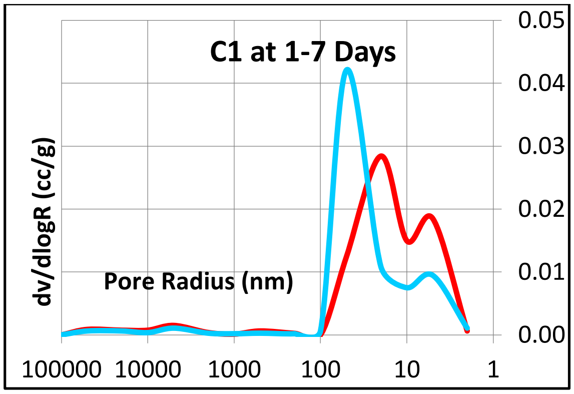

Fig.4.13 (a) MIP Results of CEM 1

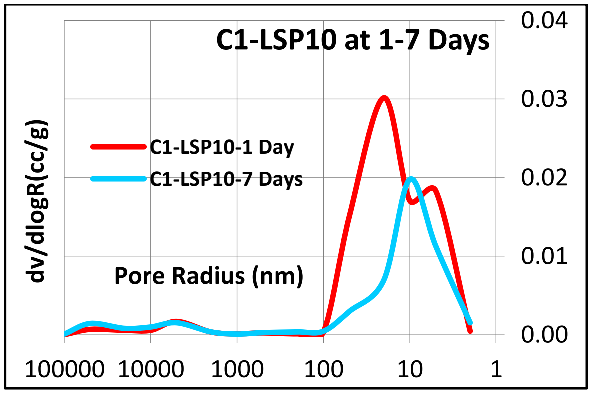

Fig.4.13 (b) MIP Results of CEM 1 with 10% LSP

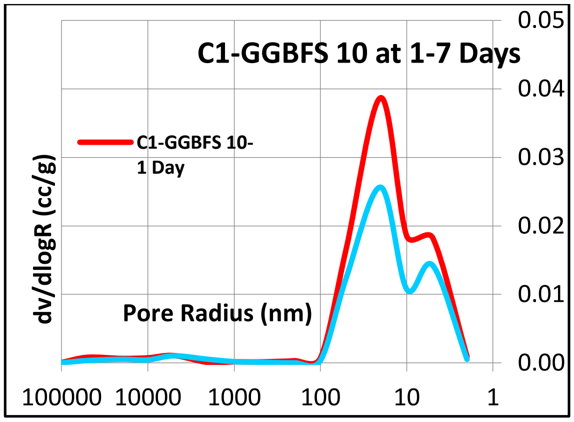

Fig.4.14 (a) MIP Results of CEM 1 with 10% GGBFS

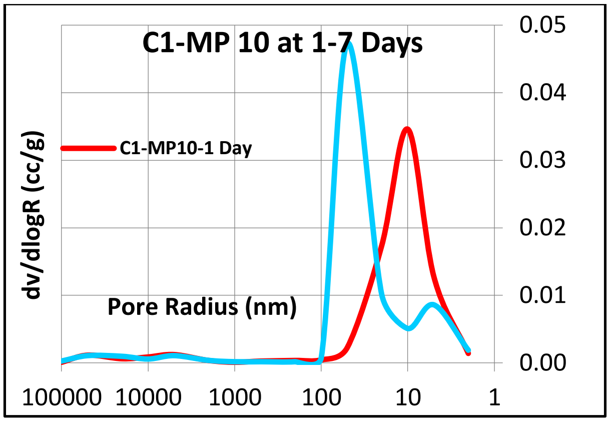

Fig.4.14 (b) MIP Results of CEM 1 with 10% MP

4.3 Tests on Self Compacting Mortar (SCM) Systems

4.3.1 General

After studying SCP systems in detail, the second phase of research continued on SCM systems. The following tests were performed on SCM system in the present study

- Flow
- Calorimetry
- Shrinkage response
- Strength

4.3.2 Flow and SP Requirements of SCM Systems

For SCM system the flow target was fixed at 31±2cm and was achieved by using Melfflux 2510 L 45.7% SP. Sand used for SCM system was Roba sand 0-2mm size. Three SRM,s were used in the study. SP demand depends on the size, shape, surface morphology and internal porosity of the SRM particles. Fig 4.15 shows graphically the plasticizer requirement for SCM Systems using various SRM,s.

