

# **HIGH-PERFORMANCE MORTARS AND CONCRETES USING SECONDARY RAW MATERIALS**

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## ABSTRACT

The American Concrete Institute (ACI) defines HPC as the concrete that meets special performance and uniformity requirements that may not always be obtained using conventional ingredients, normal mixing procedures and typical curing practices and these requirements may include enhancement of ease of placement without segregation, long term mechanical properties, early age strength, toughness, volume stability and life in severe environments. Therefore in this thesis the criterion of high performance has been taken as ease of placements or self-compaction and this is in line with the literature. Similarly flow of SCCS has been taken as an indicator of rheology. Microstructure has been studied by MIP and SEM techniques.

With the civil and structural engineering background, it was felt during the investigation stage of a fire damaged structure in Lahore that most of the damage occurred due to poor knowledge of the material performance and to its poor execution. Ignoring altogether the importance of knowledge about building materials, it is a common perception amongst structural engineers that only good structural analysis and design are the keys to satisfactory structural performance. This along with other motivating factors was responsible for undertaking this research in Freiberg.

The study on high performance cementitious systems started with selection of secondary raw materials (SRM's) after literature survey. The use of RHA in SCCS is a new idea and it could not be found in the literature so far. It was therefore decided to look into the comparative behavior of SF with amorphous and crystalline rice husk ashes (RHA and RHAP respectively) in such systems so that RHA could be recommended, if found good, for use in SCCS in the developing rice growing countries like Pakistan where SF of good quality is not likely to become economically available in the near foreseeable future while RHA could be/has been made using a very simple plant. It was also revealed during literature survey that the use of fly-ash in combination with other pozzolanic materials like silica fume is not common in Germany although their use in Scandinavian countries has proven very successful. Therefore the other dimension of the research was to investigate the role of binary and ternary binders in SCCS. The SRM's were selected and included limestone powder, fly-ash, silica fume, amorphous rice husk ash (RHA-imported from USA) and crystalline RHAP (imported from Pakistan). The study looks into flow, strength, microstructure and volume stability of SCCS in terms of linear early shrinkage measurements. The total strength increments produced by binary and ternary binders need a simple quantification which would be of a great value to the construction and structural engineers who are interested only in the total strength of a cementitious system. They are usually not interested in the strength fractions attributable to the physical and chemical processes of a material. Therefore it has been proposed to consider the relatively inert material as the base line for other pozzolanic binders and their combinations for simple strength quantification. Early volume stability was assessed in terms of total linear early shrinkage because codes of practice prescribe only the total shrinkage value of cementitious systems and not of its different parallel operating mechanisms. The study started with HP SCP systems and then SCM and SCC systems were taken up. The results could be considered more useful/adaptable as the studies on SCC, a component of SCCS, were also carried out at ready mixed concrete manufacturing plant and then during its placements in a local tunnel of a teaching mine in Freiberg based on the experience gained from prior laboratory studies.

Various new simple methodologies and concepts regarding the estimation of HP SCC's water demand, flow and strength quantification have been proposed. With the invention of superplasticizers in Germany and Japan in early 1980s, it was possible to achieve high strengths

and high durability by using suitable fillers. A formula is proposed for the indirect calculation of water demand of any filler/powder in suitable proportion with cement. Moreover the author also proposed to measure T 25 cm flow time for HP SCM/SCP systems( the ratio between 25 cm spread and bottom diameter of mini-cone is 2.5) by deriving analogy from the Abrams cone used in SCC for determining time for 50 cm slump spread. This would be a useful indirect indicator of rheological properties of SCCS. The bottom diameter of the Abrams cone is 20 cm and the said ratio is 2.5.

Based on the results it can be stated that amorphous RHA of even medium pozzolanic activity, usually obtained from the power plants using rice husks for power generation, can be safely considered as a very close equivalent of as-produced SF and could be used imaginatively in SCCS in place of SF. It has also been established that both binary and ternary binders in SCCS improve their performance and durability. It is recommended that the mixing water content of such systems should not be far away from their water demand for the sake of economy and durability.

## ZUSAMMENFASSUNG

Das American Concrete Institute (ACI) definiert Hochleistungsbeton (High performance concrete, HPC) als einen Beton der spezielle Leistungs- und Gleichförmigkeitsanforderungen erfüllt. Die Anforderungen schließen Vereinfachtes Ausbringen, verbesserte Frühfestigkeiten und mechanische Langzeiteigenschaften, Härte, Volumenstabilität und Belastbarkeit unter besonderen Umweltbedingungen ein. Diesen Anforderungen kann für gewöhnlich nicht mit klassischen Rohstoffen, normalen Misch- und Abbindeprozeduren entsprochen werden. Daher wurde in dieser Studie in Übereinstimmung mit der Literatur die Einfachheit des Ausbringens beziehungsweise die Selbstverdichtung als Kriterium für Hochleistungseigenschaften genommen.

Während einer bautechnischen Begutachtung eines brandgeschädigten Gebäudes in Lahore deutete sich an, daß die Schäden zum größten Teil durch mangelhafte Kenntnis der Materialeigenschaften und mangelhafte Verarbeitung verursacht wurden. Dies war unter anderem Anlaß für die Durchführung der vorliegenden Untersuchungen.

Die Arbeiten über Hochleistungsbetone begannen mit der Auswahl von alternativen Rohstoffen (secondary raw materials, SRM) entsprechend den Ergebnissen des Literaturstudiums. Die Verwendung von Reisasche (Rice husk ash, RHA) in selbstverdichtenden Betonen (Self compacting concrete, SCC) ist eine neue Idee, die bislang nicht veröffentlicht wurde. Deshalb wurden vergleichende Untersuchungen mit Mikrosilika (Silica fume, SF), amorpher und kristalliner Reisasche (RHA bzw. RHAP) durchgeführt. In vielen Entwicklungsländern ist Mikrosilika guter Qualität auf absehbare Zeit kaum zu vernünftigen Preisen verfügbar, während Reisasche in reisanbauenden Ländern wie Pakistan hochverfügbar ist. Bei entsprechenden Ergebnissen soll mit dieser Studie die Verwendung von RHA alternative zu SF in SCC empfohlen werden. Das Literaturstudium zeigte ferner, daß die Verwendung von Flugasche in Kombination mit anderen puzzolanischen Materialien wie Mikrosilika in Deutschland nicht üblich ist, während dies in Skandinavien erfolgreich getan wird. Deshalb ist ein weiterer Aspekt der vorliegenden Arbeit die Untersuchung der Rolle binärer und ternärer Binder in SCC. Als SRM wurden Kalksteinmehl, Flugasche, Mikrosilika sowie RHA (aus USA) und RHAP (aus Pakistan) ausgewählt. Die Studie beschäftigt sich mit Fließverhalten, Festigkeit, Mikrostruktur und Volumenstabilität (gemessen als frühes Schwinden) von SCC. Die durch binäre und ternäre Binder bewirkte Erhöhung der Gesamtfestigkeit soll möglichst einfach berechnet werden können. Die ist von großem Wert für Bauingenieure, da sie üblicherweise nur an der Gesamtfestigkeit des zementären Systems und nicht an den Festigkeitsanteilen chemischer oder physischer Komponenten interessiert sind. Es wird vorgeschlagen, das vergleichsweise inerte Material für andere puzzolanische Binder und deren Kombinationen als Ausgangspunkt zur einfachen Quantifizierung der Festigkeit zu nehmen. Es ist in der Praxis nicht üblich, die frühe Gesamtschwindung mit deren einzelnen Teilprozessen zu beschreiben. Deshalb wurde die Volumenstabilität als lineare Gesamtschwindung ermittelt. Die Arbeiten begannen mit selbstverdichtenden Pasten (High performance self compacting pastes, HP SCP), die zu selbstverdichtenden Mörteln (High performance self compacting mortars, HP SCM) und selbstverdichtenden Betonen (High performance self compacting concretes, HP SCC) weiterentwickelt wurden. Die Ergebnisse dieser Arbeiten können als anwendungsfreundlicher angesehen werden, als Ergebnisse von Arbeiten durchgeführt ausschließlich an SCC. Darüber hinaus wurden ausgehend von Laborergebnissen einige Versuche an einem Beton-Mischwerk

und anschließend während des Einbringens in einen Versuchsstollen des Lehrbergwerks durchgeführt.

Zur Abschätzung von Wasserbedarf, Fließverhalten und Festigkeit von HP SCC werden verschiedene einfache Methoden und Konzepte vorgeschlagen. Die Erfindung von Verflüssigern in Deutschland und Japan Anfang der 80er Jahre ermöglichte zusammen mit geeigneten Zuschlägen das Erreichen hoher Festigkeiten und Dauerhaftigkeiten. Es wird eine Methode zur indirekten Berechnung des Wasserbedarfs für jeden Zuschlag, der in geeigneten Mengen mit Zement gemischt wird. Weiterhin schlägt der Autor die Messung der T 25 cm Fließzeit für HP SCM/SCP-Systeme (das Verhältnis zwischen T 25 cm Ausbreitmaß und dem Kegelbodendurchmesser) in Analogie zur Ermittlung des 50cm-Ausbreitmaßes mittels Abrams-Kegel bei SCC vor. Dies wäre ein brauchbarer indirekter Indikator der rheologischen Eigenschaften von SCC-Systemen. Der Durchmesser des Abramskegels ist 20 cm und das besprochene Verhältnis ist 2,5.

Ausgehend von den Ergebnissen läßt sich feststellen, daß sicher amorphe RHA als Ersatz für SF in SCC genommen werden kann. Dies gilt selbst bei RHA mittlerer puzzolanischer Aktivität, wie sie von Kraftwerken mit Reistrohfeuerung erhältlich ist. Die Verbesserung von Leistung und Dauerhaftigkeit konnte sowohl für binäre als auch für ternäre Binder in SCC-Systemen festgestellt werden. Für gute Dauerhaftigkeit wie auch aus ökonomischen Gründen wird vorgeschlagen, daß die Menge des zuzumischenden Wassers in etwa dem Wasserbedarf entspricht.

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## LIST OF NOTATIONS

ACI	American Concrete Institute
BET	Brunauer Emmet and Teller
BFS	Blast Furnace Slag
CEM	Cement
C II	CEM II
CH	Calcium Hydroxide
C <sub>2</sub> S	Di-Calcium Silicate
C <sub>3</sub> S	Tri-Calcium Silicate
C <sub>3</sub> A	Tri-Calcium Aluminate
C <sub>4</sub> AF	Tetra-Calcium Aluminoferrite
DSC	Differential Scanning Calorimetry
EDAX	Energy Dispersive X-Ray Analysis
FA	Fly Ash
Fig/(s)	Figure/ Figures
FST	Final Setting Time
GGBFS	Ground Granulated Blast Furnace Slag
HP	High Performance
HRWRA	High Range Water Reducing Agent
HCL	Hydrochloric Acid
IST	Initial Setting Time
ITZ	Interfacial Transition Zone
LOI	Loss on Ignition
LSP	Limestone Powder
MP	Mineral Powder
MSA	Maximum Size of Aggregate
MIP	Mercury Intrusion Porosimetry
OPC	Ordinary Portland Cement
PCE	Polycarboxylate Ether
PCSIR	Pakistan Council of Scientific and Industrial Research
PSD	Particle Size Distribution/ Pore Size Distribution
P/S	Plasticizer-Stabilizer Ratio (SP/VEA)
QP	Quartz Powder
RHA	Rice Husk Ash (Amorphous)
RHAP	Rice Husk Ash (Crystalline)
RHA's	Rice Husk Ashes
RH	Relative Humidity
RILEM	International Union of Laboratories and Experts in Construction Materials, Systems and Structures.
RP	Rock Powder
SCC	Self-Compacting Concrete
SCCS	Self-Compacting Cementitious System
SCM	Self-Compacting Mortar
SCP	Self-Compacting Paste
SRM	Secondary Raw Material

SRM's	Secondary Raw Materials
SF	Silica Fume
SSD	Saturated Surface Dry
SEM	Scanning Electron Microscope/Microscopy
SP	Superplasticizer
SNF	Sulfonated Napthalene Formaldehyde
SMF	Sulfonated Melamine Formaldehyde
TC	Technical Committee
TG	Thermogravimetry
VEA	Viscosity Enhancing Agent
VMA	Viscosity Modifying Agent
W/C	Water-Cement Ratio
w.r.t	With Respect To, With Reference To
WD	Water Demand
w/b	Water Binder Ratio
w/c	Water Cement Ratio
w/cm	Water Cementitious Materials Ratio
w/p	Water Powder Ratio
XRD	X-Ray Diffraction

## **1 INTRODUCTION**

### **1.1 High-Performance Concrete (HPC)**

Despite its wide spread use now in the developed countries, it has been difficult to define high-performance concrete (HPC) in a unified way and no simple and consensus definition exists to date. American Concrete Institute (ACI) defines HPC as the concrete that meets special performance and uniformity requirements that may not always be obtained using conventional ingredients, normal mixing procedures and typical curing practices [1] and these requirements may include enhancement of ease of placement without segregation, long term mechanical properties, early age strength, toughness, volume stability and life in severe environments. Brandt [2] reports that HPC is the one, which gives 28 days compressive strength greater than, or equal to 60 Mpa and very high performance concrete (VHPC) has 28 days compressive strength in the range of 120 Mpa or greater. He states that HPC differs from ordinary concrete in terms of high strength, increased fractions of fine and very fine grains, lower W/C and use of super plasticizer (SP) to get higher flow of around 180-250 mm slump with the retention time of 1-1.5 hours and smaller fraction of coarse aggregates and smaller maximum grain dimensions. Similarly there are numerous definitions of HPC coined by various practitioners.

### **1.2 Criterion of HP**

Enhancement of ease of placement without segregation has been considered as the criterion of high performance of the cementitious systems in this thesis. Ease of placement without segregation is a special characteristic of self-compacting cementitious systems (SCCS) which do not require any mechanical vibration for their compaction. It is a desirable feature of concrete in heavily reinforced sections. This is why that many research papers call self-compacting concrete SCC as high performance concrete [3, 4, 5, 6]. Because of the importance of the role of the paste component on the overall response of mortars and concretes, the response of HP self-compacting paste (SCP) systems was studied in detail in order to start the research work. These are the one component primary cementitious systems and it is very well known that the mechanical properties, volume stability and durability of mortars and concretes depends to a great extent on the durability their paste component. Durable or high performance paste components systems are obtained by incorporating secondary raw materials.

### **1.3 Secondary Raw Materials (SRM's)**

SRM's are termed in the literature by a variety of ways like supplementary cementitious materials, fillers and powders depending upon their role in fresh and hardened state. These are less energy intensive materials, mainly industrial by-products, requiring little or no pyro-processing. 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 [7]. They help in the advancement of hydration process and especially in the improvement of hydration products. They usually replace a part of the cement. These include limestone powder (LSP), fly Ash (FA), ground granulated blast furnace slag (GGBFS), silica fume (SF) and rice-husk ash (RHA). SRM's, also called mineral admixtures, contribute to the properties of hardened concrete through physical and chemical

processes including hydraulic or pozzolanic activity. Typical examples are natural pozzolans, fly ash, ground granulated blast-furnace slag, silica fume and rice husk ash, which can be used individually with Portland cement or blended in different combinations with cements. These materials react chemically with calcium hydroxide released from the hydration of Portland cement to form cement compounds. These materials are often added to concrete to make concrete mixtures more economical, reduce permeability, increase strength, or influence other concrete properties. As their average particle size is less than 125 microns, those can also be termed as powders remembering of course that cement is also a powder but this term has been invariably applied to the SRM's other than cement in this thesis.

#### **1.4 Advantages of Using SRM's**

The use of supplementary cementing materials can significantly improve the transport properties and durability of concrete. However different dosages and combinations of supplementary cementing materials can yield dramatically different response [7]. The use of SRM's in concrete may bring lots of benefits like reduced water demand (WD), increased flow and strength and reduced shrinkages etc. but some problems may also be caused. One has to be careful regarding the selection of type and amount of SRM's to be used in an application. The uniformity of these materials may be questionable in some cases [8]. The effects of fly ash, and, to a lesser degree, that of slag and condensed silica fume on the properties are well documented. By contrast little published data and case histories are available on the performance of RHA [8]. In general SRM's have both positive and at times negative effects on water demand (WD), temperature rise, strength development, freeze-thaw resistance, chemical attack resistance, alkali-silica reaction, alkali-carbonate reaction control [8]. They also have effect on volume stability and microstructure etc. necessitating their careful selection for an application. With continuously graded aggregates, the use of SRM's in the presence of super-plasticizer usually results in minimizing the voids, paste and hence the cement requirement. They also add to the stability of the system. This could result in increased economy, high performance and increased durability.

#### **1.5 Research Focus and Objectives**

In the study of high performance self-compacting paste, mortar and concrete systems the SRM's used consisted of as produced silica fume, rice husk ash (both amorphous and crystalline), limestone powder, fly ash and some times their blends have also been used. The research focuses on the study of HP SCP and HP SCM systems using secondary raw materials to find a comparative response of RHA/RHAP and SF in such systems with a view to recommend the use of RHA as an alternate to SF, if found suitable, in the rice growing developing countries where SF may not be economically available. According to the author's information RHA has not been comparatively studied in HP SCCS before. Later on, studies were also made on SCC systems in the laboratory, at the ready mixed concrete manufacturing plant and then very useful and practical experience was gained from the SCC placements in a local tunnel of a teaching and research mine.

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

- To look into the possibility of using medium reactivity rice-husk ash (RHA), as a suitable replacement of silica fume (SF) in HP SCCS.

- To see the differences in the response of amorphous and crystalline RHA in such systems.
- To see the comparative response of various relatively inert and pozzolanic powders used alone or in suitable combinations resulting in binary and ternary binder HP SCCS.
- To study the microstructure and its significance on the properties of HP SCCS.