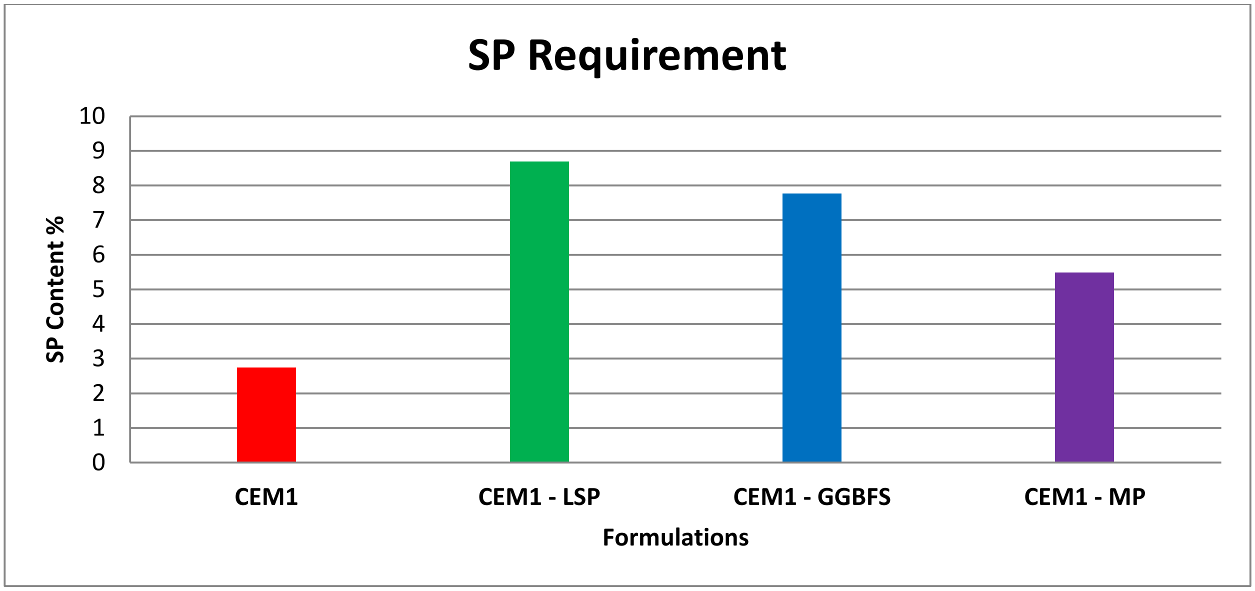

Fig 4.15 Plasticizer Requirement for SCM Systems using various SRM,s

Keeping in mind the particle shape, the relative viscosity in terms of V-funnel time and slump spread T25cm time can be understood for different formulations. Fig 4.16 is a plot between V-funnel time and T25cm slump spread time. System's viscosity can be described by using these two parameters. Fig 4.17 is a relationship between V-funnel time and total spread of different SCM system.

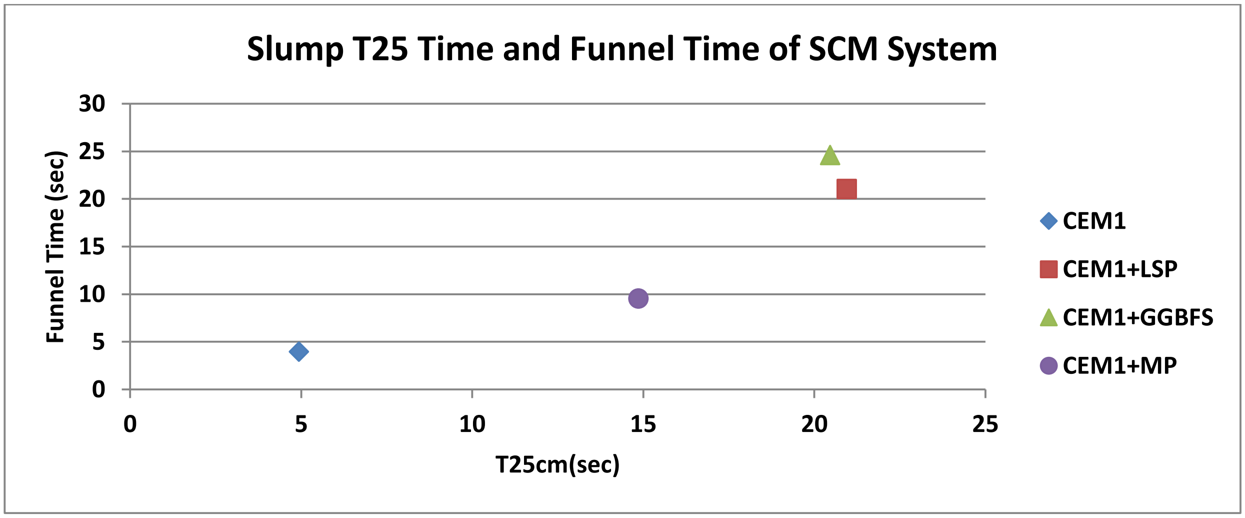

Fig 4.16 V-Funnel Time and T25cm Time of the Mini-Slump Cone Relationship for SCM System

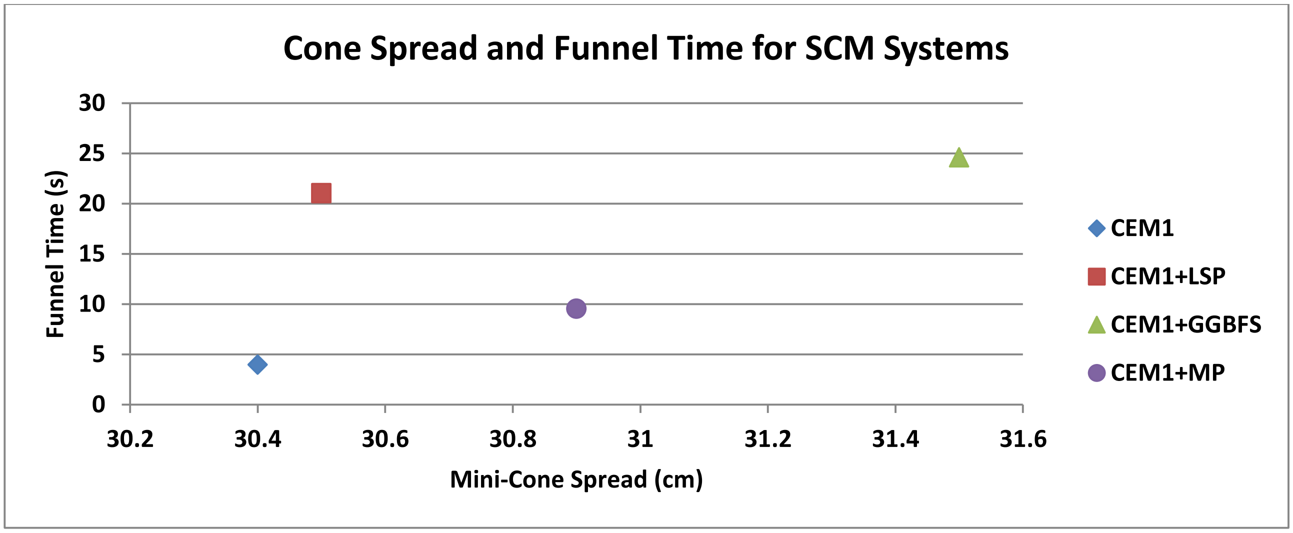

Fig 4.17 V-Funnel Time and Mini-Slump Cone Spread Relations of SCM Systems

4.3.3 Calorimetry of SCM System

This test was performed to measure the heat of hydration of various SCM systems using different SRM,s. The idea of this test was to compare the results of heat of hydration of SCP system with heat of hydration of SCM system. Fig 4.18 shows graphically the heat of hydration of SCM system incorporating various SRM,s using Calorimeter instrument.

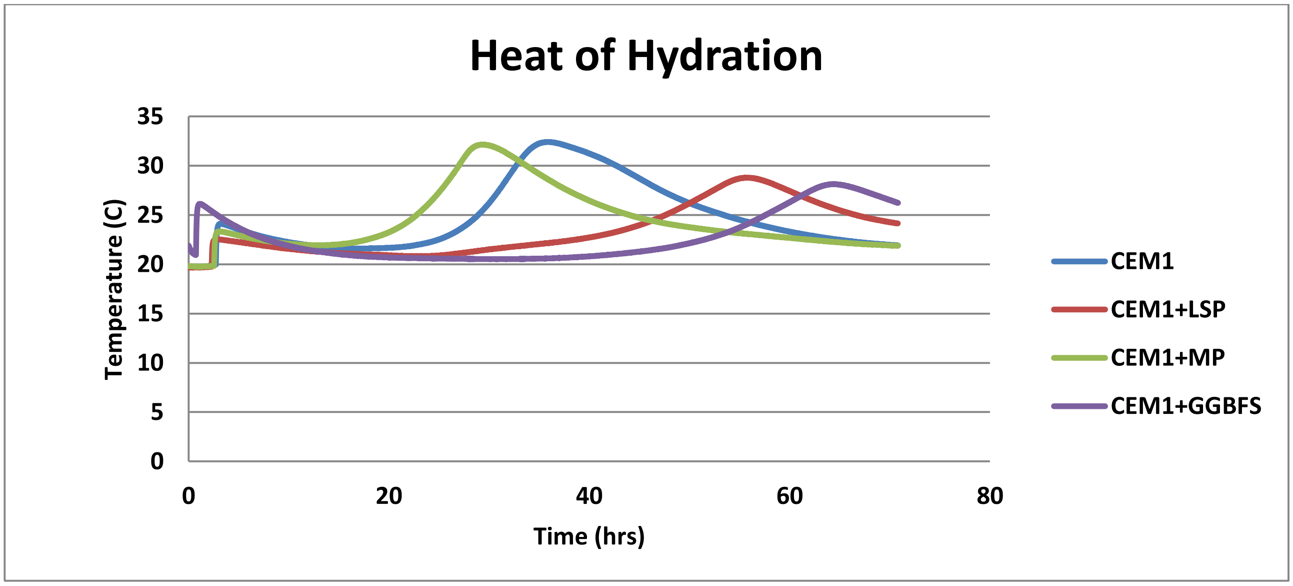

Fig 4.18 Heat of Hydration of SCM Systems using various SRM,s

4.3.4 Shrinkage of SCM System

To study the early volume stability of SCM systems shrinkage studies were done using the same procedure and equipment as explained in section 3.7. The samples were tested in uncovered condition thus approximating the field conditions. Fig 4.19 shows graphically the shrinkage of SCM systems using various SRM,s for first 24 hours.