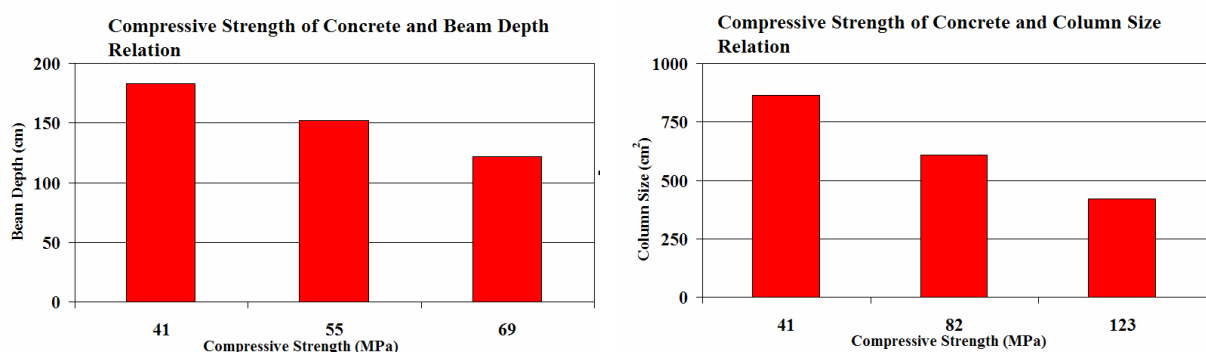
## 2 LITERATURE ON SCCS

The study encompasses three high performance self compacting cementitious systems including HP SCP systems, HP SCM systems and HP SCC systems. A brief historical development of concrete strength is first presented and thereafter these systems would be treated in order.

### 2.1 Historical Development

In early 1940's concrete strength at construction sites was around 25 MPa which rose to about 34 MPa in 1950's. In the early 1970's, experts predicted that the practical limit of ready mixed concrete would be unlikely to exceed a compressive strength greater than 43 MPa. The compressive strength of concrete largely depends on the water-cement ratio and the degree of internal packing as reflected in porosity of the system. Porosities could be minimized by continuous grading of aggregate as well as of binder phases which required large amounts of fines and hence higher water demand (higher w/c ratios) resulting in lower strength and reduced durability. Lower concrete strength also meant larger sizes of horizontal (beams and slabs) and vertical (columns and shafts) structural systems for a given load and this was not acceptable for certain functional requirements of a high-rise structure. For a given allowable bearing capacity of the supporting foundation system, increased dead loads mean reduced occupancy loads and hence reduced number of stories of a high rise building. However after the invention of superplasticizers in Germany and Japan in early 1980's the water-cement ratios could be reduced even with considerable and essential fine powder incorporations in HPC/SCC. This enabled the builders to erect two buildings in Seattle, Washington with a concrete compressive strength of 131 MPa some years ago. Fig 2.1 shows a very positive effect of increase of concrete strength on the dimensions of horizontal and vertical structural members resulting in slender sections and more useable occupancy area in a high rise building erected in reinforced HPC/SCC resulting in an efficient use of a given land size.

ACI 363R defines high-strength concrete as concrete with a compressive strength greater 41 MPa.



**Fig 2.1** Effect of Concrete Strength on Beam Depths and Column Sizes



It can be seen that increased concrete strength is more effective in reducing the column sizes than reducing the sizes of horizontal structural sub-systems. In practice higher concrete strength is specified for columns than for beams and slabs in a high rise structure.

Increased concrete strength without durability is not very desirable and is a waste of costly materials. Steps must be taken to enhance the durability of concrete. Various options are available including the use of SP, low w/c ratio and using suitable fillers. In fact pozzolanic fillers along with SP and low w/c ratio are the hallmarks of HPC/SCC systems. In HPC/SCC high amounts of fine fillers and superplasticizers are essentially used for meeting the stringent workability, strength and durability requirements. This minimizes the fluid transport within concrete mass and would result in higher strength as well. It was therefore decided to have an improved microstructure of cementitious systems by the joint application of SP and fillers in the investigations reported herein. The fillers with pozzolanic properties were found more efficient. In the lines to follow these items are discussed.

## **2.2 Basic Information on SRM's Used in HP SCCS**

The environmental aspects involved in the production and use of cement, concrete and other building materials are of tremendous importance. The manufacture of Portland cement is a highly energy intensive and environment unfriendly process requiring about 4 G J of energy per tonne of the finished product in addition to producing 0.8-1.3 ton of CO<sub>2</sub> per ton of cement produced. In an energy hungry world, considerable efforts are being made to find substitutes of cement which are called secondary raw materials (SRM's), supplementary cementitious materials or sometimes waste materials in the literature, a term which is seldom used now because of the fact that these materials can be more costly than cement at times. But this aspect does not reduce their effectiveness. These SRM's are used to replace a part of cement, an expensive material in ready mixed concrete in mortars and concretes. Reduction of cement translates into reduced shrinkage and heat of hydration. The less energy intensive SRM's being sought are industrial by-products that are easily available, require little or no pyro-processing, and have inherent or latent cementitious properties. Some specially designed supplementary cementitious materials using blends of fly-ash and bottom ash incorporating inexpensive and naturally occurring clay and limestone have also been used resulting in economic and environment improvements [9]. Use of Fly Ash in concrete is on increase. High cost of cement and pressure from environmental lobbyists are encouraging the use of SRM's to replace cement in concrete. SRM's used in this research work included SF, RHA (amorphous and crystalline), FA and limestone powder (LSP) for various SCCS. LSP is relatively inert while others are pozzolanic powders of varying activity. Their pozzolanic activity in SCCS can be arranged in ascending order as FA+RHAP, FA, FA+RHA and FA+SF respectively showing the benefits of using binary and ternary binders. FA blends were taken at 20% by FA mass.

Fillers are generally added to HP SCM/SCC systems to reduce WD, to increase paste volume and hence stability, to improve finished surface, to improve pumping etc and to reduce shrinkage. Appropriate choice of the filler is very important for the material engineer at the site for a given placement. Kronlof [10] states that traditionally, very fine particles were believed to increase the water requirement of concrete and therefore harmful to concrete. Mathematical particle packing theories, however, show the opposite. In concrete fine powder particles comprising binder and mineral powders (MP) fill the spaces between aggregate particles. The space remaining between fine powder particles is then filled with water and to a lesser extent

with air also. For workability some excess water is needed for particle mobility. The role of plasticizers and superplasticizers is to disperse the particles into spaces within their size range. The main reason between practical experience and mathematical modeling is the flocculation of small particles. In mixes without plasticizer, fine particles are flocculated and cannot fill spaces of their own class size, which is why they often require more water. The first condition that must be met for high density is the use of superplasticizers to break flocculation and hence achieve uniform packing.

The term mineral powders (MP) refers to inert fine powders formed in crushing, grinding or drilling processes of rocks from which particles greater than  $125\mu\text{m}$  have been removed. The classification of any fine MP as inert in the strongly basic environment of concrete is controversial. Even so-called inert MP may react to some extent with the reaction products of cement. Therefore the term inert may apply to MP whose reactivity is significantly lower than that of cement or any other pozzolan.

In lean concrete (cement content between  $140\text{-}200\text{ kg/m}^3$ ), it is beneficial to fill the remaining aggregate interspaced with inert MP rather than with water and air, as far as workability allows as a high particle packing density is the main requirement for achieving good quality concrete. When using rock powders, a reduction of water requirement in a superplasticized mixture is especially marked in lean mixes [10]. Incorporation of rock powders in a superplasticized lean concrete improves its strength significantly due to improved interaction of the paste and the aggregate and is attributed to a number of physical and chemical factors as follows.

- Fine materials interfere with the formation and orientation of large crystals at the paste aggregate interface (ITZ)
- Large amounts of small particles may alter the rheology, reducing internal bleeding at the paste-aggregate interfaces (ITZ)
- The wall effect does not weaken the contact between the paste and the fine aggregate particle; thus its function approaches that of unreacted cement particle core.
- The components (paste and aggregate) are homogeneously mixed, lowering the stress peaks.

Crushed aggregate particles are irregular in shape and pack more poorly together than naturally formed gravel. The space between them being comparatively large requires more water and cement to meet workability and strength requirements. In order to reduce cement quantity mineral powders (MP) looks like a possible solution. The function of MP particles derives from their filler and binder effects and for this, the particles have to be extremely fine. In practice MP's are mainly industrial by-products. The filler effect includes particle packing and involvement in chemical reactions as nucleation sites. The binder effect results from reaction products of true chemical hydration and pozzolanic reactions. However separating these while researching chemically reactive particles is extremely difficult.

Very fine mineral additives having insignificant chemical reactivity upto 28 days are used widely in blended cements. Fly ash, fine limestone is used in blended cements in Europe especially in France. In Finland, the blended cements started having limestone and blast furnace slag instead of fly ash in 1994. It has been suggested that the moduli of elasticity of rocks is the controlling factor of the modulus of elasticity of resulting concrete. In other words, concrete with higher modulus is only obtained with rocks of higher modulus from which aggregates are made.

An increase of 172.5% in the modulus of elasticity of rocks may result in corresponding 48% increase in the modulus of elasticity of concrete [11].

### 2.2.1 Role of SRM's in Strength Enhancement

Inert and pozzolanic mineral admixtures modify the physical and chemical properties of mortars and concretes and the compressive strengths can be separated into fractions of strength related to physical and chemical effects of mineral admixtures. When mineral admixtures are added, three effects can be quantified including, dilution, heterogeneous nucleation (physical) and pozzolanic reaction (chemical) depending on the amount and solubility of amorphous silica. Heterogeneous nucleation is a physical process leading to a chemical activation of hydration of cement such that mineral admixture particles act as nucleation centers for the hydrates thus enhancing cement hydration. A smaller amount of powder has an optimum efficiency and results in a large increase in compressive strength while the use of large amount of powder has a smaller effect [12]. Therefore only 20% mass of FA was replaced with both types of RHA and SF in SCM systems. Pozzolanic powders equal to only 10% of the cement mass were used in HP SCP systems in a replacement mode. LSP particles being finer act as nucleation centers for hydration products and also adsorb SP in its porous structure with bottle neck pores. Low purity of LSP in terms of  $\text{CaCO}_3$  content will also adsorb more SP [13]. Incorporation of FA in cement based materials generally reduces the water demand, increases the setting times and reduces the early shrinkage due to the delayed hydration. Packing effect is dominant for FA systems during 3-28 days [14] and pozzolanic effect becomes more pronounced thereafter and that the pozzolanic reaction of FA decreases with increase in its particle size. Quantification of SF in concrete systems has shown that upto an age of 7 days, physical effects contribute to the compressive strength while beyond that chemical effects become significant [15]. Increase in the strength of a cementitious system brought about by the inclusion of amorphous RHA in a replacement mode is due to its packing effect, pore refinement effect, reduction of effective w/c ratio due to absorption of water in internal porosity of RHA particles, improvement of cement hydration and to the pozzolanic reaction between silica and  $\text{Ca(OH)}_2$  [16]. By virtue of its reduced pozzolanic activity, crystalline RHAP shows lesser strength enhancement than amorphous RHA and its filler effect dominates the pozzolanic one.

LSP has been very often used in self-compacted cementitious systems in addition to fly-ash. The use of RHA or SF in form of FA substitutive blends in HP SCCS has not been undertaken as yet. It is surprising to mention that in Germany the combined use of FA with other admixtures like silica fume etc. in concrete seems to be generally unusual although in Scandinavian countries such combination of both materials had proven successful in practice [17] and literature also verifies the benefits of such combinations [18].

### 2.3 Superplasticizers

Superplasticizers (SP) are chemical admixtures which increase the workability of cementitious systems at low mixing water contents and are therefore considered to be essential for durability of structures made in HP SCCS. Superplasticizers are the break-through invention relevant to the cement based materials and unfortunately the information on their mechanism of action is not available in a single publication. Such information is provided here to understand

their mechanism of action and to know how they could affect the response of cement based materials in both fresh and hardened state.

Even amongst engineering community SP's are considered to be workability enhancers only but their main role of durability enhancement is often ignored. A normal water reducer is capable of reducing water requirements by about 10-15%. The advent of high-performance concrete (HPC) and self-compacting concrete (SCC), which are recent technologies, were possible only due to the availability of chemical admixtures and especially of superplasticizers or high-range water reducing agents (HRWRA) which are capable of reducing water requirement by up to 30%. Electron microscope examination reveals that in water suspensions of cement, large irregular agglomerates of cement particles are formed. By the addition of superplasticizer, the cementitious material is dispersed into small pieces. Concrete pumping is also very much facilitated by using superplasticizers because it decreases the friction at the interface of pipe and pumped concrete. SP's have also been found successful in the application for underwater placements of SCC using tremie pipe. They can however, show greater slump loss at times especially if the mixing water content is less than the water demand of the system or due to incompatibility problems.

By definition an admixture influences the properties of fresh and/or hardened cementitious systems and is generally added during the mixing process.

Both HPC and SCC are characterized by a dense particle packing, a high or medium amount of powder and low water-cement (w/c) or water-binder (w/b) ratio ( $\leq 0.4$ ). Both HPC and SCC use high amounts of powder to improve packing, to reduce water demand, to increase flow, to reduce heat of hydration and shrinkage especially at early ages. The type of powder to be employed for a given application should be carefully selected considering the advantages/disadvantages it brings with it.

For the industrial production of cement based products, like in the pre-casting industry, the setting time is very important as it is connected with the form removal. Therefore, the admixture used should have as small an effect on setting as possible.

### 2.3.1 Types of Water Reducing Agents

There are three different groups of chemical substances influencing workability of cement pastes, mortars and concretes. These include lignosulfonates (LS), sulfonated naphthalene and melamine formaldehyde condensates (SNF /SMF) and Polycarboxylate ethers (PCE). These classes are also called first, second and third generation of plasticizers respectively. The first category of lignosulfonates brings about a water reduction of at least 5% so these are not suitable for HPC or SCC. They are side products of cellulose extraction from wood with molecular weights between 500 to 100,000 g/mol and on the average between 20,000-30,000 g/mol [19]. The second category of superplasticizers brings about a water reduction of 12% at least. In construction technology mostly the sodium, magnesium and calcium salts of lignosulfonates are used.

Attractive forces exist in cement particles suspended in water without SP due to difference in the surface charges of various phases of cement. The SP polymer molecules bind on the surface of cement grains and decrease surface potential which becomes negative for all phases of cement. Thus electrostatic repulsive forces are created between cement grains. This is the mechanism of action through which agglomeration is prevented. The manufacture of SP is a Hi-tech industry based on nano-technology with multi-million Euros investment.

The second generation SNF or SMF condensates are polymers with five to ten repeating units. For use in cementitious systems the sodium and calcium salts are used. Every unit is sulfonated which explains the better dispersing effect of this type of SP and higher water reductions at the same dosage level compared with LS. At higher dosages both types can have a retarding effect. SMF condensates are polymers with an average molecular weight of 30,000 g/mol. These are used as sodium salts. The effectiveness of SMF condensates in terms of reductions of water demands and increasing the workability of cementitious systems is the same as that of SNF condensates but their “open-time”(time to maintain workability) is less with lesser effect on setting time of cementitious systems at higher doses.

The third generation PCE type of SP's were developed in Japan and Germany in the late seventies or early eighties of the last century [20]. Those are essential ingredients of HPC or SCC and are used to bring down the water demand and to regulate the open-time and setting time. Their basic structure is like a “comb-type” molecule. The poly-carboxylate is called the trunk or main chain of the molecule and the polyether groups are connected to the Polycarboxylate trunk by chemical bonds. The polyether group is also called “side chains” or “grafts”. Their name suggests the possible connection between the Polycarboxylate and ether groups. Three types of grafts or side chains of ethers are common and are called ether, ester or amide. Amongst them ester group is very common. Because they are more effective than LS, SMF and SNF, they are called “super-plasticizers”. SP's are also responsible for lowering the porosity of cementitious systems in hardened state [21].

### 2.3.2 Mechanism of Action of Superplasticizers

There are four main clinker phases of cement namely  $C_2S$ ,  $C_3S$ ,  $C_3A$  and  $C_4AF$  and it is reasonable to think that the chemical compounds of these SP's get grafted on them. In a fresh cement paste without SP,  $C_2S$  and  $C_3S$  have a negative zeta-potential while  $C_3A$  and  $C_4AF$  have a positive zeta-potential. This leads to a faster coagulation of the cement grains.

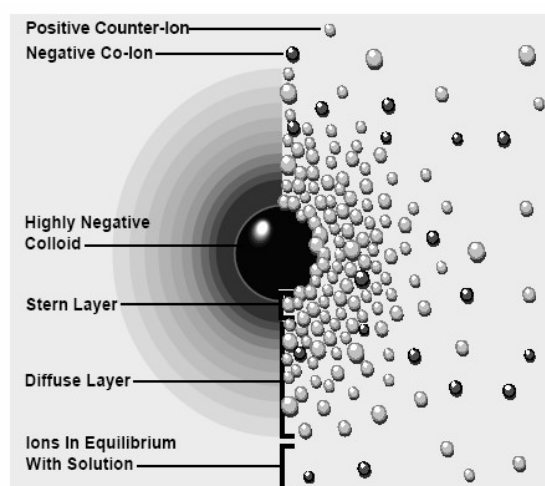
Cement particles act like a colloid in suspension. Each colloid carries a “like electrical charge”. Particle charge can be controlled by modifying the suspending liquid characteristics. Modifications include changing pH of liquid or changing the ionic species in solution. Another more direct technique is to use surface active agents (SP) which directly adsorb to the surface of colloid and change its characteristics. It is reported that cement aluminate content ( $C_3A$  &  $C_4AF$ ) along with cement fineness affects the fluidity in addition to  $C_3A/CaSO_4$  ratio [22]. Deflocculation test as described in [22] is able to predict more accurately, the minimum active dosage of an admixture to retain fluidity. A simpler hydrometer test is also proposed to assess the relative effectiveness of the plasticizing admixtures[23]. The literature also cites that lower alkali content along with lower  $C_3A+C_4AF$  and higher  $SO_3$  contents give higher fluidity[24]. These are the conditions suiting the SP to remain in the solution. Some studies on sulfonated polymers of naphthalene, melamine and styrene show that the polymer which is least adsorbed(with highest molecular weight) gives highest negative zeta potential and higher dispersing capacity[25]. However, this is not true for PCEs' which have lower zeta potential than SNF and SMF type of super-plasticizers. The addition method (time of addition) of traditional superplasticizers is an important factor determining workability of SMF and SNF type superplasticizers. To obtain high workability, their addition should be delayed and the optimum time is the beginning of dormant period. However with PCE's the time of addition is less important to obtain higher workability [26]. The enhanced effect of superplasticizer when added



a few minutes after the mixing water can be explained in a simple way. When SP is added along with the mixing water, the SP is rigidly attached in substantial amounts to  $C_3A$ -gypsum mixture leaving only small amounts for the dispersion of silicate phases. By late addition the SP is adsorbed 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.