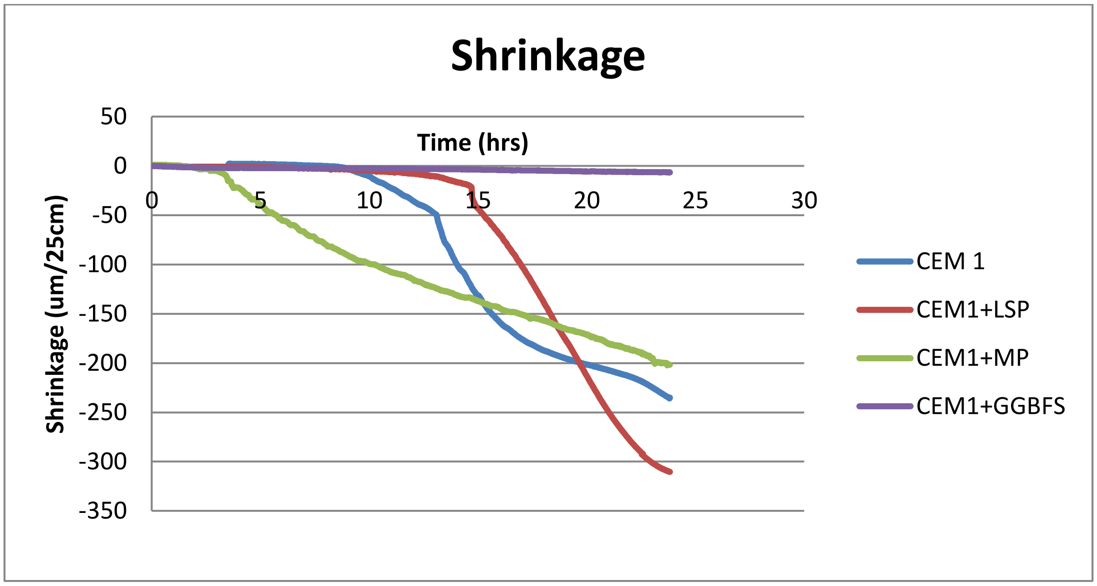

Fig 4.19 Shrinkage of SCM Systems using various SRMs

4.3.5 Strength of SCM System

The specimens were tested for strength in SSD condition at the age of 28 days. The development of flexural and compressive strength of specimen at specified age is shown in fig 4.20 and fig 4.21.

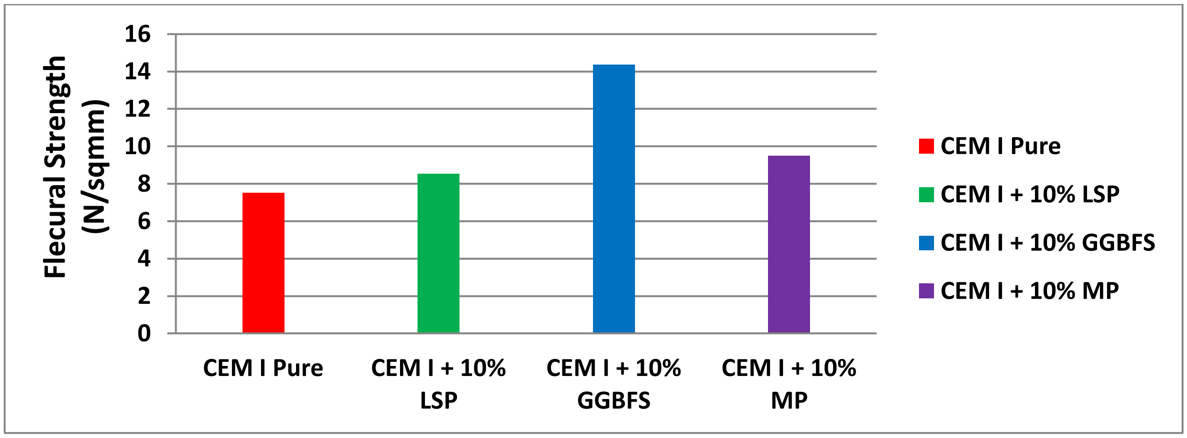

Fig 4.20 Flexural Strength of SCM Systems with various SRMs

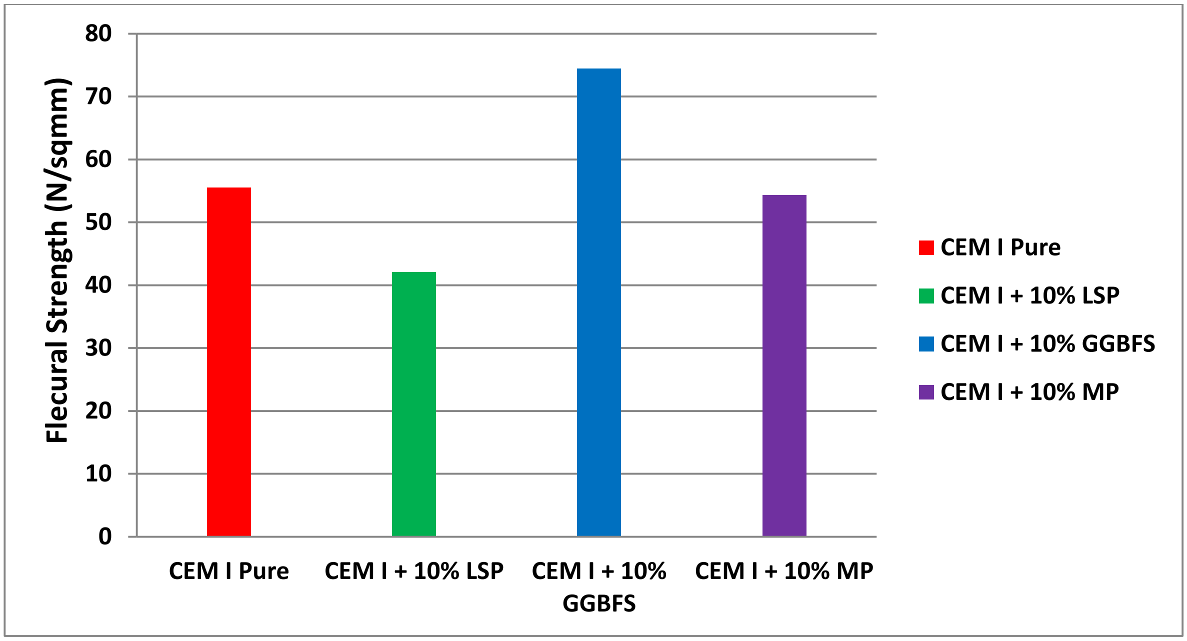

Fig 4.21 Compressive Strength of SCM Systems with various SRMs

CHAPTER 5 – DISCUSSION

5.1 SRM Characterization

5.1.1 Particle Size of SRMs

SRMs particle size plays a very important role in the packing of the mix due to physical and chemical effects. If it is two orders less than the cement particles it can pack the binder phase effectively and hence become very instrumental in reduction of porosity of cement based systems in hardened state. The SRMs which had particle size three times smaller than cement particle can pack completely (particle size which can pack the SRMs themselves are very uneconomical and impractical) in the smaller voids between the cement grains and consequently reduce porosity thereby increasing strength [25]. The particle size of LSP used in the present study is 7.353 micron which is smaller than particle of GGBFS, the particle size of which is 8.603. The MP used in present study has size 4.275 micron. The particle sizes in the present study are determined using Laser Granulometry. Smaller size also increases the specific surface area of the whole mix translating in to higher water demand to wet the surface area. WD of a packed system decreases as the voids between cement grains are filled with SRM and less space is available for water or air to occupy.

5.1.2 Particle Shape of SRMs

The particle shape and size of secondary raw materials are very important parameters for determining their role in terms of water, super plasticizer demands and mechanical properties of self compacting paste systems. The scanning electron microscopic images of secondary raw materials used in the study are shown in Fig 4.1(a), 4.1(b), 4.1(c) and 4.1(d). The particles of GGBFS are rough, angular shaped, broken, elongated and flaky with smoother surface. The particles of LSP are also broken, angular and flaky with rough surface and seem to have some internal porosity and are likely to give high internal friction during flow. Due to such characteristics GGBFS show higher water demand but superplasticizer demand for the target flow is higher for LSP particles due to very rough surface and angular shaped particles. The particles of MP are small, with moderate rough and porous surface. The particles of CEM1 also seem to be rough and angular in shape. Among all SRM,s used in the present study, the particles of LSP seem to be more rough and angular in shape.

5.2 Water Demand and Super Plasticizer Demand of Self Compacting Paste (SCP) Systems

Particle shape, size and morphology of secondary raw materials plays an important role in understanding the role of SRM,s in terms of water and super plasticizer demands, flow, strength, shrinkage and microstructure of self compacting paste systems. The water demand of CEM1 is the lowest while the GGBFS shows the highest water demand. MP shows the lowest water demand of all the three SRM,s used in the present study. Although there is not significant amount of difference in the water demand of these SRM,s. LSP water demand is lesser than GGBFS but it is higher than MP as cab seen in Fig. 4.2. GGBFS shows the highest water demand because the size of the GGBFS particle is larger than LSP and MP. It has already been stated that SCC systems should have the mixing content equal to the WD of the system which is the divorcing content below which system is uneconomical and gives rise unwanted effects while a water content more than the water demand of the system would adversely affect the strength and durability [10]. WD of a packed system decreases as the voids between cement grains are filled with SRM and less space is available for water or air to occupy. Smaller will be the particle size, the voids between cement grains will be less and lesser will be the water demand. The water demand of marble powder is lowest while GGBFS shows the highest water demand as can be seen in Fig.2. The smallest size of marble powder efficiently fills the voids between cement grains and the water demand of the system gets reduced. Due to larger particle size of GGBFS as compared with other SRMs used in the present study show the highest water demand. LSP particle size is larger than MP therefore its water demand is more than MP, because of the larger particle size of LSP more water will be required to fill the voids between cement particles.

The super plasticizer demand of LSP is highest as compared with GGBFS and MP as can be seen in Fig. 4.4. CEM 1 shows the lesser SP demand of all the formulations. LSP shows the highest SP demand because morphology of LSP shows irregular particles with broken edges and rough surface, so when it is used as SRM it offers higher internal resistance to meet the target flow. The MP shows higher SP demand than GGBFS and CEM 1 due to porous and rough surface as can be seen in Fig. 4.1 (c). The porous surface of MP absorbs water and rough surface of MP offers internal resistance to meet the target flow. Also one reason for increased SP demand of MP as compared with GGBFS could be is its increased specific surface area as compared with GGBFS due to the smaller particle size of MP. GGBFS shows higher SP demand as compared with CEM1 due to its irregular and broken particles of GGBFS. Furthermore, it has already been documented [27, 28, 29] that certain amount of super plasticizer is also adsorbed by secondary raw materials depending upon the morphology and surface texture of the particles.

5.3 Initial and Final Setting Times

MP shows the lesser initial and final setting times compared with other SRM,s as can be seen in Fig. 4.3. While GGBFS shows the higher initial and final setting times. The reason for decreased initial and final setting times of MP is the smaller particle size and higher CaO content. Another reason for decreased setting time of MP was the porous surface as can be seen in Fig. 4.1(c).With 10 percent replacement, the voids between the cement grains are effectively filled with the smaller particles of MP and these particles acts as the centre of nucleation for deposition of products of hydration, hence accelerates the setting. LSP also shows decreased setting times as compared with GGBFS and CEM 1 because LSP particle size is smaller than GGBFS and CEM1. Also the LSP particle surface has some pits that may also absorb some water and decrease the setting time. The reason for increased setting time of GGBFS was the larger particle size and more water demand.