### 2.3.3 Double Layer Model

A “double layer” model explains the electrical repulsion mechanism and helps understand the definition of Zeta potential. A colloid (negative ion, co-ion) will be surrounded by positive ions (counter ions) in the solution. The attraction from negative ion forces some of the positive ions to stick to its surface around colloid. This layer of counter ions is called “stern-layer”. Additional positive ions are still attracted by the negative colloid, but with a small equilibrating force, and are now repelled by the stern layer counter ions and by other counter ions which are trying to approach the colloid. This dynamic equilibrium results in the formation of a “diffuse layer” of counter ions over-lapping the stern-layer. Diffuse layer is followed by a layer of ions which are in equilibrium with solution. Fig. 2.2 shows the model.



**Fig. 2.2** Double layer Model of SP mechanism of action.

In a similar but opposite fashion, there is a lack of negative ions in the neighborhood of the surface because they are repelled by the negative colloid. The concentration of co-ions gradually increases with the distance as repulsive forces of colloid are screened out by the positive ions until equilibrium is again reached.

The diffuse layer can be visualized as a charged atmosphere surrounding the colloid. The stern layer and diffuse layers are called double-layer. The double layer is formed to neutralize the charged colloid and in turn causes an electrokinetic potential between the surface of the colloid and any point in the mass of a suspending liquid. This is called surface potential and is measured in milli-volts. The electrical potential at the junction of stern and diffuse layer is called “zeta-potential” and is related to the mobility of the particle. Zeta-potential can be quantified by tracking the colloid particles through a microscope as they migrate in a voltage field.

Van der Waals attraction is the result of forces between individual molecules in each colloid. This effect is additive. Subtracting attractive curve from the repulsive curve, the net interaction curve is obtained. In order to maximize repulsion to get dispersion, the colloids should be kept at a minimum prescribed distance, by over coming Van der Waals “attraction”. This is done by adding surface active agents like SP.

Due to the addition of SP, the surface potential of all cement phases becomes negative and they start repelling each other. PCE's adsorb more selectively to  $C_3A$  and  $C_4AF$  than to  $C_2S$  and  $C_3S$ . That's why PCE's need a smaller dosage to achieve the same reduction in water content. In addition, long polyether side chains lead to a steric repulsive effect between the cement particles and increase the workability. Longer main and side chains lead to better dispersing and water reduction effect while having a relatively small effect on setting times.

### 2.3.4 Polymeric (Steric) Forces

When a polymer layer is present at the surface of particles (either adsorbed or chemically grafted), a repulsion force can be created when the layers on two neighboring particles overlap. This happens whenever the polymer molecules would rather become more compact as the two layers are squeezed together. Polymeric repulsion occurs only when polymeric stabilizer layers overlap. The thickness of these layers is often of the order of 10 nm. In contrast, electrostatic double layers can be much thicker if the ion concentration of the medium is low and polymer repulsion potential is quite steep.

### 2.3.5 Effects on Fresh and Hardened Concrete

In fluidized concrete, the SP facilitates escape of air. Typically 1-3% air is lost out of a total of 5-8% entrained air. Setting is also retarded [20], the extent of retardation depends on the type and dosage of SP. SP gives enhanced effect when added a few minutes after the mixing water has been added to the concrete [20] because doing so SP would be adsorbed to a lesser extent and there will be enough SP in the solution to promote dispersion of the silicate phases and to lower the viscosity of the system.

Literature cites that compared with the control mortars, the hardened HRWRA mortars (with dosages 0.3 and 0.75%) had lower overall porosity, higher compressive strength due to improvement in the interfacial zone relative to the corresponding bulk paste[21]. Effect of SP on the early volume stability of HP SCP systems containing inert and pozzolanic powders has been studied in the laboratory for different exposures conditions and will be discussed in the next chapters.

The SP added was of the powder type Melflux 1641 F and 2651F by Degussa Germany in HP SCP and HP SCM systems. The positive effect on early volume stability in terms of shrinkage reduction was noticed.

After having discussed these basic issues, the specific information on the inert and pozzolanic SRM's used in this study would be provided in the following articles.

## 2.4 Production of SRM's

### 2.4.1 Rice-Husk Ash (RHA)

Like many other countries, rice is the most important food grain in Pakistan after wheat. Its Basmati quality is world famous and has become one of the main export items over the years. Basmati rice has various classes but in general it is an expensive rice quality liked for its aroma, flavor and taste the world over. Rice is mainly grown in Pakistan in the province of Punjab (although other provinces also produce this magnificent crop) in the districts of Sialkot, Sheikhpura, Gujranwala, Faisalabad, Multan, Sahiwal and Vehari and the overall area under rice cultivation is over two million hectares. Rice husk is the outer covering part of the rice kernel and consists of two interlocking halves. It is removed from the rice grain because husk is not edible. Rice husk is a by-product of the process of obtaining rice grain. Bulk of the husk is disposed off by setting it on fire in fields (which creates environment related issues) although small quantities are used as a low-grade fuel in brick kilns and in low-pressure steam generation etc. In the developed world, husk is used to produce electricity through steam generation and resulting ash is used as a value added product in making HP SCCS. Agro-Industrial wastes are abundant in Pakistan and in those rice husk is probably one of the biggest. It can therefore be converted easily into a value added item to be used in concrete and especially in HP SCCS. Table 2.1 gives the physical properties of the rice-husk.

**Table 2.1: Physical Properties of Rice Husk [27-28]**

Parameter	Nature/Value
Color	Golden
Length	4.5 mm (average)
Hardness	6 Mohr's Scale
Density (Bulk)	96-160 kg/m <sup>3</sup>
Thermal Conductivity	3.3 K Cal-cm/g m <sup>2</sup> /° C
Angle of repose	35 <sup>0</sup> (ungrounded)
Fuel value	2800-3700 K-cal/kg

### 2.4.2 Nature of Rice Husk

Rice husk is composed of both organic and inorganic matter. Organic matter consists of cellulose, lignin, hemi cellulose and some proteins and vitamins while the major component of inorganic mineral is silica. The actual composition of rice husk varies with the type of paddy, inclusion of bran and broken rice in husk, geographical factors, crop season, sample preparation and relative humidity etc [27-28]. Moisture content of rice husk is about 9% at corresponding relative humidity of air less than 50%.

Yoshida et al [29] state that silicon component is taken up from soil by roots of plant as monosilicic acid. This soluble silica moves to outer surfaces of plant where it eventually polymerises to form a cellulose-silica membrane. The organic matter decomposes during combustion of the rice husk and residue is ash rich in silica.



### 2.4.3 Composition of RHA

Rice husk has a cellular structure. On combustion, the cellulose-lignin matrix of rice husk burns away leaving behind a porous silica skeleton with extremely small domains of 3-120 nm in size [30]. This structure would yield very fine particles if ash were ground. The highly porous structure of ash gives rise to a large surface area, which is mostly internal, depending strongly on burning regime parameters like temperature, its duration and environment. James and Rao [31] have reported changes in surface area with temperature and its duration. They state that at 500<sup>0</sup>C, the surface area reached a maximum value of 170m<sup>2</sup>/g. Within 500-600<sup>0</sup>C, the surface area decreased but actual values remained quite high (100-150m<sup>2</sup>/g).

Ibrahim et al [32-34] boiled the rice husk with water, washed it and then dried. For a constant burning time of 3 hours, the surface area was found to increase from 200 to 274 m<sup>2</sup>/g on heating husk from 500 to 600<sup>0</sup>C. Beyond 600<sup>0</sup>C, the surface area and total pore volume decreased with increasing temperature of thermal treatment.

Treatment with diluted hydrochloric acid before burning the husks was reported to be very effective for obtaining ashes with a large internal surface area [30, 35]. The surface area of an ash sample produced by burning the acid treated husks at temperature 600<sup>0</sup>C for 3 hours under inert atmosphere, followed by the combustion of residue carbon in oxygen atmosphere was found to be 260m<sup>2</sup>/g [30]. Liou and Chang [35] have reported a surface area of 261 m<sup>2</sup>/g for an ash sample obtained by burning acid-treated husks at temperature of 900<sup>0</sup>C for an hour. Various researchers have suggested a variety of burning regimes for producing high surface area ash.

### 2.4.4 Rice-Husk Combustion

Fluidized bed reactors are reported to be very suitable for the utilization of heat value of rice-husks [36]. The reactors can be used either for combustion or for gasification of rice husk. Since the bed temperature can be kept below the crystallization temperature of silica, the ash produced is amorphous and hence highly reactive [37]. A research was undertaken in Delft/Vietnam by using ash produced in a drum type incinerator (burner) developed by PCSIR (Pakistan Council of Scientific and Industrial Research, Peshawar centre [38-39] which was modified to increase its capacity to 1 m<sup>3</sup>.

The drum and detachable chimney of the incinerator were made from galvanized iron sheet. The incinerator is lightweight and can be easily carried by two persons. The fire is started from bottom using a small amount of waste papers or wood. The husks burn themselves once ignited. No control is required during burning process. The highest recorded temperature was 780<sup>0</sup>C and the carbon contents were found to be 5% for 20 experimental runs.

Haxo and Mehta [40] argued that the porosity is the primary factor controlling the surface area of RHA. Unburnt carbon particles are very porous; hence an ash sample with greater unburnt carbon content will have higher internal surface area. Since the pore volume mainly controls the specific surface area of RHA, collapsing the pore structure will result in a decrease of the surface area. This would happen when particle size is reduced to a value similar to the average micro-pore spacing. The mean diameter of RHA particles burnt below 800<sup>0</sup>C is about 50-60 μm. It can be expected that when particle size of the ash approaches 5-10μm due to milling process, a noticeable drop in specific surface area will occur.

### 2.4.5 Role of Unburnt Carbon in RHA

Since unburnt carbon has a very large surface area, the water demand is higher for the ash samples with a higher unburnt carbon content. A carbon rich ash is considered to be a pozzolanic material of lower quality because unburnt carbon particles increase specific area and hence the water demand and this increase in carbon content decreases silica content [39]. A high LOI (loss on ignition) value needs a higher dosage of superplasticizers for a given level of workability.

### 2.4.6 Fuel Value of RHA

The fuel value of husks is reported to range from 13.8 to 15 M J /Kg. By way of comparison, oven dry timber averages 18.8 M J/Kg while typical values for coal and fuel oil are 29.7 and 39.8 M J/kg. Hence the fuel value of one tonne of rice husks is equivalent to 0.48 tonnes of coal or 0.36 tonnes of fuel oil.

In addition, rice husk has good insulating properties. Depending upon its degree of compaction, its thermal conductivity ranges from 0.036 to 0.086 Wm<sup>-1</sup> K<sup>-1</sup>. This compares with 0.041 Wm<sup>-1</sup>K<sup>-1</sup> for shredded asbestos, 0.03 for mineral wool and 0.028 for granulated cork [38]. Table 2.2 gives the ash and silica content of various plants in Pakistan.

**Table 2.2: Ash and Silica Contents of Various Plants**

Plant	Part of Plant	Ash%	Silica%
Rice Husk	Grain sheath	22.1	93.0
Wheat	Leaf sheath	10.5	90.50
Sorghum	Leaf sheath epidermis	12.5	88.7
Rice Straw	Stem	14.6	82.0
Breadfruit tree	Stem	8.6	81.8
Bagasse	-	14.7	73.0
Corn	Leaf Blade	12.1	64.3
Bamboo	Nodes(inner portion)	1.5	57.4
Sunflower	Leaf and Stem	11.5	25.3
Lantana	Leaf and stem	11.2	23.3

Amongst the agricultural wastes, rice husk has a very high potential for the production of a very effective secondary raw material. It is mainly due to its random availability, very high silica content and relatively low cost. More than 100 countries in the world produce rice, the current production of which is estimated at more than 600 million tons. After burning rice husk in controlled temperature and duration using properly designed small plants, 20 % of mass of husk is converted into high quality value added ash which is a unique secondary raw material. After milling process, about 20% of the mass of rice is obtained as husk. The production and research on RHA started in Pakistan in early seventies and the Asian countries have produced world famous researchers in this field. Some of them got recognition and a world authority status later on after working in a conducive western research environment.

RHA resembles SF in terms of high silica content and its large surface area is mainly due to its internal voids and certainly not due mainly to its particle size. However SF has sub-micron level particle size, as identified in SEM, which also gives rise to high surface area. Inclusion of RHA in cement based systems improves its properties [41-44]. By using a new stirring type furnace

with controllable air flow and husk feeding rate, instead of routinely used rotary kiln, and in the temperature ranging between 500°C to 700°C, the specific surface area decreased with increase in the incineration temperature. The best ranges of temperature and duration were given as 450°C to 550°C and 50-100 minutes respectively to burn out fixed carbon [45] and to get very high surface area (150m<sup>2</sup>/g). The pore refinement effect of RHA results in reduced pore sizes which adds to durability [46].

The production of ash using small laboratory scale plant as reported in [45] may however be economically unjustified. There is a considerable controversy regarding the temperature at which amorphous silica gets converted into crystalline form [39]. However based on the literature, a crystalline ash is obtained if the incineration temperature exceeds 900°C with prolonged durations [39]. Some other details concerning use of RHA containing cement specially suited for rural areas are also given in the literature [47, 48]

#### **2.4.7 RHA Reactivity**

Reactivity and water demand are the two main parameters of RHA. The reactivity of RHA depends on the content of amorphous silica and on its porous structure. If porous structure gets minimized by milling process in an effort to reduce particle size, the reactivity decreases. The reactivity of RHA contributes to the strength of RHA containing cement based materials by pozzolanic reactions between silica and calcium hydroxide liberated during cement hydration process. These reactions produce additional amounts of CSH that makes denser microstructure of RHA containing cement based materials. The water demand depends on the specific surface area and pore volume. Since the unburnt carbon has very high specific surface area due to its very porous particles, the water demand is higher for ash samples with higher unburnt carbon content [39]. Compared with ash samples free of carbon, a carbon rich ash has lower pozzolanic reactivity due to two reasons. As mentioned earlier unburnt carbon particles in RHA increase specific surface area which increases water demand and reduces the silica content of ash.

#### **2.4.8 Hydration Mechanism of RHA Paste**

The penetration resistance coincides with the growth of CH upto 8 hours and is similar to behavior of ordinary cement paste [46]. The formation of CH at the surface of RHA may be due to adsorption by cellular structure of RHA. In such case bleeding water will be significantly reduced especially in unplasticized systems. The adsorbed water enhances the reaction inside the inner cellular spaces and results in significant strength gain. After the formation of CH, the pulse velocity increases rapidly. After 40 hours, the pozzolanic reaction further binds SiO<sub>2</sub> in RHA with CH to form CSH and solid structures. This mechanism gets changed in HP SCP due to the interaction of SP with the constituents of paste.

#### **2.4.9 Comparative Use of RHA in SCCS**

As mentioned in earlier sections that the use of RHA has resulted in various improvements in the performance of cementitious systems. However, the author is not aware of any literature wherein RHA has been studied in comparison to SF in HP SCCS. Therefore one of the main dimensions of this investigation was to explore the use of RHA instead of SF (which is not likely to be locally produced economically in the near future in developing rice producing

countries) in HP SCCS. This would also reduce the environmental problems associated with the current open field burning of the husk. SF is not economically available even in developed countries therefore efforts may be made to encourage the use of RHA in HP SCCS.

## 2.5 Limestone Powder (LSP)

As stated earlier suitable SRM's can be added in cement to reduce its water demand. They are able to do so because of their filling effect in cement and because of their lower water requirement to wet their surfaces and the fact that they do not hydrate themselves but improve hydration of cement rather indirectly.

To verify this point, a side investigation was made on the Vicat water demands and setting times of three cements including Holcim (CEM I 52.5R), Dyckerhoff (CEM I 42.5R) and Lafarge (CEM I 42.5R). Three selected LSP's were from Medenbach (MB), Lengefeld (SAX) and Schonedorf (Schon). MB was calcium carbonate while the other two were dolomite powders. Cements were studied in pure state as well as with 50 % mass replacement with LSP's. An indirect formula to calculate the water demand (WD) of any mass % (w.r.t cement mass) of a SRM is also given as equation 1 of Appendix-A. When LSP was used in HP SCM systems its  $\text{CaCO}_3$  content was found to be 92.3 % and it showed highest SP demand to meet a target flow. The particles were studied by SEM and MIP was also done for the solid SRM powders. These tests showed why LSP needs highest SP dose, in comparison with other SRM's used, to produce the target flow. It is mentioned in another study that LSP not only had a physical effect but also represented a certain degree of chemical activity in terms of producing carboaluminates when used in cement pastes [49].

## 2.6 Fly-Ash (FA)

Fly ash or pulverized fuel ash is a residue derived from the combustion of pulverized coal in furnaces of thermal power plants. The characteristics of FA vary according to the combustion operation system as well as the coal composition. The combustion temperature is high (approximately 1200°C) and the ash, which is usually less than 100 microns in diameter, is carried in the air stream and is collected by electrical or mechanical precipitators while it is quickly cooled. FA produced in modern dry method is rather more homogeneous in terms of particle size than that produced by wet process. The pozzolanic activity of FA is largely due to glass content of FA which reacts with lime in the presence of water. Since 1970 fluidized bed combustion process is employed as it needs lesser temperature and has a high heat transfer rate. In recent years in order to reduce air pollution, LSP is introduced into the combustion chamber to absorb sulphur released from burning high sulphur coals. If oxides of silica, iron and alumina are greater than 70%, the ash is classified as class F according to ASTM C 618. These ashes usually belong to burning of anthracite (burning with little smoke) coal and bituminous coal (burning with high smoke). Class C fly ash will have this oxides sum greater than 50%. Class C FA's are normally produced from lignite or sub-bituminous coal. Class C FA's have some cementitious properties in addition to pozzolanic ones. It is stated that for FA cement based systems, the water binder ratio is related to water- cement ratio by the following relation [50]. The degree of FA pozzolanic activity is related to its particle size with smaller size being more reactive.

$$\frac{W}{C+F} = \frac{W}{C} \left(1 - \frac{F}{C+F}\right) \quad (2.1)$$

Where W, C and F are water, cement and FA respectively.

It means that keeping the water binder ratio constant, the concrete with more FA has higher effective w/c ratio for a given mixing w/c ratio. FA containing systems show higher bleeding and retard setting [51]. CH crystals form preferentially on FA particles because of latter's "nucleation center effect". This effect along with pozzolanic reaction between silica of FA and CH released by cement hydration form the hydration mechanism of FA containing cement based materials.