5.4 Flow of Self Compacting Paste (SCP) Systems

Particle size, shape, morphology and internal porosity of secondary raw materials all have a very significant effect on the overall response of self-compacting systems [30, 31]. Previously it was thought that only the cement particles absorb SP while the SRM,s do not, which is incorrect. For the present study mixing water content for the paste system was equal to the water demand of the system. Because if the mixing water content is less than WD of system, very high SP doses are required to meet the target flow which not only disturbs the economy but also delays the setting times. And if the mixing water content is more than the WD then it affects the durability due to higher maximum pore sizes [13]. Limestone powder based self compacting paste system required the highest super plasticizer content to meet the target flow level as can be seen in Fig. 4.4 due to irregular, rough, broken and patchy particle characteristics resulting in increased internal friction during flow. The slump flow test using mini slump cone aims at investigating yield stress, deformability and the unrestricted filling ability of self compacting cementitious systems. It basically measures two parameters; the total flow spread and a suggested flow time T25 cms and T30cms. The former indicates the free unrestricted deformability or the yield stress and the later indicates the rate of deformation within a defined flow distance. The smaller value of flow time indicates lesser internal friction offered, during the flow, by the powder particles and translates into higher deformation. From Fig.4.5 it can be seen that T25 cm time was highest for CEM1 while lowest for MP. Among the three SRM,s used GGBFS shows the highest T25cm time while MP shows the lowest. The reason for GGBFS highest time is its larger particle size and rough and angular particle shape. MP shows the lowest T25cm time because of the least rough and angular size particles as compared with other SRM,s used in the study.LSP also have the higher T25cm as compared with MP because of the rough, broken and angular surfaces. Fig.4.6 shows the T30cm time. GGBFS shows the highest T30cm time while MP shows the lowest. Though the LSP particle shape is more angular and rough as compared with GGBFS and MP but the lower T25cm and T30cm time for LSP can be explained for the reason that LSP has higher SP content and therefore more SP is available to graft the surface. In general, this specifies the positive effect of secondary raw materials replacement on the self compacting cementitious systems that is low yield stress and higher viscosity. From Fig 4.7 it can be seen that LSP formulation has the larger mean diameter due to higher SP content while MP formulation have the lower mean diameter due to lower SP content.

5.5 Calorimetric Study of Self Compacting Paste Systems

Heat liberated over time due to hydration reactions is measured with this technique. The peaks of liberated heat are then considered reactions and hence reaction kinetics is known [13]. The hydration of cement phases and consequently the heat flow in the process is a complex phenomenon and depends upon various factors. It can influence concrete workability, setting behavior, strength gain rate and pore refinement; hence affect the early age behavior as well as long term performance of concrete. The knowledge and measurement of heat flow is also necessary to get an estimate of quantity of formed hydrates [32] and to get an idea about the curing regime [13].

Calorimetry is one of the techniques used to measure this heat flow with time. The Calorimetry curves shown in Fig 4.8 and heat of hydration measurement in Fig.4.9 represent the heat flow of various formulations. To understand the heat flow during hydration process and the effect of secondary raw materials on heat evolution, it is necessary to have the knowledge of the pattern followed by the curves. These curves show various phases or peaks. The initial phase or the first peak represents the initial reaction of the aluminate phase. Here almost all the clinker phases especially aluminate phase throw their ionic species into the solution. It is followed by the dormant or induction period where the hydration reaction slows down at a rapid rate and allows the concrete to be placed before the onset of main reaction leading to setting, hardening and the strength gain by the concrete. The actual reason for this dormant period still remains unclear. However, two theories exist to explain the process. According to the first theory, a protective layer forms around the reacting grains just after the initial high heat release which prevents the further reaction till the onset of acceleration period. The main problem with this theory is that no evidence of formation of such layer has yet been obtained and there is no satisfactory explanation for disappearance of the layer with commencement of acceleration period. The second hypothesis denies the presence of any real induction period and specifies it with slow development of hydrates by nucleation and growth. Drawbacks of this theory includes that neither it explains the drastic slow down of the rate of reaction just after the initial very high heat release nor there is any clarification of the reason of slow reaction of highly soluble Alite [32, 33].

The dormant period ends after few hours due to the onset of growth of two main hydration products, calcium hydroxide (CH) and calcium hydrate silicate (CSH). This marks the start of acceleration period where the calorimetric curve again ascends and reaches a second peak. This acceleration can be related to C_3S hydration which continues for 15 to 20 hours. The start of the acceleration period can also be related to the initial setting time by Vicat. The hydration of C_2S is much slower usually starts after 15 hours hence after reaching the second peak the again there is deceleration, but the hydration process of C_2S continues with a steady rate and decreases gradually [34].

From Fig.4.8 it can be seen that GGBFS shows the higher heat of hydration while LSP shows the lowest heat of hydration. For measuring the heat of hydration by calorimeter the samples were enclosed in boxes and were put in the separate channels. To measure the heat of hydration close to real condition shrinkage samples were casted; the sensors of the Testo 177-T4 instrument were immersed in the shrinkage channels.Fig.4.9 measures the heat of hydration in open condition more closely related to real condition. CEM 1 shows the higher heat of hydration while GGBFS shows the lowest heat of hydration. Fig 4.9 shows that MP reaction kinetics starts earlier than other formulation that is the reason why initial and final setting time of MP was earlier. GGBFS shows the delayed reaction kinetics and lowest heat of hydration that is why it shows delayed initial and final setting times. LSP heat of hydration is more or less similar to MP but LSP shows delayed reaction kinetics as compared with MP. LSP heat of hydration is more than GGBFS because of the smaller particle size of LSP as compared with GGBFS.

5.6 Early Volume Stability of Self Compacting Paste Systems

Shrinkage or expansion in volume or length can be caused either by chemical reactions during and after hydration process due to removal of water from the pores within the system. Shrinkage occurring while a concrete or mortar is not yet solid is referred to as plastic shrinkage [35]. Total shrinkage of self compacting paste formulations is the sum of various parallel and over lapping simultaneously operating mechanisms including plastic shrinkage, chemical shrinkage, autogenous shrinkage and drying shrinkage [34]. The lower the W/C ratio, the greater the number of capillaries of smaller diameter in the concrete in hardening phase which accelerates the development of autogenous shrinkage [35]. The paste phase is mainly responsible for the shrinkage / expansion of the cementitious systems. Greater the cement content in the paste phase greater would be the shrinkage due to higher consumption of water during hydration process. Fig. 4.10 shows the shrinkage of all the paste systems used in the present study. The shrinkage has been studied for initial 24 hours. MP shows the early and higher shrinkage of all the paste systems studied because of the smaller particle size and higher calcium carbonate content. This fact is also evident in the heat of hydration results as marble powder shows early heat of hydration. GGBFS shows the delayed and lesser shrinkage as compared with other SRM,s used in the present study. This fact is also evident in initial and final setting times because GGBFS showed delayed initial and final setting times due to its larger particle size as compared with LSP and MP.LSP powder shrinkage is more than GGBFS and CEM1 because of smaller particle size of LSP as compared with GGBFS and CEM1.

5.7 Strength of SCP Formulations

Maximum pore size, degree of pozzolanic activity and packing of constituent materials affect strength of self compacting paste system. Higher the pore size, lower pozzolanic activity and loose packing which will ultimately result in the reduction and lowering of strength. Fig 4.11 shows the flexural strength. CEM1 shows the higher flexural strength for 1,3,7 and 28 days. Among the three SRM,s used for 1,3and 7 days LSP shows the higher flexural strength but for 28 days the GGBFS shows the higher flexural strength. The results of flexural strength of GGBFS are contradicted to that reported in [25]. MP shows the lower flexural strength as compared with other SRM,s used. Fig 4.12 shows graphically the compressive strength. For 1 and 3 days compressive strength of CEM1 is highest while LSP shows the lower strength. Among the three SRM,s for 1day and 3 days MP shows the higher compressive strength due to smaller particle size as is also evident from the initial and final setting times and the early shrinkage. For 7 days MP shows the higher compressive strength while LSP and CEM1 show the lowest. But for 28 days GGBFS shows the higher compressive strength due to increased pozzolanic activity. The strength increase for GGBFS is due to combined filler and pore refinement effect. While LSP shows the lower 28 days compressive strength. LSP shows the lower compressive strength due to high SP content and coarser pore structure. Higher maximum pore sizes and lower pozzolanic activity are the reason for reduction in 28 days compressive strength of LSP and MP as compared with GGBFS. The particle size of Secondary raw materials along with its chemical composition plays an important role in the packing of the mix (physical effects) and pore refinement (chemical effects). If the size is two orders less than the size of cement particles it can pack the binder phase effectively and porosity get reduced. Porosity, being the function of degree of packing, always controls the strength. The secondary raw materials which have smaller particle size than the cement particles can pack efficiently in the smaller voids between the cement grains and hence result in better packing and consequently better strength [25]. The average particle size of GGBFS was smaller than CEM1 which gave better packing efficiency of binder phase and lower porosities in specimen due to physical, chemical and site nucleation effect therefore it gave higher compressive strength.

5.8 MIP of SCP Formulations

Fig.4.13 (a) show the MIP result of neat cement paste. At the age of 1 day for CEM 1 the intruded volume is less but for 7 days the intruded volume is more but for 7 days it is showing continuous porosity. Fig.4.13 (b) shows the MIP result of CEM1 with 10% replacement of LSP. Though the pore size is higher at age 1 but it is uniformly distributed throughout the matrix. At the age of 7 days the intruded volume is lesser for LSP. Fig. 4.14 (a) shows the MIP results of CEM 1 with 10 % GGBFS replacement. The intruded volume is higher for 1 day but it is lesser for 7 days for GGBFS formulation. Fig.4.14 (b) shows the MIP results of CEM 1 with 10 % MP replacement. The intruded volume is lesser for 1 day but it is higher for 7 days for MP formulation. For all formulations the pore size distributions shift to smaller end of the proe range. Pore refinement effect of all pozzolanic materials increases with respect to the degree of pozzolanic of powders and with the age of course.

5.9 Flow of Self Compacting Mortar (SCM) Systems

Three types of SRM,s were used in the present study. It has already been mentioned that particle shape, size, surface morphology and internal porosity affects the SP demand of the formulation. To get the target flow of 31±2cm Melfflux 2510 L 45.7% SP was used. Fig 4.15 shows the SP requirement of SCM systems using various SRM,s. LSP shows the highest SP demand to meet the target flow while CEM1 shows the lowest. Among the three SRM,s used in the present study MP shows the lowest SP demand. LSP because of its highly abrasive, irregular and broken surface requires higher SP demand to get the target flow. This behavior confirms the importance of particle shape on the flow response and SP demand. Also it has been stated in [13] that LSP had relatively higher maximum pore sizes so SP content absorbed into such pores is no longer available for cement particle dispersion that is the reason why LSP shows higher SP demand. GGBFS shows higher SP demand as compared with MP because of its highly irregular, abrasive and broken surface. CEM1 shows the lowest SP demand because of its non porous surface and more SP is therefore available for particle dispersion. Fig. 4.16 is a plot between V-funnel time and T25 cm slump spread time. Both of these parameters describe the viscosity of the system. The yield stress determines the stress above which the material becomes a fluid. The plastic viscosity is a measure of how easily the material will flow, once the yield stress is overcome. The physical interpretation of this factor is that the yield stress is the stress needed to be applied to a material to initiate flow. The yield stress term is a manifestation of friction between solid particles while the plastic viscosity term results from viscous dissipation due to the movement of water in the sheared material. From Fig.4.16 it can be seen that GGBFS gives the highest V-funnel time due to highly irregular surface while CEM1 gives the lowest V-funnel time due to less porous surface so more SP is available to graft the surface. Among the three SRM,s used in the present study MP shows the lowest V-funnel time. LSP T25 cm time is more than GGBFS but its V-funnel time is less than GGBFS. This means that yield stress of LSP is more than GGBFS while LSP plastic viscosity is less than GGBFS. MP shows lower yield stress and lower plastic viscosity as compared to GGBFS and LSP. Fig. 4.17 shows relationship between V-funnel time and mini slump cone spread. GGBFS shows the maximum spread and higher V-funnel time while CEM 1 shows minimum spread and minimum V-funnel time. GGBFS spread is more than LSP means that GGBFS yield stress is less than LSP which is also evident in Fig.4.16. It is concluded from these results that flow of SCM system depends to higher extent on the shape and surface morphology of the SRM particles.