Two hard coal fly ashes were used. FA1 was from Opole -Poland and other FA2 was from Letvice-Czech Republic. From the oxides contents it is clear that both ashes are of type F according to ASTM classification. Because FA particles are larger than cement particles (based on d50 size), have a comparatively smooth surface and have a smaller absorption capacity, less water is required to wet them and those can pack both the binder as well as sand phases (of course the lower sizes). This reduces the water demand of a cementitious system wherein FA is used as cement replacement material to get obvious benefits. It is mentioned however that there is a huge difference in the quality of FA produced at various facilities and there are even batch variations of a single facility. This variation is mainly due to the differences in the coal quality, burning process and variations in the power demand on the electricity grids.

## 2.7 Silica Fume (SF)

The Interest in the use of silica fume (SF) started with the strict enforcement of air pollution controls in many developed countries due to which ferro-silicon industry had to stop releasing silica fume along with other flue gases into the atmosphere.

SF is an industrial by-product mainly from ferro-silicon producing industries during reduction of high purity quartz with coal or coke in an electrical arc furnace during reduction of silicon metal or ferro-silicon alloy. The SiO<sub>2</sub> content of SF is highly dependent on the type of alloy product [52].

**Table 2.3 Silica Content of SF in Different Alloy Making Industries [52]**

Alloy Type	SiO <sub>2</sub> Content of SF
50% ferrosilicium	61-64%
75% ferrosilicium	84-91%
98% silicon metal	87-98%

SF comes in various forms including powder SF, slurried SF, densified SF and pelletized SF. SF generally produces filler and pozzolanic effects when added into cement based materials. The pozzolanic activity is due to the reaction between silica of SF and the CH produced due to cement hydration.

The transition zone, also some times known as interfacial transition zone (ITZ) is the inter-phase between aggregate and the hydrated cement paste. It is very important both from the view point of mechanical strength as well as durability. With the increase of w/c ratio, both the thickness of ITZ and the degree of orientation of CH crystals is increased due to internal bleeding. Addition of SF improves the microstructure in ITZ and also controls ASR if SF replacement level is 15% or more [52].



## 2.8 Aggregate-Paste Interfacial Transition Zone

When inert particles are added to concrete as aggregate, the area of interfacial transition zone increases significantly. This zone is considered to be the “weak link” in concrete, lending major importance to its strength and durability properties. It has been established that paste structure in the interfacial transition zone differs markedly from that of the bulk paste and constitutes the weakest part of concrete both chemically and structurally. Presence of weakest part around strongest part (aggregate) limits stress transfer to aggregate [10]. Depending upon the method of determination, the thickness of transition zone is generally estimated around 20-50 nm.

### 2.8.1 Pore Structure in the Interfacial Transition Zone

The inhomogeneous structure of the paste develops initially in the plastic state, when excess water collects around aggregate particles. This is thought to be the result of looser packing of cement particles at the interface, the so-called “wall effect”, and internal bleeding which favors porosity beneath aggregate particles. Cement particles existing in the close vicinity of the aggregate are very less in number. Therefore, since calcium silicate hydrate (CSH) precipitates on cement particles, the main hydration product near the transition zone is calcium hydroxide (CH) [10].

In reinforced concrete, the loads are transferred to the reinforcement through the bond between reinforcement and surrounding concrete and therefore a “wall-effect” is expected at the interface. It has been reported that at this interface water gets accumulated under the reinforcement. The resulting interfacial transition zone (ITZ) becomes therefore the weakest link in the reinforced concrete composite. The strength and durability of such a composite depends on these properties of the ITZ. The ITZ between cement paste and aggregate (or fiber) and around steel reinforcing bars has been an area of particular interest associated with engineering and durability properties of cementitious composites and structural reinforced concrete. As a result of its more porous and heterogeneous/anisotropic nature, the ITZ was recognized to be the “weak link” in cement and concrete composites affecting their engineering and durability properties.

Between aggregate particles and cement paste, and for that matter between any two phases with different properties, there exists a distinct micro-structural phase called interfacial transition zone (ITZ). This region separates the aggregate particle from bulk of the paste and possesses micro-structural properties often significantly different from the bulk paste. Sometimes an interfacial separation crack has also been observed between the aggregate and surrounding paste [53]. The ITZ is a thin layer between the aggregate particle and the hydrated cement particle (hcp) and is caused by the “wall-effect” which prevents adequate packing of the cement grains close to aggregate surface [54] and gives rise to depletion, of anhydrous cement particles in the ITZ, approaching zero at the aggregate surface [55]. The literature mentions the influence of aggregate size and water-cement ratio on the microstructure of ITZ. Reducing the aggregate size tends to reduce the ITZ porosity and reducing the w/c from 0.55 to 0.40 resulted in an ITZ with characteristics that were not distinguishable from those of bulk paste [56]. This effect has also been confirmed by the author while studying the effects of sand coarseness on the MIP response of HP SCM systems. This could be the reason why HPC is stated to have a maximum W/C ratio of about 0.40 in an effort to avoid bigger pore sizes. In another study of ITZ in mortars, it was mentioned that sand content of 45% seems to be the threshold value. Above this critical sand content the ITZ became linked together or percolated [55]. The study gave direct evidence of the

fact that the higher porosity in the ITZ results in the porosity being more interconnected and confirms that ITZ has an important effect on the transport properties of concrete [55]. In cement based materials, microstructural defects and discontinuities occur, which cause stress concentrations under load. In ordinary concrete, aggregate is the least deformed due to its higher modulus while the paste would deform more due to its lower modulus of elasticity. Because there should be no crack between aggregate and paste, requiring that these two phases must have the same deformation for strain compatibility making the induced stresses to be proportional to the respective moduli. Therefore stress levels in paste and aggregate would be different. It means that aggregate attracts higher stress levels than the surrounding paste. The transmission of this stress gradient through weaker ITZ is a complex issue as large flat  $\text{Ca}(\text{OH})_2$  crystals form within it perpendicular to the surface of aggregate grains resulting in the formation of a highly porous structure favoring the formation of micro cracks and their propagation [57]. The sizes and micro strain of the CH crystallites decrease with increasing distance from the aggregate-cement paste interface. These values are reported to be  $0.26\text{ }\mu\text{m}$  and  $3.7 \times 10^{-4}$  respectively [58]. Literature reported SEM studies have shown this region with the following characteristics.

- (a) Deposition of calcium hydroxide crystals (CH) with some degree of preferential orientation with respect to the aggregate surface (c-axis parallel to aggregate surface).
- (b) Hadley grains or hollow shells that sometimes contain anhydrous grains of cement.
- (c) Calcium silicate hydrate (C-S-H having a rod or needle like morphology).
- (d) A duplex film of thickness between  $0.5\text{-}1.0\text{ }\mu\text{m}$ , is deposited on the aggregate surface and is composed of two layers, one being of CH and other of C-S-H.
- (e) A higher porosity compared to the bulk paste.

Diamond [58] has shown that in conventional concrete the estimated average span of ITZ between the surface of aggregate particles and the bulk mortar is  $75\text{ to }100\text{ }\mu\text{m}$ . If this is true then 50% of the matrix is typically dominated by microstructure and properties of ITZ.

Another study on mortar samples kept in  $\text{CO}_2$  free environment using environmental scanning electron microscope with field emission gun (SEM FEG) is reported in the literature [59] that showed "Sheaf of wheat" morphology in paste-aggregate interface within first 5-10 minutes which turned into a needle/rod like microstructure believed to be C-S-H type I at 10 days of age. Mixing regime was also believed to influence the ITZ properties. Increased mixing energy causes densification of paste-aggregate interface. It was believed therein that ITZ in field concrete is fundamentally different from ITZ observed in laboratory studies [59].

The principal product of hydration of a cement paste is itself porous. Two types of porosity can be defined. (1) capillary porosity, the larger porosity and (2) gel porosity, the finer porosity that as a first approximation is entirely contained within C-S-H. Roughly gel pores are smaller than  $10\text{ nm}$  in diameter. The finer porosity is implicated in shrinkage and creep mechanisms while the larger pores influence strength and permeability [60].

In freshly compacted concrete, water films form around large aggregate particles and the effective w/c ratio becomes higher closer to larger aggregate than in the bulk mortar. In the vicinity of coarse aggregate, crystalline hydration products like ettringite (AFt), monosulfate

(AFm) and calcium hydroxide form a more porous framework than in the paste or mortar matrix. By the age of 56 days, pores get concentrated in the aggregate edge, ranging from 0 to 15  $\mu\text{m}$  [53]. It was also shown there that CH content increases upto 14 days age and then drops between 14-28 days after which it starts increasing again at a slower rate and the pulse velocity shows similar trend. Sometimes galvanized iron has been used, in place of ordinary reinforcing steel, as an extra safety against corrosion in structures. It showed a higher porosity of interfacial transition zone (ITZ) at the very young age (19 hours) but at 28 days there seems to be no difference in the porous structure of ITZ of these two types of reinforcing bars [61]. While determining ITZ porosity, the sample thickness also effects the results of pore size distribution with the thicker samples giving inaccurate information on the porosity of ITZ as measured by MIP with a thickness less than 1 mm gave good results. It is also inferred that with a simultaneous presence of different types of powders in the mass of cementitious systems, different type of porosity would develop as seen in MIP investigations of such systems. In a comparative study on normal and self-compacting concrete [62] it was shown that the elastic modulus and micro strength in the ITZ were significantly lower on the bottom side of horizontal reinforcement than on the top side.

## 2.9 Thermal Analysis

Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) were carried out using Netzsch STA 409 PC machine on powdered HP SCP/SCM formulations with a heating rate of 10°C per minute and upto 1000°C. The machine used was Netzsch STA 409 PC. From TG curves mass loss of  $\text{Ca}(\text{OH})_2$  was calculated using a formula mentioned in the literature [63].

$$CH = \left[ \frac{4.11dW_{480}}{W_{120}} \right] (100) \quad \text{- Mass \%} \quad (2.2)$$

Where

CH= Calcium hydroxide (mass %)

dW<sub>480</sub> = Mass loss at 480°C

W<sub>120</sub> = Mass at 120°C

It will be shown later that the quantity of calcium hydroxide so calculated yields a linear relationship with the peak reference intensity of XRD of same formulation. According to another source [53] CH mass can be calculated by the following formula.

$$WCH = 4.11(W_{440} - W_{580}) + 1.68 \frac{(W_{580} - W_{1007})}{W_{1007}} 100\% \quad (2.3)$$

Where

WCH is the weight ratio of  $\text{Ca}(\text{OH})_2$  in the cement paste. W<sub>440</sub>, W<sub>580</sub> and W<sub>1007</sub> are the weights of the specimen at 440, 580 and 1007°C respectively. The mass ratio of 1 mol of  $\text{Ca}(\text{OH})_2$  to 1 mol of  $\text{CO}_2$  is 1.68.



## 2.10 XRD Study of HP SCCS Systems-Background

XRD is the most powerful technique when applied to crystalline materials but can yield important data when applied to amorphous solids and liquids. XRD revealed that crystals are composed of atoms or groups of atoms arranged in a regular and repeated pattern. The term amorphous solid is reserved for those substances that show no crystalline nature. Glasses, certain resins and polymers fall in this class. They give a liquid type diffraction pattern and are to be regarded as super cooled liquids of great viscosity. The term solid is synonymous to crystalline and metals as polycrystalline. Most mineral matter occurs in crystalline form. Much of the beauty displayed by fine crystal specimens originates from their symmetry of form, which is by far the most striking external evidence of their regular internal structure. If a crystal is rotated about an imaginary line through its center and it gives exactly the same appearance more than once, then that line is called axis of symmetry. The symmetry axis is twofold, threefold, four fold or six folds depending on whether the crystal is brought into a similar position every 180, 120, 90 or 60 degrees during rotation.

Bragg's law, given below, is the fundamental in XRD experimentations.

$$N \lambda = 2d \sin \theta \quad (2.4)$$

Where N is an integer denoting order of reflection,  $\lambda$  is the wavelength of X-rays, d is the inter-planar spacing between the successive atomic planes in the crystal and  $\theta$  is the angle between the atomic plane and both the incident and reflected beams. The following points should be kept in mind while performing XRD studies of a powdered material.

- The powder diffraction pattern is characteristic of the substance.
- Each substance in a mixture produces its pattern independently of the others.
- The diffraction pattern indicates the state of chemical combination of the elements in the material.
- Only a minute amount of sample is required.

An unknown substance can not be identified unless its pattern was available in the library records. A joint committee of ASTM and the American Society for X-Ray and Electron Diffraction undertook the task of standardizing the procedure and of publishing a card file of the pattern data. This file was updated over the years and is called Powder Diffraction File (PDF) containing over 21500 numeric patterns of crystalline materials. Afterwards a Joint Committee on Powder Diffraction Standards (JCPDS) was set up as an international organization in 1969. As the file increased in size, and more complex compounds were added, it was desirable to use longer X-ray wavelengths, such as copper, iron, cobalt and chromium radiations in order to spread out the pattern as much as possible. Now  $\text{CuK}\alpha$  is the predominant radiation used in preparing patterns in the PDF [64].

Study of the hydration process and products in concretes and mortars by XRD is complicated by the presence of aggregate which are also crushed while making powders so most of studies are made on pastes. Calcium hydroxide (CH), calcium silicate hydrates (CSH) and ettringite are common hydration products which can be detected by XRD technique.

This technique is now widely used for the study of various crystal systems present in the powdered cementitious systems. In this investigation it has been used qualitatively for the

detection of the quantity of  $\text{Ca(OH)}_2$  in combination with thermal analysis like thermogravimetry (TG) and differential scanning calorimetry (DSC) for RHA/SF containing pastes and mortars. In the later chapter on self-compacting mortar systems it would shown that  $\text{Ca(OH)}_2$  quantity as indicated by XRD in terms of reference intensity and by thermal analysis (TG and equation 2) enjoys a linear relationship for Portland cement based HP SCCS. Therefore it would be possible to use only XRD peak reference intensity for the qualitative assessment of relative increase or decrease of  $\text{Ca(OH)}_2$  content in the Portland cement based systems containing various types of SRM's. This has been done for HP SCP systems.

## **2.11 Studies of Microstructure**

### **2.11.1 Scanning Electron Microscope (SEM)**

Scanning electron microscopy is becoming a very versatile tool for the study of microstructure, interfacial transition zone (ITZ) and hydration progress. Selected specimens were studied by SEM technique to have a closer look at the microstructure and to look for hydration products and their morphology which could lead to some indications on shrinkage and strength etc. The sample preparation was done in laboratory after stopping hydration by oven heating the samples broken in flexure at  $105^\circ\text{C}$  for 24 hours. FEI XL 30 environmental scanning electron microscope with field emission gun (ESEM FEG) was used to study the microstructure.

### **2.11.2 Mercury Intrusion Porosimetry (MIP)**

Kjellsen [65] mentions existence of hollow shell pores of 1 to 15  $\mu\text{m}$ , in addition to gel and capillary pores, in systems with SF even at later ages resulting in reduced capillary porosity. In this research porosity studies were made by MIP technique for various paste and mortar systems employing various SRM's. Oven heating has been employed for stopping hydration before MIP sample preparation. It forms one of the techniques, may not be the best, for stopping hydration [66].

Maintaining lower water contents (as in HPC) whilst achieving an acceptable level of workability, results in higher strengths for a given cement content as well as in lower permeability and reduced shrinkage [67]. The permeability of the cement paste with RHA is reported in the range of  $1 \times 10^{-11}$  cm/sec [46]. The literature reports that the porosity in the interfacial zone of RHA composite was higher than that of SF composite [68] and this study confirms it in terms of maximum pore diameter obtained from the porosimetry studies. MIP studies were made on carefully prepared samples after hydration had been stopped to have an idea about the relative maximum pore sizes and pore refinement effect brought about by the incorporation of inert and pozzolanic SRM's. These studies are more suited to paste systems because of the absence of aggregates and therefore HP SCP systems with CEM III were studied in detail.

## **2.12 Rheology**

Eugene Bingham, a chemistry Professor and a colloid chemist coined this term after observing an unusual flow behavior in concentrated suspensions like paints. Thus rheology means the study of flow and deformation. In construction field terms like workability,

flowability and cohesion are used sometimes interchangeably. Various researchers have given their definitions of workability, consistency and plasticity. These are based or defined on the basis of feelings of a person and are not based on physical behavior of a material. With the availability of modern equipment it appears that all these should be discarded in favor of physically measurable parameters. Tattersall [69] summarizes very clearly the concrete workability terminology.

Workability is defined either qualitatively as the ease of placement or quantitatively by rheological parameters [70]. The most commonly used test to determine workability in practice is the slump cone test. Either the vertical slump distance or the horizontal spread of the concrete can be measured. Most of the existing tests measure only one parameter either related to viscosity or yield stress.

### 2.12.1 One-Factor Tests

Tests like slump, Penetrating rod, Kelly ball, Vicat and Wigmor, K. slump test, Vebe time or remolding Powers apparatus and Flow-Cone are all one factor tests.

In slump test, the stress is composed of weight of concrete per unit area. "The concrete will slump or move only if yield stress is exceeded and will stop when stress (weight of concrete per unit area) is below yield stress. Slump test is related to yield stress. The variability in slump test measurements is mainly due to operator and due to variations in mix proportions. "A modification of the slump test, used for concretes with very high slump as high as 300 mm minus the coarse aggregate diameter is to measure spread instead of drop."

In Germany (DIN 1045) the slump cone is placed on a special metal sheet. It is filled and then lifted; the metal sheet is given a pre-determined number of mechanical drops. The spread of concrete is measured. This version of slump cone is related to viscosity and not to yield stress because dropping the metal subjects the concrete to a stress that is greater than yield stress. Therefore measurement is related to the flow of concrete when yield stress is exceeded. If the concrete does not slump or spread, then this means that yield stress was not exceeded and therefore concrete did not flow.

Recently slump cone test procedure was modified to allow the estimation of both the yield stress and viscosity. Since the final slump is related directly to the yield stress, it is reasonable to assume that the time-dependence of slump is likely to be controlled by the plastic viscosity. There are tests measuring both parameters but they are neither cheap nor easy to carry out. Rheology, aside from measuring flow of concrete, is concerned with prediction of flow from the properties of components.