5.10 Heat of Hydration of SCM System

The hydration of cement phases and consequently the heat flow in the process is a complex phenomenon and depends upon various factors. It can influence concrete workability, setting behavior, strength gain rate and pore refinement; hence affect the early age behavior as well as long term performance of concrete. Fig.4.18 shows the heat of hydration of SCM system. MP shows the early heat of hydration same behavior was studied in SCP system studies. The reason for early reaction kinetic of MP is its smaller particle size as compared with other SRM,s used in the present study. This was also the reason that MP shows the early initial and final setting time and early shrinkage in paste systems. GGBFS shows delayed reaction kinetic because of the larger particle size. Among the three SRM,s used MP shows the higher heat of hydration while GGBFS shows the lower heat of hydration. . LSP shows delayed reaction kinetics as compared with MP. LSP heat of hydration is more than GGBFS because of the smaller particle size of LSP as compared with GGBFS.

5.11 Early Volume Stability of Self Compacting Mortar Systems

Shrinkage occurring while a concrete or mortar is not yet solid is referred to as plastic shrinkage [35]. Total shrinkage of self compacting paste formulations is the sum of various parallel and over lapping simultaneously operating mechanisms including plastic shrinkage, chemical shrinkage, autogenous shrinkage and drying shrinkage [34]. The lower the W/C ratio, the greater the number of capillaries of smaller diameter in the concrete in hardening phase which accelerates the development of autogenous shrinkage [35]. Fig.4.19 shows the shrinkage of SCM mortar system. The shrinkage has been studied for initial 24 hours. MP shows the early and higher shrinkage of all the paste systems studied because of the smaller particle size and higher calcium carbonate content. This fact is also evident in the heat of hydration results as marble powder shows early heat of hydration. GGBFS shows the delayed and lesser shrinkage as compared with other SRM,s used in the present study.LSP shows delayed shrinkage as compared with MP and CEM1 because of higher SP content.

5.12 Strength of Self Compacting Mortar Systems

The structural and construction engineers are mostly interested in the strength enhancement associated with powders and not in the assessment of the contributions of physical and chemical factors towards the total strength of system [13]. Fig.4.20 shows the flexural strength of SCM system. GGBFS shows the higher flexural strength while CEM 1 shows the lowest. Among the three SRM,s used in the present study LSP shows the lower flexural strength. Fig.4.21 shows the compressive strength of SCM system. It can be seen that GGBFS shows the higher compressive strength while LSP shows the lowest compressive strength. Higher maximum pore size of LSP is the reason for lower strength as compared with other SRM,s. LSP is relatively inert and usually does not take part in chemical reaction [36]. The same behavior was reported in [30] that SCM systems using LSP as SRM gave the lowest 28 day compressive strength with all cements and also showed the largest pore sizes. MP compressive strength is also higher than LSP because of smallest particle size of MP.

CHAPTER 6 – CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

Particle shape and surface morphology plays an important in determining the overall response of SCP and SCM systems. So before using any SRM in SCC systems its particle characterization should be exactly known to determine its overall response on water demand, strength, flow, early volume stability and heat of hydration. The present study provides useful information about the use of various SRM,s in SCP and SCM systems. Based on this research work following conclusions can be drawn

1. LSP has been extensively used in SCC by different researchers. In the present study LSP shows higher SP demand and lowest strength as compared with GGBFS and MP.
2. GGBFS gives higher strength as compared with LSP and MP but it also gives higher flow timings due to particle shape and its size. Hence in order to get better flow response, the fineness of GGBFS must be increased to get an optimum particle size which should results in better flow characteristics of the formulation as well as packing efficiency of the binder phase.
3. MP gives lowest SP demand of all the SRM,s used in the present study but it also gives higher shrinkage in SCP and SCM system and lesser initial and final setting times due to its particle size and shape.MP also shows early reaction kinetics and higher heat of hydration as compared with LSP and GGBFS.
4. Use of MP in SCP and SCM system not only gives better flow response but it also shows better strength response as compared with LSP.

6.2 Recommendations

1. The studies for GGBFS and MP should be extended for SCC formulations as they give comparatively good results for SCP and SCM formulations.
2. Studies should be made for GGBFS and MP to find their optimum percentages that can be used for SCC.
3. A study should be made to find the effect of type of SP on the behavior of GGBFS and MP formulations.

4. A study should also be carried out to find the effect of different types of cements on the behavior of GGBFS and MP.
5. A particular secondary raw material, depending upon its individual morphology, shape, size and chemical composition, exhibits improvement in certain properties of modern concretes while the other may enhance certain other properties of the self compacting concrete systems. Hence, in order to get a better overall response of self compacting concrete systems, the blends of GGBFS and MP may be investigated.

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