Laboratory rheometers are sophisticated and expensive while most field tests are easy to use and inexpensive. Even if the rheological behavior of the concrete is reduced to two parameters (yield stress and plastic viscosity), the array of current rheological tests for field use does not permit them to be evaluated, except very roughly. While the slump test, the grandfather and the most widely used of all tests, provides an indication that is reasonably well correlated to the yield stress, the other tests like DIN flow table and VEBE apparatus etc. provide results that are not very useful in terms of characterizing the rheological parameters. In most of these tests, the concrete flows under the effect of a dynamic loading. Thus, the behavior of the concrete under vibration is brought into play, although nothing indicates that this is related directly to the behavior of the unvibrated concrete (as illustrated by the Bingham parameters). A survey of the state of the art methods showed that none of the current "field" tests (in distinction to rheometer) makes it possible to assess the plastic viscosity of the concrete. However, this parameter is

assuming increasing importance in modern concretes. For high-performance concretes, it frequently constitutes the critical parameter that controls pumpability, and ease of finishing.

Concrete flow properties need to be characterized by more than one parameter because concrete is a non-Newtonian fluid. The most commonly used model is the Bingham equation that requires two parameters, i.e., yield stress and plastic viscosity. 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 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.

Literature describes that rheological properties of cement pastes vary with the change of test geometry, friction and gap. There is a need to standardize rheological test methods for comparing inter-laboratory results. [71, 72]. Generally for various rheological models, a reduction in water-binder ratio results in higher plastic viscosity. Fresh concrete is a complex non-Newtonian material that possesses a yield stress and a shear rate dependent viscosity, both of which change with time. As concrete sets, the yield stress and viscosity increase gradually [73]. Air-entraining agents are frequently used to enhance freeze-thaw resistance of concrete. Literature reports a study which showed that by increasing air content, the yield stress increased and the plastic viscosity decreased [73]. The increase in yield stress was an unexpected result because increasing air is well known to cause an increase in slump, and yield stress and slump are negatively correlated (as yield stress increases, slump decreases). It was argued therein that in pastes containing HRWRA, the bubble bridges dominate over any fluid action of air entrained bubbles. Modern high performance concrete or self-compacting concrete require high amounts of superplasticizer because of their high filler contents. But it is worth mentioning that different superplasticizers give different rheological response of the same system [74]. At small separations (gaps) SP have a large effect [75]. Their time of addition is also important. Usually an increase in the addition time of the admixture reduces the shear stress, the yield stress, and the plastic viscosity of cement pastes. The optimum delaying time of admixture is found to be 10-15 minutes which is independent of cement and superplasticizer type [76]. In normal undisturbed concrete a high yield stress prevents the settlement of coarse aggregates, although its density is higher than the suspending mortar. But it will sink when vibrated due to reduction of yield stress. It implies that coarse aggregates sink only during vibration [77]. A study on mineral admixtures including finely ground blast furnace slag (BFS), fly-ash (FA) and silica fume (SF) showed that the rheological properties of one-component system (OPC) were improved with increasing the SP dose while for two components, yield stress and plastic viscosity decreased when OPC was replaced by BFS and FA. In case of OPC-SF system, yield stress and plastic viscosity steeply increased with increasing SF. For three component system, both OPC-BFS-SF and OPC-FA-SF systems improved rheological properties, compared with the sample having SF [78]. This improvement may be due to the shape effect of FA, SF and BFS particles. The author also observed the same phenomena rather indirectly when tests on self-compacting mortars systems incorporating various SRM's were performed. Generally in the presence of superplasticizers, the finer the microfiller the lower was the flow resistance and torque viscosity of the mixture. It has been reported that upto 20% ground silica or limestone did not increase the superplasticizers requirement to achieve a constant workability, even though one of the fillers had a surface area of 10,000 m<sup>2</sup>/kg [79]. SF, however, while being the most effective SRM from rheological point of view, increased the SP demand at a constant workability. This suggests that high surface area is the sole parameter influencing the SP demand of SF mixtures and that SF may have a strong

affinity for multi-layer adsorption of SP molecules [79]. However this study showed that there are some other factors also responsible for the increased SP demand especially the type of internal porosity of powder. In summary, concrete is a suspension including particles that may range from less than 1 $\mu$ m to over 10 mm. The flow properties are described approximately using a Bingham model, defined by two factors including plastic viscosity and yield stress as under.

$$\tau = \tau_o + (\mu \dot{\gamma}^o) \quad (2.5)$$

Where  $\tau_o$  is the yield stress and  $\mu$  is the plastic viscosity. No flow occurs until the shear stress exceeds  $\tau_o$ . The most common rheological parameters used to qualify workability are the yield stress and plastic viscosity as defined by the Bingham equation [80]. There are a number of publications on self-compacting concrete proportioning, properties and applications but very few attempts focus on rheology of paste and mortar [81].

### 2.13 pH of Mineral Solutions

Literature [82-83] states that the inclusion of SF and RHA reduces mortar bar expansion due to alkali-silica reaction and brings about other useful changes. It is possible only through improved microstructure and/or with the flow of alkali ions from such powders into the solutions so that a decrease in pH due to pozzolanic reaction is replenished by the alkali ions provided by pozzolanic powders to the solution. The pH value of pore solution has a direct bearing on this type of volume stability and therefore it is imperative to study the pH of SF/RHA solutions as close to the actual conditions as possible

### 2.14 Calorimetry

Conduction calorimetry was done on cement pastes with and without plasticizers in parallel with setting times and with or without RHA or SF. The objective was to see the effect of addition of these mineral admixtures on the heat released and on the reaction kinetics. By adding SP equal to that required for producing 200% flow at WD, 40% and 60% mixing waters, the magnitude of heat peaks is expected to slightly increase and their occurrence is likely to be delayed for both CEM I and CEM 111. This delay is expected to be greater for CEM 111 pastes. The time of occurrence of peaks at WD's and 40% water mixing water would be almost the same for both cements because of their close proximity at 10 % cement replacement level.

72 hours differential conduction calorimetry would be done on the samples with and without superplasticizers/mineral admixtures at various mixing water contents to know the reaction kinetics of SF and RHA in cement pastes.

### 2.15 Shrinkage

In HP cement pastes having low w/cm ratio, the internal relative humidity decreases with the water consumption resulting in increased shrinkage especially for SF containing pastes [84]. In cement-based composites, the cement paste is the major source of shrinkage [85]. Being a volume change, it can be studied either by volumetric experimental methods, linear methods or by digital imaging techniques. These methods have their relative advantages and disadvantages. The advantage of volumetric method is that it measures shrinkage as per its true definition of a



volume change. Its disadvantages include sucking-in of any entrapped air from within the membrane into the sample and thus falsely showing an increase in shrinkage. The bleeding resulting in the loss of contact of sample with the membrane is another disadvantage. The advantage of the linear method is that it is done in an apparatus of constant cross-sectional areas so that the volume change can almost be considered as a linear change in length. Disadvantage includes that an appreciable shrinkage/expansion is registered only after the onset of hardening. In this study a modified version of German classical “Schwindrinne” meaning shrinkage channel apparatus measuring 4x6x25 cm was used at  $20\pm1^{\circ}\text{C}$  and RH of  $31\pm5\%$  with specimen uncovered and then fully covered conditions. Calorimetry and setting times were also done on selected specimens. Conflicting results about shrinkage found in the literature are due to interpretational differences based on concepts, definitions and measuring techniques [86]. However it has now been shown that both techniques are valid and give almost similar results [165]. In general for HP SCCS early age volume changes or shrinkage is of prime importance because such systems incorporate high SRM's of various types. Moreover the literature reports measurement of various types of shrinkage by using either volumetric or linear measurements, each technique has its own plus and minus points. However very little data is available about self-compacting cementitious systems containing pozzolanic powders. Structural or construction engineers are concerned with the total amount of shrinkage and certainly not in that of its various individual parallel operating mechanisms. That's why most codes only prescribe the total amount of shrinkage. Morin et al [87] report volumetric increase of shrinkage with increase in amount of super-plasticizer and accompanying delay and reduction of chemical activity. In this study it was revealed (at 40% mixing water) that if moisture movement is prevented, swelling occurs in neat cement pastes for both CEM 1 and CEM 111 in the absence of plasticizer due to hydrates and thermal effects. However if the moisture movement is allowed (uncovered case), shrinkage gets reduced for both cements when super-plasticizer is present due to reduction of surface tension. In both covered and uncovered conditions having controlled environmental parameters, it was not be possible to assign or to distinguish between various parallel shrinkage mechanisms using the available apparatus as well as the contributions of such mechanisms could not be evaluated considering their already known and well documented definitions. Plastic shrinkage will always be present along with drying or chemical shrinkage in formulations with mixing water content greater than the system's water demand. It was also interesting to know the effect of stopping evaporation on the total early shrinkage response of various cementitious systems. In construction, depending upon its quality of site supervision and adherence to the specifications, freshly placed cementitious system may have only two possible exposures and the extremes being the situations where evaporation is either allowed or is prevented by the immediate use of some curing membranes/ procedures. The emphasis in this thesis has, therefore, been clearly on measuring the total shrinkage of various HP SCCS in two stated exposure conditions rather than on measuring the contributions of different parallel operating shrinkage mechanisms.

## 2.16 Comparative Hydration of SF/RHA Pastes

Although mortars and pastes using mineral admixtures have been routinely employed, cement paste systems with mineral admixtures have very rarely been investigated regarding their suitability for making high performance concrete (HPC) which has also been defined elsewhere[88] and its details are also given in the literature [2, 89]. In HPC or SCC, high powder

content with low mixing water in the cementitious systems is generally the basic requirements. Such systems have high water demands which are generally reduced by using the third generation superplasticizers based on poly carboxylate ethers [19]. The comparative response of RHA and SF based cement pastes has been studied to look into the possibility of replacing silica fume (SF) by rice-husk ash (RHA) for making HPC/SCC especially in rice growing countries.

The most critical part in HPC recipe lies in the paste [90] and the other aspects are rapid slump loss and plastic/chemical shrinkage. The particle size and surface area of these mineral admixtures are traditionally considered to be responsible for their higher water demands [91, 92]. Mixing also influences all the properties especially flow and rheology [93]. The mechanisms through which SF and RHA improve some of the properties of resulting concrete are still unclear. Some interactions have been postulated. These include densification of hydrating gel structure, filler action, pozzolanic action between silica rich SF particles and Portlandite, a by-product of cement hydration, resulting in pore size refinements with SF particles acting as nucleation sites for Portland cement hydration [94]. Traditional literature [95-96] would suggest that SF reacts readily with calcium hydroxide produced during early cement hydration. However Mitchell et al. [97] state that digestion of SF in calcium hydroxide solution for upto 120 days showed it to persist in the form of agglomerates coated with amorphous calcium silicate hydrates. High surface area RHA is sometimes more pozzolanic than SF and its pozzolanic activity can still be further increased by treating husk with 1N HCL aqueous solution [98] so that about 50% of the lime reacts within first 24 hours. Almost similar improvements in concrete performance using RHA have been reported as those containing SF and these include improvement in workability with small RHA additions (<2-3% of cement mass), pore refinement due to filler action, resistance to acidic environment, indirect improved corrosion resistance through reduction in permeability [91], improved sulphate resistance, better freeze-thaw resistance than similar SF concrete [91] and higher compressive strengths.

Strengthening mechanisms suggested by Yu et al [16] include reduction in pore size, reduction of the effective w/c ratio of RHA concrete compared with control due to adsorption of a portion of free water in the great number of pores existing in RHA particles, improved cement hydration and more C-S-H gel formation in RHA concrete. Bui and Sugita's work [39, 99] provides more useful information on the topic.

### **2.17 Shrinkage and Microstructure of HP SCP Systems**

Performance of concrete is generally controlled to a large extent by the properties of its constituent paste system [100-104]. The pore structure of various paste systems determines their strength, volume stability and durability performance [105] which is related to the microstructure which has been studied in this investigation by MIP and SEM. Some corrections need to be applied to MIP results to make them comparable with other works [106]. It is mentioned in [107] that none of the shrinkage codes enables modifications to be made for the presence of mineral or chemical admixtures. Generally, the higher the surface area of particles is, the higher is the tensile capillary pressure and hence more is the plastic shrinkage [108]. The factors effecting shrinkage of paste systems, its basic mechanisms and control techniques can be found elsewhere [2,109,110] and many theories exist for explaining shrinkage mechanisms but none has gained universal acceptance as more than one mechanisms operate in parallel and dominant mechanism is probably not the same for different ranges of relative humidity. Under some conditions dominant mechanism may be hard to distinguish. CEM 111 with 70% blast furnace slag is

known to show higher 24 hour shrinkage than CEM 1 (OPC) in uncovered conditions. It shows lower shrinkage than CEM I in sealed condition probably due to delayed setting, relatively greater free water content within the matrix [166] and prevalence of 100% relative humidity etc.

### **2.18 Background-HP SCM Systems**

Self-compacting mortars (SCM) find numerous applications while the published work on such systems is rather limited especially for those having pozzolanic powders which are incorporated in HP/SCCS (self-compacting cementitious systems) to make a variety of improvements like reduction in water demand, increased flow or strength, reduced peaks of liberated heat, early shrinkage control and reducing the fluid transport through improved microstructure resulting in enhanced durability etc. Essentials of SCCS including high fluidity and sufficient segregation resistance are in general contrary to each other and appear to be diagonally opposite. SRM's and SP have to be used imaginatively to achieve these contradictory requirements. In case of mortar it has been proven that the relationships between slump spread and yield stress and also V-funnel time and plastic viscosity are very close [111]. Detailed information on the flow, strength, microstructure and shrinkage of cementitious systems can be seen in other works by the author [112-114]. In Germany the combined use of FA with other admixtures like silica fume etc. in concrete seems to be generally unusual although in Scandinavian countries the combination of both materials had proven successful in practice [17] and literature also verifies such combinations [18]. Generally the cement systems in which SF is included show greater liberated heat in comparison with the control cement while incorporation of FA reduces the heat evolution [115].

### **2.19 Background-HP SCC Systems**

Self-compacting concrete or self-consolidating concrete (SCC) was pioneered in Japan about 12 years ago. Research on this type of high performance concrete is going on in the universities of the developed world ever since and now significant progress has been made and it is hoped that unified specifications for SCC would soon become available. SCC has been rightly described as technology of the decade. The development of SCC is considered to be a milestone achievement in concrete technology due to its high performance in fresh and hardened state. The Architectural Institute of Japan established standard specifications for SCC in 1997 as well as guidelines which made SCC use very common. Three basic criteria are required to achieve self-compaction: high deformability, high passing ability and high resistance to segregation. To secure good deformability, it is important to reduce the friction among solid particles during flow. Aggregate interparticle contact can decrease by reducing the aggregate content and increasing the paste volume to maintain high passing ability among closely spaced obstacles. Adequate cohesiveness can be achieved by incorporating viscosity-enhancing agent (VEA) along with HRWRA to control bleeding, segregation and surface settlement. Another way to enhance the cohesion of SCC is to reduce free water content, increase the volume of fines and cement paste or both. Fine materials and fillers with greater surface area than cement can reduce free water content. The incorporation of VEA in the presence of HRWRA requires greater HRWRA content for a given flow level due to reduction of free-water resulting from the long chain polymer molecules of VMA that absorb and fix part of the mixing water thus increasing the viscosity of the mixture. The dynamic and static stabilities of SCC are also the main functional



requirement for adequate production and use of such class of concrete. The former prescribes the resistance to segregation during transport and placement while the later refers to the resistance of the fresh concrete to segregation and bleeding once the concrete is cast into place and until onset of hardening. In author's opinion it is the static stability which is more difficult to insure than the dynamic stability especially with FA powder. The dynamic stability is assessed by V-funnel flow time, J-ring, L-box, U-Box and pressure bleed tests. For static stability surface settlement, aggregate segregation and monitoring the in place changes of electrical conductivity can be carried out. The SCC technology is based on adding or partially replacing cement with fine materials like fly-ash, blast furnace slag and SF without modifying the water content. This process changes the rheological behavior of concrete. In order to achieve a balance between flowability and stability, the particles  $<150\ \mu\text{m}$  should be between  $520\text{-}560\ \text{kg/m}^3$ . High powder content improves cohesiveness. SCC offers environmental, social and economic advantages in addition to offering better performances than normal concrete due to increased cementitious materials content and denser ITZ (Interfacial Transition Zone between aggregates and pastes), faster construction, noise elimination and placements without skilled labor. HRWRA lowers mostly the yield value but results in a limited drop of viscosity also making it possible to have highly flowable concrete without significant reductions in viscosity or without significant reduction in cohesiveness.

Reduction in w/p ratio results in reduction of deformability of cement paste while an increase in w/p secures high deformability but can reduce cohesiveness of paste and mortar necessitating a balance in w/p ratio to enhance deformability without substantial reduction in cohesiveness. Inter-particle friction increases when the concrete spreads through restricted spacing due to greater collisions between various solid particles. This increases viscosity thus requiring greater shear stress to maintain a given capacity and speed of deformation.

It is also essential to reduce the coarse aggregate and sand volumes, and increase the paste volume to enhance deformability. Continuously graded cementitious materials and fillers can also reduce inter-particle friction.

Self-compacting concrete offers a rapid rate of concrete placement, with faster construction times and ease of flow around congested reinforcement. The fluidity and segregation resistance of SCC ensures a high level of homogeneity, minimal concrete voids and uniform concrete strength, providing the potential for a superior level of finish and durability to the structure. SCC is often produced with low water-cement ratio providing the potential for high early strength, earlier demoulding and faster use of elements and structures.

The elimination of vibrating equipment improves the environment on and near construction and precast sites where concrete is being placed reducing the exposure of workers to noise and vibration. The improved construction practice and performance combined with the health and safety benefits make SCC a very attractive solution for both precast concrete and civil engineering construction.

The reduction in aggregate content necessitates the use of a higher volume of cement that increases cost and temperature during hydration. Therefore SCC often contains high-volume of cement replacements like fly-ash, blast furnace slag, limestone filler, or stone dust to enhance fluidity and cohesiveness and also limit the temperature rise due to hydration. The combined use of HRWRA and VEA can insure both high deformability and adequate stability resulting in high filling capacity, good bond with reinforcement and uniformity of in-situ mechanical properties. Commonly used VEA in concrete include cellulose derivatives and polysaccharides of microbial

sources, in particular welan gum, which improves the capacity of the paste to suspend solid particles.

Mixes containing VEA exhibit shear thinning behavior whereby the apparent viscosity decreases with the increasing shear rate. Once in place shear rate decreases, the apparent viscosity increases resulting in a greater stability. Materials less than 0.125 mm (125 microns) are termed as powders or fillers and include SF, Fly-ash, RHA and limestone powder (LSP) etc. The fillers should have at least 75% material passing through the 0.063 mm sieve.

SCC finds typical applications in congested reinforced sections like mat foundations, tunnel lining sections, heavily reinforced columns, repair of underside of beams and girders and in basement constructions. It has been reported that SCC mixtures entrap less air than thoroughly vibrated control concrete having identical volumes of water and cementitious materials. Moreover statistically insignificant differences have been observed between the in situ  $f_c'$  values of both types of concrete [116]. Viscosity modifying admixture (VMA) not only increases the viscosity but also provides mixture robustness and overcomes effects due to poor aggregate shape and grading [117]. It is also stated that at ready mixed concrete manufacturing plant even a limited failure in the aggregate humidity measurement system will typically generate 10-20 liters excess of water per  $m^3$  of concrete causing bleeding and segregation in the absence of viscosity agent [118]. The cracking performance and behavior under load suggested that in general cast in place compressive strengths of SCC were closer to standard cube strengths than those of ordinary concrete. Also the crack width was wider and had greater depth for ordinary concrete beams than for SCC beams [119]. Based on a study encompassing 70 SCC formulations with w/cm ratio in the range of 0.35-0.42, performance based specifications have been formulated for structural applications of SCC [120]. Fillers for SCC are very important and brief information on such powders is given in the next article.

## 2.20 A Note on SRM's for SCC

Various SRM's have been reported in the literature including limestone powder (LSP), fly-ash (FA) and ground granulated blast furnace slag (GGBFS). These SRM's modify the rheological properties of SCC in fresh state and also those in the hardened state. When high volumes of limestone filler were added to SCC mix, the required self-compacting properties were achieved at a lower water/ (cement +SRM) ratio. Twenty eight day compressive strength is also increased due to filler effect resulting in improved fine-particle packing [121] with LSP particles acting as sites for the nucleation of CH and CSH reaction products. It is reported that the replacement of large volumes of cement by limestone filler (on the order of  $100 \text{ kg/m}^3$ ) is shown to reduce the cement content needed to achieve a given slump flow, viscosity, and compressive strength at early age. The increase in limestone filler content can reduce the HRWRA demand necessary to secure a given deformability. For a given dosage of HRWRA the loss in slump flow is shown to decrease with the increase in limestone filler in mixtures containing  $360 \text{ kg/m}^3$  of cement and the opposite trend was reported for concrete with  $290 \text{ kg/m}^3$  of cement [122]. It will be shown in the later chapters that calcium carbonate based LSP decreased the WD and setting times while dolomite based LSP decreased WD lesser than calcium carbonate based LSP and had no significant effect on setting. The author while making a comparative study on the use of different SRM's like LSP, FA and FA blends with SF and RHA found that the use of limestone filler in self-compacting systems required the greatest amount of SP for a target flow, gave the least strength, highest linear shrinkage and also had higher

maximum pore size [123]. One study suggests that limestone filler used in SCC does not contribute to strength gain in SCC and is mainly used to increase paste volume without generating excessive heat [124]. Therefore sometimes conflicting results have been reported about the behavior of LSP in terms of various properties. Mainly it is the per cent  $\text{CaCO}_3$  content and the per cent and the nature of other left-over elements in per cent (100- $\text{CaCO}_3$  %) which dictate the overall LSP response. It is also reported in the literature that SCC columns would have greater ductility but 10% lower strength than similar normal vibrated concrete. It is probably due to higher paste content in SCC columns which reduces the modulus of elasticity in comparison to aggregates it replaces. After a formulation has been arrived at in the light of literature [125-126], the first step is to carry out the flow tests and these are described in the next chapter.

### **2.21 Viscosity Agents**

There are two types of viscosity agents. The first type attaches itself onto powder grains (adsorptive -They reduce flow to some extent) and the second type acts in water (non-adsorptive). It is possible to control viscosity by using non-adsorptive viscosity agents without reducing flow. Details on such types of VEA's can be found elsewhere [127,128].

### **2.22 Pumping Effects**

The slump flow and air quantity of SCC may change during pumping. In general, the slump flow tends to decrease while the air quantity is reduced in some cases [129]. The pipe resistance during concrete pumping also differs according to the type of SCC. When the viscosity of SCC is high, the pipe resistance increases and in some cases pipe resistance may be far greater than that for ordinary concrete of slump of around 18 cm [129].

### **2.23 Structural Applications**

SCC has been successfully used in civil engineering structures like basements, repairs in aluminum plants, anchorages for long span suspension bridges [129-132]. It is hoped that SCC would almost replace the conventional vibrated concrete in the near future at least in the developed countries starting from pre-casting industry to the special applications and massive in-situ placements.

### **2.24 Types of SCC**

The literature describes three types of SCC. It includes powder type, viscosity agent type and combination type. Each differing in the way segregation resistance is achieved. In powder type very high powder content is provided. But it is neither economical nor wise to use such high amounts of uneconomical and environmental unfriendly cement which can give volume stability problems. Therefore it is generally replaced by high volumes of FA, LSP or some other suitable materials. This type uses only the SP admixtures for enhancing deformability.

The viscosity agent type SCC uses high contents of viscosity agent and smaller powder content. The combination type of SCC uses both moderate contents of powder and viscosity agent. This is considered to be more robust and can tolerate small variations in grading and

surface moisture of aggregates. However, the experience of making SCC at semi-automated plant suggests that for irregular and rather elongated aggregates even combination type of SCC can be sensitive to aggregate surface moisture conditions. In such cases it is advisable to increase the sand content (0-2mm) to about 50-55% of the total aggregate mass content as allowed by the European guidelines for self-compacting concrete.

### 3 EXPERIMENTAL PROGRAM

#### 3.1 General

Keeping in view the objectives of the research, the experimental program comprised of carrying out necessary tests pertaining to:

- (a) HP SCP systems
- (b) HP SCM systems
- (c) HP SCC systems

This chapter describes the materials, methods and procedures pertaining to above mentioned systems which are taken up in order.

#### 3.2 Investigation on Pastes

##### 3.2.1 Materials for HP SCP Systems

The materials comprised of three types of cements (by Schwenk Germany) including normal Portland cement (CEM 1 42.5 R) and two others having 30 and 70% blast furnace slag contents (CEM 11-B/S 32.5R and CEM 111/B 32.5 N NW/HS/NA) respectively at four mixing water contents including 20%, WD, 40% and 60% of mass of cement. The cement content with CEM I 42.5R for the neat paste and with pozzolanic additions is shown in Table 3.1. RHA/SF was taken at 10% of the cement mass in a replacement mode.

**Table 3.1** Cement Content for Various Mixing Water Contents

Formulation	Cement Content (kg/m <sup>3</sup> ) at the Mixing Water Content (%)		
	20	40	60
Neat cement paste	1932	1394	1089
Cement +10% RHA	1779	1312	1040
Cement + 10% SF	1787	1316	1042

The mineral admixtures selected in the study for comparison purposes included as produced dry silica fume powder (SF provided by RW-Fuller Silicium GmbH Germany) and imported rice husk ashes (RHA-amorphous and RHAP-crystalline imported from USA and Pakistan respectively). Third generation powder superplasticizers (Melflux 1641F and 2651) made by Degussa Germany were used to reduce the water demand and to obtain the target flow (200%, 30±1 cm spread of mini cone) of resulting durable HP self compacting cement paste systems.

##### 3.2.2 Physical and Chemical Properties of the Powders

The measurements for particle size and BET surface area were made on Beckmann Coulter LS 230 laser granulometer using nitrogen gas. Dingsøyr et al [133] state that the original size of micro silica particle is in sub-microns and those are usually agglomerated as primary agglomerates, of 0.05-1.0 micron range and possess a high degree of resilience even to mechanical influence. The secondary agglomerates consist of particles of somewhat uncertain

microstructure with diameters in range of 1.0-100 microns. They further state that by laser diffraction it is the size of an equivalent sphere or ellipsoid, as formed by the rotating particles, that is measured. RHA was imported from Agriletric International Technologies, Lake Charles, LA, USA in different plastic buckets. This plant uses husk for energy generation and resulting ash can be used in cement based materials as a value added item. RHA particle size and milling time relation will be shown later. It was decided to have a RHA particle size of about 7 microns.

Incidentally each bucket had different particle sizes which were measured and the coarser ash was milled in the Process Engineering Department of the TU Freiberg. After milling, the particle size got reduced possibly at the expense of reduced internal porosity and pozzolanic activity. The required particle size of RHA has to be decided by the material engineer considering what properties are to be improved. RHAP had smaller surface area than RHA, after both had been ground to required particle size, and hence lesser internal porosity. Physical and chemical properties (per cent values) of the powders used are given in Table 3.2.

**Table 3.2** Physical and Chemical Composition of Cements and Mineral Admixtures

Parameters	FAI	CEM I	CEM II	CEM III	RHAP	RHA	SF
Specific Gravity	2.317	3.15	2.9961	2.9713	2.45	2.26	2.36
Particle Size (d50), $\mu\text{m}$	26.59	18.42	21.13	14.38	6.17	6.8	12.16
BET Surface Area, $\text{m}^2/\text{g}$	1.6	1.098	1.229	3.231	2.52	28.92	20.46
<b>Chemical Analysis</b> ( per cent )							
Loss on Ignition	2.0	2.75	5.45	0.75	0.28	4-6	1.6
Silicon Dioxide	51.44	19.17	22.17	28.13	87.96	90.0+	95
Aluminum Oxide	26.13	5.21	7.08	10.02	3.73	<0.01	0.2
Ferric Oxide	5.55	2.39	1.66	0.94	1.67	0.032	0.05
Calcium Oxide	4.03	61.12	52.44	43.28	1.49	0.60	0.25
Magnesium Oxide	2.51	2.78	4.39	8.36	0.90	0.37	0.4
Sulfur Trioxide	1.89	3.30	4.04	5.98	0.21	0.14	-
Sodium Oxide	1.23	1.25	1.00	0.94	0.78	0.14	0.1
Potassium Oxide	2.63	1.01	0.99	0.78	1.26	2.30	1.2

If short term strength gain is the aim, then probably filler action gets the priority and RHA can be milled accordingly to get a particle size of about 5-10 microns for packing the binder phase. RHA and SF had bulk densities of  $288.45 \text{ kg/m}^3$  and  $330 \text{ kg/m}^3$  respectively. RHA was black in color and was found amorphous after XRD examination. The black color is due to its carbon content. RHAP was found to be crystalline with a pale white color and SF was light grey in color.

All materials were local except the amorphous and crystalline RHA's. Amorphous RHA was imported in two batches because it became clear that this SRM deserves a detailed and perhaps a deeper look. Every time its particle size was determined first. If RHA was found coarse for binder packing, it was ground to the required particle size. After milling process RHA in all buckets was mixed mechanically using a mechanical mixer so as to obtain a homogeneous mixture with the final particle size and surface area as shown in table above.



### 3.2.3 SRM Shapes

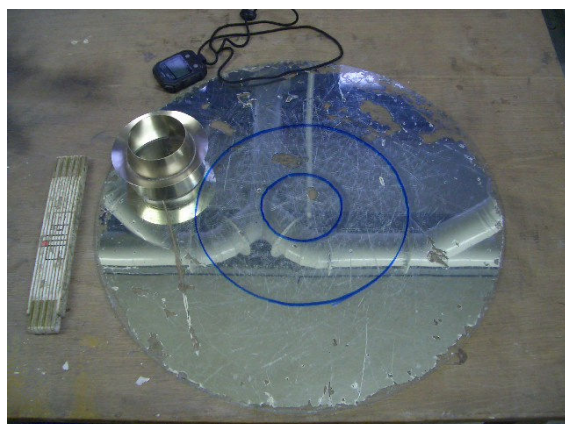
The shape and particle size of SRM's is very important in terms of water demand, SP demand and mechanical properties of cement based composites. The scanning electron microscopy (SEM) was done to obtain the shapes of pozzolanic powder particles. These shapes shall be shown in the next chapter. It is stated in the literature that amorphous RHA particles are abrasive, rough and have internal porosity. The particle shapes of SF and FA are expected to be circular. It would be seen that RHA particles are highly irregular and broken and are likely to give high internal friction during flow. Silica Fume (SF) particles are of submicron size if viewed through SEM and BET d50 measurement gives the size of primary agglomerates (and not of individual particles) as SF particles are interwound and interpenetrated due to some electrical bonds. The circular shape is useful for flow but due to extreme fineness and internal porosity their SP demand for a given flow level would be high.

### 3.2.4 Water Demands and Setting Times of Pastes

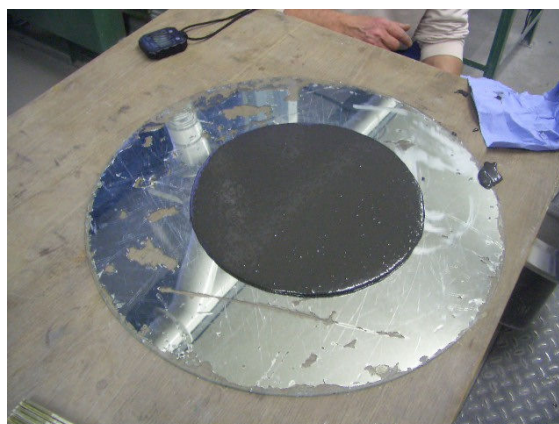
Water Demands (WD) and setting times (ST) of neat cements and cements with pozzolanic additions were determined by standard Vicat apparatus at  $20 \pm 1^\circ \text{C}$  and at  $20 \pm 5\%$  RH in laboratory in accordance with EN 196-3:1994 D. The details of water demands and setting times of various powders in paste systems can be seen in Tables 1-4 of Annexure-A. It can be seen there that in general by increasing the SF content (in terms of cement mass), the water demand and setting times increase for all cements. This increase is more for CEM III due to its finer particle size and lower clinker content. The larger is the specific surface, the higher is the water demand. As reported in the literature, it is confirmed that water demand of mix increased almost linearly by the same percentage as was the percentage of SF added [134]. The water demands of equal percent additions of RHA for cement pastes were slightly lower than those of corresponding SF cement pastes. This is in agreement with an earlier work by Nehdi et al. [135]. However in cement replacement mode, RHA increased the setting times significantly, mainly due to its carbon content. WD of cement with a known mass of SRM can be calculated as per equation 1 of Appendix A.

### 3.2.5 Flow Measurements

These measurements were made using mini-slump cone and other apparatus as shown in Figure 3.1. The target flow level was  $30 \pm 1$  cm. At various mixing water contents, the plasticizer content required to give the target flow was determined by trials. Table 5 of Annexure-A shows the plasticizer content required for obtaining the desired flow level of various HP SCP formulations. The mixing was done using Hobart Toni Technik mixer. The dry constituents of pastes along with SP were manually mixed first and then were fed into the bowl of mixer containing the required mixing water. Slow mixing (145 rpm) was done for 30 seconds and then interior of the bowl was cleaned. Thereafter, the formulations received 150 seconds of fast mixing (285 rpm). The RHA formulations needed more time and looked very viscous due to irregular, abrasive and internally porous particles of RHA.



**Fig 3.1(a)** Mini-Cone Flow Apparatus



**Fig 3.1 (b)** Flow Spread After Removal of Cone

Fig 3.1 (a) shows the apparatus and two circular marks of 10 cm and 30 cm diameter. The cone is placed on the glass so that its bottom rim rests on the 10 cm diameter mark. It is filled with HP SCP/HP SCM system. After the cone is removed the pastes/mortar flows outwards. Usually a symmetrical circular spread as shown in Figure 3.1(b) is obtained. It is measured in two orthogonal directions and the mean is recorded as the flow or the spread. For HP SCM, the diameter of the outer circle was 25 cm and T25 cm (sec) was also measured.

### 3.2.6 Strength of the Paste Systems

Prisms for flexural and compressive strength measurements comprised of 4x4x16 cm dimensions and were cast and cured as per EN 196-1. Strengths of the paste systems were determined as per EN 196-1: 1994 at the age of 1, 3, 7 and 28 days. The flexural strength at any age was an average of three specimens while compressive strength was an average of six specimens. In total 252 prisms of HP SCP were cast for paste systems with CEM I and CEM III in laboratory at a temperature of  $20 \pm 2^\circ\text{C}$  and relative humidity of  $35 \pm 5\%$ . The specimens were tested in SSD condition after weighing them for water absorption test. The strength results are given in Tables 6-9 of Annexure A. Table 10 of Annexure-A gives the theoretical paste densities and powder contents of various systems.

### 3.2.7 Calorimetry

72 hours conduction calorimetry was done on the cement pastes with and without plasticizers/mineral admixtures in parallel with the setting times. The objective was to see the effect of addition of these mineral admixtures on the heat released and on the reaction kinetics. Because only a small sample mass (say 5 gm) is required, it is advisable to take it out from shrinkage dry mixes and to possibly run both tests in parallel. Manual hand mixing of water can be non-uniform and the lids of the crucibles may not be air tight making this test rather just qualitative. However if a suitable software allows the plotting of total cumulative heat generated over time, it can be of some quantitative significance. By adding SP equal to that required for producing 200% flow at WD, 40% and 60% mixing waters, the magnitude of heat peaks may slightly increase and their occurrence may be delayed for both CEM I and CEM III. This delay

was greater for CEM III pastes. The time of occurrence of peaks at WD's and 40% mixing water remains almost the same for both cements because of only 3 % difference between these two mixing water contents. As the first peak occurs immediately after the addition of mixing water, it is normally the occurrence of second and third peaks which are of interest and are normally considered for comparison purposes and for the selection of curing procedure.

The sample for calorimetry had mass of 5 grams and was derived from a bigger dry mixed sample powder. The mixing water was added manually by using a syringe after weighing it on a balance of 0.1 g sensitivity. The mixing was done by hand so in cases of very low water contents and especially with pozzolanic powders, the mixing time was around 4-5 minutes. The calorimeter had four channels; the fourth being a reference one (dummy) allowing simultaneous testing of three samples. The calorimetry results in combination with setting times and early shrinkage results help understand and reason out some of the phenomena observed due to pozzolanic additions.

### 3.2.8 Microstructure

MIP and SEM tests were done on selected typically prepared specimens. MIP was done with the help of Autoscan 33 Porosimeter. The contact angle was taken as 140°. Specimens were oven dried at 110°C for 24 hours. A pore refinement effect is also clearly visible in Figs. 1-6 of Annexure-A. Figs 7-14 of the same annexure show SEM details of typical HP SCP systems. The differences in the shape, size and morphology of hydration products of different formulations are visible.

### 3.2.9 Shrinkage Response of HP SCP Systems

In cement-based composites, the cement paste is the source of shrinkage while other components are inert and may well control shrinkage deformation [2, 109]. Being a volume change, it has usually been studied by volumetric, linear or lately by digital imaging procedures. Time-zero may be taken as setting time and is recommended for simple comparison purposes. Acoustic emission detection is also useful for zero-time determination [167]. All methods have their relative advantages and disadvantages. The advantage of volumetric method is that it measures shrinkage as per its true definition of a volume change. Its disadvantages include sucking-in of any entrapped air from within the membrane into the sample and thus falsely showing an increase in shrinkage and the bleeding can result in the loss of contact of sample with the membrane. The external pressure exerted by the membrane on the paste is also a source of error. The advantage of the linear method is that it is done in an apparatus of constant cross-sectional areas so that the volume change can almost be considered as a linear change in length. Disadvantages include registering an appreciable shrinkage/expansion only after the onset of hardening and with some equipments.

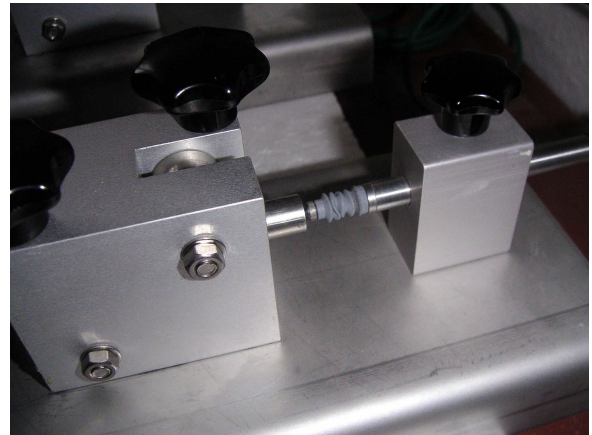
In this study a modified version of German classical “Schwindrinne” meaning shrinkage channel apparatus measuring 4x6x25 cm was used at 20±1°C and RH of 31±5% with specimen uncovered/unsealed and fully covered/sealed. Conflicting results about shrinkage found in the literature are due to the interpretational differences based on concepts, definitions and measuring techniques [114]. Plastic shrinkage will always be present along with drying or chemical shrinkage especially in the formulations with mixing water content greater than the system's water demand. Again due to contradictory results reported in the literature, the effect of



plasticizer on the shrinkage response was also studied. Some researchers report an increase of shrinkage while others report its reduction with SP addition. It is said that such differences arise due to differences in measuring technique, due to the absence of information about WD (w.r.t mixing water), due to differences in types of SP and their compatibility with cement and other powders and due to interpretation of results. It was also interesting to know the effect of stopping evaporation on the total early shrinkage response of various paste systems. Only total value of early shrinkage is of interest in construction and codes also prescribe it. Hence in all shrinkage measurements only the total linear shrinkage has been studied under various exposure conditions. Figure 3.2 shows the details about the shrinkage apparatus used in this study.



**Fig 3.2 (a)** Details at Rear End of Shrinkage Apparatus



**Fig 3.2 (b)** Details of Spring at Rear End of Shrinkage Apparatus



**Fig 3.2 (c)** Details of Apparatus and of Exposure Conditions



**Fig 3.2 (d)** Condensation in Covered Condition (Without Insulation Topping)

Fig 3.2(a and b) show very clearly the details of the empty channel and the shrinkage registering mechanism at the rear end of the channel. Fig 3.2(c) shows the details of networked apparatus while fig 3.2(d) shows the condensation noted in plastic covered condition. It was eliminated by applying a further topping of insulation foam. A factor of about 0.8 was

established in typical measurements of shrinkage/expansion in insulated and covered/sealed conditions shown in Fig 3.2(c). After knowing this factor remaining measurements were made in two exposure conditions only. The apparatus is interfaced with computer and is capable of recording translations of the order of 0.31 microns or a micro strain of 1.2 microns/meter. The system is networked and the shrinkage/expansion readings can be obtained from a web site established for this test.

### 3.2.10 pH of Mineral Solutions

Literature [82, 83] states that the inclusion of SF and RHA reduces mortar bar expansion due to alkali-silica reaction and brings about other useful changes. The pH value of pore solution has a direct bearing on this type of volume stability. To get an idea about the change in pH value of water due to SF and RHA addition to demineralized and tap water having initial pH of 6.26 and 8.29 respectively, 24 hours of pH monitoring was done in an open cylinder in laboratory with the help of Mettler Toledo-MP 220 pH meter without continuous agitation and in the laboratory environment with environment related CO<sub>2</sub> changes in order to approximate the mixing conditions at site. 1% and 5% solutions of SF/RHA were prepared after 1 minute of manual stirring. Literature [39] contains similar measurements but in a closed environment and with continuous stirring. Such conditions are difficult to be realized in actual constructions where concrete using RHA would have some possible placement. So conditions closer to the actual situation were approximated in this study. The measurements showed that SF slightly reduced the pH of the tap water while RHA marginally increased it. It should be kept in mind that CO<sub>2</sub> in the air has a direct bearing on the pH measurements. Before the start of measurement, the pH meter was calibrated against three standard solutions having pH values of 4.01, 6.86 and 9.18.

The sample remained in the laboratory and maximum measurements were taken during the possible day times. The tap water supplied in Freiberg has pH in the range of 8.2-8.5. It was found to be 8.29 while that of demineralized water was 6.26.

### 3.2.11 XRD Study of HP SCP Systems

This technique is now widely used for the study of various crystal systems present in the powdered cementitious systems. While studying the comparative use of RHA and SF in HP SCP systems, it has been used qualitatively for the detection of Ca (OH)<sub>2</sub> quantity in combination with the thermal analysis like thermogravimetry (TG). Later in the chapter it would become apparent that Ca (OH)<sub>2</sub> quantity as indicated by XRD in terms of reference intensity and thermal analysis enjoys a linear relationship for Portland cement based HP SCM systems. Therefore it would be possible to use only XRD peak reference intensity for the relative qualitative estimation of Ca (OH)<sub>2</sub> in the HP SCP systems using Portland cements.

XRD reference intensity impulse corresponding to 2θ value of 34.1° for CuKα radiation within 4-70 degree sweep for CH has been obtained by using the Diffractometer of Philips PW 3710 series. Earlier hydration of specimens was stopped by oven drying at 105°C for 24 hours and the specimen pieces of about 2-4 mm size were made and were ground. Their powder was used for the XRD experimentation.

### 3.2.12 Rheological Measurements

Rheological studies were made to know the role of RHA in cement paste in terms of viscosity and yield stress. Earlier it was felt during mixing of RHA paste systems in Hobart type mixer that RHA paste systems needed more time for producing a fluid mass and seemed to require more energy for adequate mixing. It was obviously due to the typical particle shape and morphology of RHA particles which offered high internal friction and hence resulted in a very high viscous paste flow which could creep for quite some time.

Therefore tests were done on RHA paste systems using Haake RS Rheo-stress rheometer using serrated parallel plates PP 35 Ti with 1 mm gap. Samples were prepared using powder type PCE SP for giving the target flow level of 200% (or 30 cm spread on Hagermann's mini slump cone). The total mixing time using a small rotating vane type mixer was 5 minutes. The water was added to the dry ingredients which were mixed in a glass cylinder for one minute at a slow rate (120 rpm). The interior of glass cylinder was then cleaned and the formulation was mixed again at 500 rpm for the remaining three minutes. Yield point measurement could be made from deformation-shear stress response on a log-log scale. The time or flow curve would generally measure the viscosity as a function of time at constant shear rate. The cement was Schwenk CEM I 42.5R.

### 3.2.13 Water Absorption of Pastes

After first 24 hours of moist air curing specimens were demoulded, numbered and weighed. Thereafter these were put in water at room temperature. Before being tested for strength at different ages, these were taken out of water. The surface water was removed by using tissue papers and samples were weighed in SSD condition. The weight difference gave water absorption of paste systems and it is shown in Figs 15-17 of Annexure-A.



### 3.3 HP SCM SYSTEMS

#### 3.3.1 General

In the mortars, aggregate component is also present within the paste component though the requirements for self-compaction remain similar including high deformability and high segregation resistance. High deformability is usually achieved by using a good superplasticizer while stability or high segregation resistance is achieved by either using high powder contents (low water-powder ratio) or by using moderate powder content with a viscosity agent. In any case SRM's are required to reduce water demand, to increase packing and to reduce shrinkage etc.

#### 3.3.2 Materials Used in HP SCM Systems

These included three cements from Lafarge, CEM I 42.5 R, CEM II/A-LL 32.5R (pr EN 197-1, 6-20% limestone) and CEM III/B 32.5 N-NW/HS/NA (70% BFS) and five SRM's, viz, limestone powder (LSP), fly-ash (FA) and three of its 20% by mass blends of RHA, RHAP and SF. Two types of sands were used. S1 consisted of naturally occurring locally available Roba sand 0-2 mm size with fineness modulus (FM) of 2.39 and S2 consisted of 80% 0-2 mm and 20% 2-4 mm size fraction and had a FM of 2.78. Grading plays an important role in SCCS and per cent material passing sieve 1 mm has a direct bearing on their segregation resistance. For fillers alone, the percent passing sieve 0.063 mm is very significant and it is recommended to be more than 70% [141]. Table 3.3 presents the physical and chemical analysis of the powders used.

**Table 3.3** Physical and Chemical analysis (in terms of per cent) of Powders Used

Oxides	Powders							
	RHAP	FA	LSP Lafarge	CEM I 42.5R- Lafarge	CEM II/A-LL 32.5R- Lafarge	CEM III/B 32.5 N-NW/HS/NA (Lafarge)	RHA	SF
SiO <sub>2</sub>	87.96	51.44	7.07	18.92	18.74	31.01	90.0+	95
P <sub>2</sub> O <sub>5</sub>	1.78	1.89	-	-	0.38	-	-	-
Fe <sub>2</sub> O <sub>3</sub>	1.67	5.55	0.88	2.27	2.23	0.89	0.32	0.05
MgO	0.90	2.51	1.13	1.72	1.38	7.50	0.37	0.40
CaO	1.49	4.03	48.57	63.18	58.97	44.90	0.60	0.25
TiO <sub>2</sub>	0.18	0.99	0.10	0.21	0.23	0.68	-	-
Al <sub>2</sub> O <sub>3</sub>	3.73	26.13	2.53	5.09	4.78	8.86	<0.01	0.2
Na <sub>2</sub> O	0.78	1.23	0.47	1.48	1.25	0.86	0.14	0.1
K <sub>2</sub> O	1.26	2.63	0.68	1.35	1.01	0.70	2.3	1.2
B <sub>2</sub> O <sub>3</sub>	-	0.64	-	-	0.62	-	-	-
Cr <sub>2</sub> O <sub>3</sub>	-	-	-	0.01	-	-	-	-
LOI	0.28	2.71	38.32	2.34	7.09	0.19	4-6	-
SO <sub>3</sub>	0.21	-	0.28	3.48	3.2	3.76	0.14	-
Particle size(μm)	6.17	26.59	7.176	18.91	16.9	11.82	6.8	8.66
BET Area (m <sup>2</sup> /g)	2.53	1.65	4.986	0.812	1.353	1.648	28.92	20.45
Density,g/cc	2.45	2.317	2.748	3.1688	3.1085	2.986	2.2641	2.35

S1 and S2 had passing percentages at 1 mm sieve of 73.37% and 58.47% respectively which itself would suggest about the passing range required for sands for SCM systems. SP was PCE type Melflux 2500 L with 30% total solids content. Grading of aggregates is very important for any HPC/SCC system. For the stability of a SCM system, the per cent of aggregates passing sieve size of 1 mm is very significant as it shows the adequacy of the quantity of fine material needed for stability and segregation resistance. Fine sands can pass sieve of 1 mm size in the range of 70-82 % and based on the experience this passing percentage seems to be good for the stability of SCM systems using such sands.

### 3.3.3 Composition of Mortars

The mortar systems had 1:1:2 mix proportions (cement: SRM: sand) by mass with 40% w/c and 20% w/p ratio. Such a low w/p ratio was selected to ensure adequate segregation resistance. The SRM's used were LSP, FA and 20% mass blends of FA with RHAP, RHA and SF to investigate the role of binary and ternary binder systems on flow, strength and microstructure of HP SCM systems. Fig 3.3 gives the grading curves of the two sands.

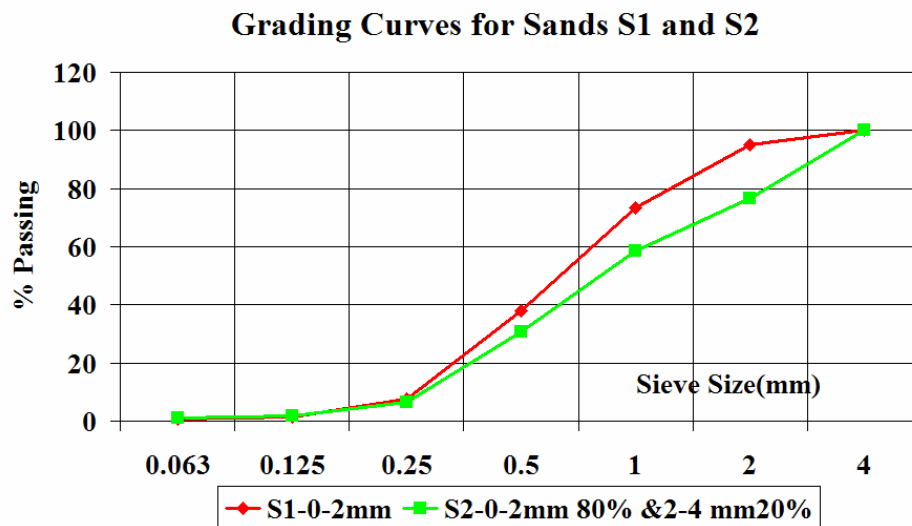


Fig 3.3 Gradation Curves of Two Sands S1 and S2 Used in SCM Systems

### 3.3.4 Mixing Regime

Mixing was done to get a target flow spread of  $31 \pm 2$  cm for SCM systems incorporating various powders. Mixing regime consisted of 30 seconds of dry mixing of materials at slow speed in a 10L Erisch mixer (Selected gears gave 900 rpm in slow and 1800 rpm in fast mode) followed by 80% of the total water addition and mixing at slow speed for 30 seconds and then for 60 seconds at fast speed. The interior walls etc of the mixer were then cleaned and remaining 20% water and SP were added. SP was added in a single dose for workability retention [140]. Three minutes of additional mixing at fast rate was done making the total mixing time of 5 minutes which is and should be higher than that for normal concrete [141,142]. Table 1 of Annexure-B gives the water demands and setting times of cements used in HP SCM system.

### 3.3.5 Flow Measurements

Literature suggests that the indices of deformability and segregation resistance are mini-slump cone spread and V-Funnel time [136, 137]. In some other work it has been proven that the relationships between slump spread and yield stress and those between V-funnel time and plastic viscosity are very closely related [138]. Various types of cements are available and any suitable one can be used depending upon the desired goals. It is known that CEM II is particularly useful for the improvement in corrosion resistance [139] while CEM III is useful for improving microstructure and for reducing excessive early heat of hydration. Mixing sequence is also very important for getting a target flow obtained by adding SP very imaginatively at a suitable moment of time during mixing, which has to be found by trial process based on experience. Firstly flow trials were made by mixing the ingredients in Hobart type of mixer. In this investigation on HP SCM, it was observed that delayed incorporation of SP after 80% of the total mixing water had already been mixed resulted in a good flow thereby minimizing the required SP content. The mini-slump cone spread and V-funnel time was measured on two batches of the same formulation. SP had been confirmed to be activated in 5 minutes of mixing in Eirich tilting mixer. Therefore this mixing regime was adopted. It indicated that the shear rate and total mixing time along with proper sequence of admixtures additions is essential for SCCS for the sake of economy and durability.

Eirich mixer was used because a larger mass was required for the flow measurements, casting of specimens for strength and shrinkage measurement from the same mixed material to avoid batch variations. This was not possible with Hobart mixer which would have required lots of mixings thus giving rise to higher batch variations in the fresh and hardened states. It is recommended that mini-cone slump spread should be measured after a fixed pre-decided time; say 2 or 3 minutes, for all formulations to obtain the seizure of flow. This would enable even viscous mortars, which keep on creeping for sometime, to give accurate flow times. In the absence of such time, T25 cm in seconds seems to be a better flow index for the comparative flow response of SRM's in HP SCM systems. T25 cm time has been proposed by the author and was not found in the literature. It is based on the analogy with Abrams cone having a base of 20 cm and T50 cm time is recorded there. The ratio of these two diameters is 2.5. The mini-slump cone had a diameter of 10 cm so the spread time was selected for 25 cm flow again at a diameter ratio of 2.5.

FA and LSP's have been used extensively by the researchers for reducing the water demand of cementitious systems. The particle size of LSP is very fine so it would pack even the spaces within cement grains but because of its highly abrasive, irregular and rough surface morphology, it gives rise to high internal friction and hence higher SP content to give a target flow. Because of its surface morphology it would give a poor packing within the particles of its own size class. This also highlights the importance of particle shape for increasing the flow and for reducing the SP content. Adding 20% RHA in FA would increase the SP content because of irregular and porous particle shape of RHA. The amorphous RHA requires higher SP to give the target flow than the crystalline one because amorphous RHA has higher internal porosity and seems to have more irregular shape than crystalline RHA. Adding SF in FA (by 20% mass of FA) would increase the SP demand due to very fine particles of SF and due to high intruded volume of mercury in SF suggesting it to possess numerous small pores. Both LSP and FA+RHA systems require SP content which is higher than the maximum specified by the manufacturer (3 % of cement mass based on total SP content and 1% based on total solids content of SP). Despite the

highest SP requirement, no setting problem could be observed with LSP formulation though some other fillers showed it to varying degrees. Tables 2-4 of Annexure-B provide the details of flow data

### 3.3.6 Powder Porosimetry

During initial experiments to determine the SP content required to give  $31 \pm 2$  cm flow, it was observed that LSP required the highest amount of SP while FA needed the lowest. Addition of RHA's in FA increased the SP demand due to high surface area of RHA which depends on its internal porosity. Therefore after initial flow experiments, it was thought to make MIP of the dry SRM's to get an idea about their pore structures and morphology in an indirect way so that the relative SP demand of various powders could be better understood and explained.

### 3.3.7 Strength and its Quantification for HP SCM Systems

The casting, curing and strength testings were made as per EN 196-1 of 1994. The curing consisted of putting the castings in moist air with 90%+ relative humidity for the first 24 hours after which they were demoulded and were put into water at 20°C after weighing. Specimens were tested in SSD condition at the prescribed ages. The strength results of these formulations had 95% statistical acceptance level. LSP is stated to be relatively inert [141] and it is proposed by the author to consider it as base line material for simple quantification of strength increments obtained with other more reactive powders.

The cast specimens had  $4 \times 4 \times 16$  cm<sup>3</sup> dimensions. For flexure the average of three specimens of a typical formulation at a given age was taken as strength at that age while for compressive strength the average of six samples (obtained from three broken samples in the flexure) was taken as the mean strength. Table 5 of Annexure-B provides the 28-day strength quantification of SCM's with CEM III using different SRM's.

### 3.3.8 Early Volume Changes and Dimensional Stability

Total shrinkage may be considered as the sum of the plastic, chemical and drying shrinkages. Autogenous shrinkage is the one that occurs due to internal consumption of water during hydration at a constant maintained temperature without moisture loss to the environment. Drying shrinkage is caused by the loss of water to the environment [141]. It is mentioned that literature contains too many papers on the estimation of a particular type of shrinkage using complex apparatus and conditions which can probably never be realized at a construction site. Structural and construction engineers are only interested in the total amount of early shrinkages of HPC/SCC systems due to their low w/c and w/p ratios. This is precisely the reasons that codes specify only the total maximum allowable shrinkage values and not the maximum allowable values of different types of parallel operating shrinkage mechanisms. Therefore in this research work emphasis is clearly on the estimation of total early shrinkages produced by several overlapping and simultaneously acting mechanisms in various paste, mortar and concrete systems using different SRM's. Early shrinkage values of HP SCM systems are given in Table 6 of Annexure-B.

### 3.3.9 Microstructure

Almost all short and long term properties of cementitious systems depend upon their microstructure which can be studied by MIP, SEM and image analysis techniques. In this investigation it was studied by MIP and SEM techniques. For both, the samples were made after drying the broken flexural test samples, in an oven for 24 hours at 105°C to stop the hydration process. There can be many other procedures for stopping hydration including the use of acetone and isopropanol and D-drying etc. Special care was exercised so that sample to be viewed remains representative.

#### 3.3.9.1 MIP

Mercury Intrusion Porosimetry (MIP) is a widely used method for measuring the pore size distribution of porous media. It is based on the fact that for squeezing out a non-wetting fluid in a pore of the diameter  $d$ , a pressure  $P$  inversely proportional to the diameter of this pore, must be applied. For a cylindrical pore this pressure is given by the Washburn (Laplace) relation as given below:

$$P = -4\gamma \cos \theta / d \quad (3.1)$$

Where  $\gamma$  is the surface tension of the liquid and  $\theta$  is the contact angle in degrees. Various researchers have used different values of angle but in this investigation  $\theta$  has been taken as 140 degrees.

#### 3.3.9.2 SEM

Scanning electron microscopy has become a very versatile tool for the study of microstructure, ITZ and hydration progress. The machine used was FEI XL 30 environmental scanning electron microscope with field emission gun (ESEM FEG). It was capable of giving spot chemical analysis EDAX (energy dispersive X-ray analysis) of cementitious systems which appears to be just of qualitative nature and no definite quantitative results should be expected due to high variation in material from point to point in cement based systems.

### 3.3.10 Thermal Analysis of HP SCM Systems

Thermogravimetric (TG) and DSC were carried out on powdered HP SCM formulations with heating rate of 10°C per minute and upto 1000°C using Netzsch STA 409 PC machine. The mass of  $\text{Ca(OH)}_2$  was calculated using TG curves and a formula mentioned in the literature [63]. Table 7 of annexure B gives the results of CH mass for various HP SCM formulations.

### 3.3.11 Water Absorption of SCM Systems

Like HP SCP systems, the water absorption of HP SCM systems was also recorded and it appears in Figs 1-3 of Annexure-B.

### 3.4 Study of HP SCC Systems

Self-compacting concrete (SCC) is the technology of the decade. Various types of SCC are known including powder type, viscosity agent type and combination type each differing mainly the way the segregation resistance is achieved. In the powder type SCC a low water-powder ratio guarantees adequate segregation resistance while the same role is played by viscosity enhancing agent (VEA) in the viscosity agent type of SCC. The combination type of SCC allows the production of a robust SCC obtained with slightly reduced powder and VEA contents respectively when compared with the earlier mentioned two types of SCC. This type is believed to have an excellent segregation resistance and was therefore selected for experimentation and site placements. It is mentioned elsewhere that to enhance the segregation resistance, the difference between the densities of paste and aggregate components should be minimum [143], which is not easy, and it may have affect on static stability of SCC.

#### 3.4.1 SCC Mix Design Concepts

Several SCC mix design approaches exist with each being drastically different from the others. However continuous aggregate grading is mostly used in SCC mix designs as it requires lesser paste to fill the voids and to give mobility to the aggregates and is therefore preferred.

The knowledge of volume characteristics enables to combine the aggregates to obtain mixes with high packing density. Comprehensive investigations have shown that the appropriate aggregate volume of SCC can be calculated directly by taking into account the measured volume characteristics. In some studies pre-selection of the aggregate volume and aggregate composition, particularly sand content, was based on the flowability tests on concrete mixes with varying aggregate volumes and sand-to-aggregate-ratios [144,145]. According to reported results, aggregate volumes of  $640 \text{ dm}^3/\text{m}^3$  and  $615 \text{ dm}^3/\text{m}^3$  and five different aggregate compositions with sand contents of 30-40% were chosen by the investigators. In these studies water demand of a certain concrete constituent was defined as the amount of water required to completely cover all particles surfaces with a thin water layer (In the opinion of the author, such a WD would be an upper-bound result of SSD WD). It is stated therein that the minimum water demand of mortar equates to about 95% of the SCC's total water amount so that the water demand of the coarse aggregates would amount to approximately 5% of the total water content of the SCC mix. The author's suggested procedure given in Table 3.7 also verifies this point though the procedure used is simple and different from that reported [144,145] wherein WD of coarse aggregate was determined by centrifuging the water cured aggregates. It was assumed in [144,145] that the centrifuging process will remove all extra water other than that absorbed and that which chemically sticks onto the coarse aggregate particle surfaces, a condition very near to SSD condition. The WD of aggregate compositions in the vicinity of  $0.0135\text{-}0.0155 \text{ dm}^3/\text{dm}^3$  reported in [144,145] had been determined using fairly sophisticated equipment. Therefore a suitable and simple procedure has been suggested by the author in the following articles to establish the WD of SCC system. The experience with the SCC mixes shows that as a first starting step, aggregates can be selected with reasonable accuracy by keeping in view the European guidelines for SCC 2005 [141]. Of course the powder content (cement, fillers and their ratio) would be selected based on the best engineering judgment in view of the desired target properties of SCC in fresh and hardened state. Water-cement ratio can be selected from strength of local cements and seeking help from certain codes of practice considering the service use and



exposure requirements during the service life of structure. Later on plasticizer and viscosity agent contents can be adjusted considering flow targets possibly starting with the average manufacturer's specified ranges. The appropriate sand content appears to be in the range of 50-55% of the total aggregate volume especially for rather elongated coarse aggregates for stability purposes.

After selecting the powder and aggregate contents, the WD of SCC systems can be estimated as suggested and can also be compared with the mixing water available from selected w/c ratio to avoid possible bleeding and segregation.

Various sources have made recommendations regarding the selection of coarse and fine aggregate content of SCC. These are given in Tables 3.4 and 3.5 respectively. Total aggregate content, to start with, can be taken in the range of  $0.615\text{--}0.64 \text{ m}^3/\text{m}^3$  [144,145] with a sand content of 50 % of the total aggregate mass has been found satisfactory for SCC [146]. The powder content and the water-cement ratio can also be selected considering guidelines and required properties in the light of strengths given by local cements [3,141]. Adjustments are then made till the desired test values are obtained.

The other recommendations for SCC-mixtures about the fraction of aggregates as well as sand (0-2 mm) passing the 1 mm sieve can be seen in Table 3.6.

**Table 3.4** Volume of Coarse Aggregates

Reference	Volume of coarse aggregate w.r.t SCC volume ( $\text{m}^3/\text{m}^3$ )
[147]	0.28-0.36
[3]	0.266-0.281
[141]	0.27-0.36(750-1000 $\text{Kg}/\text{m}^3$ )
[144,145]	0.313-0.359

**Table 3.5** Volume of Fine Aggregates

Reference	Volume of fine aggregate w.r.t SCC volume( $\text{m}^3/\text{m}^3$ )
[144,145]	0.256-0.327
[141]	48-55% of total aggregates mass

Experience shows that the per cent material passing 1 mm sieve is of tremendous importance for the stability and flow of SCC mixes using MSA of around 16-20 mm.

**Table 3.6** Recommendations on Fine Material Required For SCC

Reference	Fraction < 1 mm in %	
	of total aggregates	of sand (0-2 mm)
Generally recommended	30-45	70
[148]	39	67
[122] CSA (A23.2-2A)	42	82

To increase cohesiveness and stability, the sand content may be increased keeping the total aggregate content constant. Good workability is usually achieved by reducing the aggregate content (resulting in reduced internal friction) and by increasing the paste volume as has been stated earlier. This may, however, slightly increase shrinkage and reduce strength of SCC mix.

### 3.4.2 Calculation of Water Demand of SCC Systems

The calculation of system's water demand is often the first required SCC design step [141]. Therefore a simple procedure suggested by the author, suiting field conditions also, can be used instead of procedures using sophisticated equipments [144,145]. For the production of durable SCC mixtures, it is important that the mixing water content does not exceed the water demand of the system by a big margin. The importance of making SCCS at a mixing water content close to system's WD have already been established in the previous articles.

The total WD of SCC system is the sum of individual water demands of the powder and the aggregate components. The WD of the powder component can be determined by mixing cement and other SRM's in the selected mass proportions to be used in SCC composition and a test can be made with Vicat needle. For various size fractions of coarse and fine aggregates simple procedures outlined in ASTM C 127 and 128 can be followed. The results can then be added to get the systems WD as shown in Table 3.7

The following amounts of materials were used in a typical SCC formulation and application. The water demand of 1 m<sup>3</sup> of SCC according to the proposed procedure is given in Table 3.7.

**Table 3.7** Calculation of the Water Demand of 1 m<sup>3</sup> SCC

Material	Amount in SCC mixture (kg/m <sup>3</sup> )	WD of material (% of mass)	WD (kg/m <sup>3</sup> )
Cement : fly ash (1 : 0.387* by mass)	(380 +147) 527	27.5	145
Aggregate size 0/2 mm	824	1.73	14.25
Aggregate size 2/8 mm	412	0.933	3.84
Aggregate size 8/16 mm	412	1.06	4.37
Total system's WD			167.5
Mixing water (w/c=0.45)			171
Difference			3.5

\* Based on engineering judgment

### 3.4.3 Materials Used in SCC Mixes

Many cement types and two FA types were used in various SCC mixes designed for different flow levels. However most of the data is based on hard coal FA1 (Opole-Poland). Table 3.8 gives the physical and chemical (in per cent) properties of some of the powders used.

**Table 3.8** Properties of Powders used

Powder	Particle Size (μm)	BET Area (m <sup>2</sup> /g)	Density (g/cc)	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	LOI	SO <sub>3</sub>
CII	16.90	1.353	3.11	18.74	2.23	1.38	58.9	4.78	1.25	1.01	7.09	3.20
FA1	26.59	1.65	2.31	51.44	5.55	2.51	4.03	26.13	1.23	2.63	2.71	-

The Bogue's potential parameters of CEM II/A-LL 32.5R were C<sub>2</sub>S= 19.56, C<sub>3</sub>S= 51.18, C<sub>3</sub>A= 10.5 and C<sub>4</sub>AF= 6.87.

In general, the aggregate shape requirements for both normal concrete and SCC are the same stating that no more than 15 % of aggregates could be elongated. According to DIN EN 933-4, aggregate is considered elongated if the ratio of length to the minimum dimension is more than

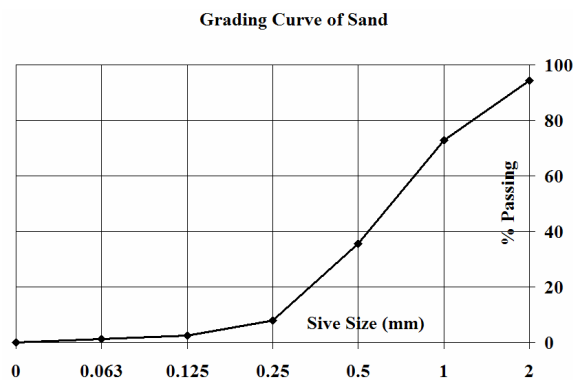
3.0. A random sample of 8-16 mm size fraction was evaluated. It had 15% elongated aggregates and therefore could be considered as a border line aggregate.

Fig. 3.4 shows the shape of a random sample of 8-16 mm size of coarse aggregates used in SCC. These elongated aggregates can cause increased internal friction, voids and also pipe blockings at times. Such blockages may also caused by bleeding, high coarse/fine aggregate ratio, and using the pipes with different wear [149]. A high elongated aggregate content also needs a higher paste volume for filling the voids and for the SCC conveyance because paste is the vehicle for the aggregates.

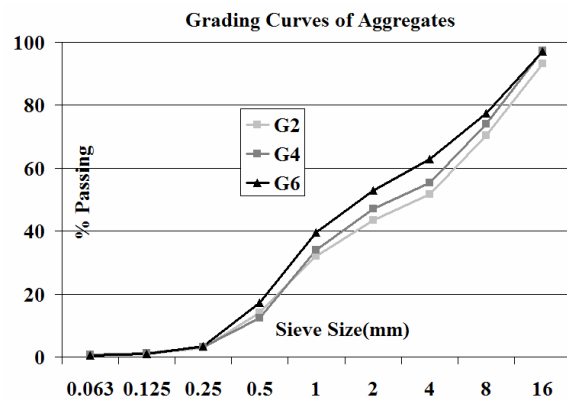


**Fig 3.4** The Shape of 8-16 mm Size Fraction Random Aggregate Sample

Siliceous sand (0-2 mm) and natural gravel (2-8 mm and 8-16 mm) was used for the SCC-mixes. The grading curves of aggregates used in this research work with a maximum aggregate size of 16 mm falls within the limits of German standards DIN EN 206-1 and DIN 1045-2 [150]. Figure 3.5(a and b) show the grading curves of sand and of total aggregates.



**Fig. 3.5 (a):** Grading Curve of Sand (0-2 mm)



**Fig. 3.5 (b)** Gradings of Total Aggregate Used for SCC. Contents of fractions (0-2:2-8:8-16 mm): G1 (39:33:28), G2(45:27:28), G4(50:25:25), G6 (55:22.5:22.5)

### 3.4.4 Mixing Procedure

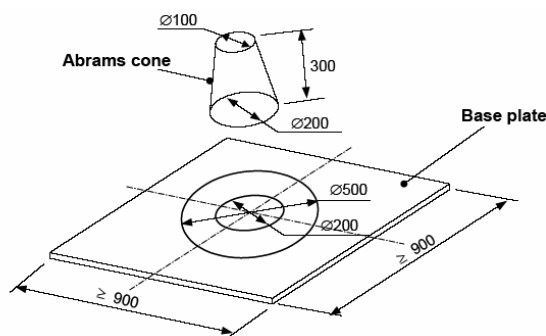
The mixing procedure for both laboratory and plant SCC mixes consisted of:

1. Mixing of dry constituents for 30 seconds
2. Then adding water, superplasticizers and viscosity agent at the same time.
3. Mixing the ingredients for another 90 seconds. The total mixing time was 2 minutes.

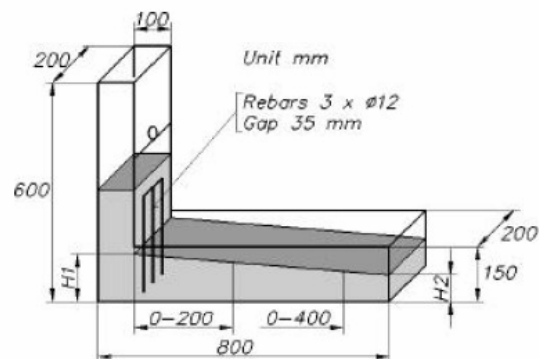
In laboratory, after initial two minutes of mixing, concrete was kept undisturbed for seven more minutes and then was given one minute final mixing before starting flow tests for insuring SP activation. Other possible alternative could have been to have a higher mixing time of around 4 minutes for the same purpose. At ready mixed concrete manufacturing plant, after two minutes of mixing SCC was transferred to a mixing truck which kept rotating at slow speeds for seven minutes and then one minute of fast truck mixing was given before flow testing. From plant to site continuous truck agitation at slow speed was observed en-route. It is mentioned that the followed mixing regime may not be the most efficient but it had to be observed due to stringent plant mixing routines which normally do not allow the use of optimal mixing procedures as recommended elsewhere [141].

### 3.4.5 Description of SCC Flow Tests

In the fresh state the tests including slump spread (cone standing on narrow end), V-Funnel time; L-box and J-ring (blocking ring) were carried out in sequence. After that air content was measured. The average time spent on completing the flow tests was around 20 minutes by three men party. In laboratory, the sample was agitated again for 5 seconds each before starting some other flow test after slump test. Same mixing regimes were followed both in the laboratory and at ready mixed concrete manufacturing plant. It is therefore suggested that slump should be taken after insuring the activation of the superplasticizers only especially in the laboratory otherwise the slump test values (T50 cm and spread) will be incorrect and its comparison with J-ring may not be accurate. This can be done in many ways including higher mixing time or leaving the mixed material in the pan for some more minutes and then finally mixing for some more time after initial mixing. Figs 3.6 (a to f) show the apparatus used for various routinely performed SCC flow tests.



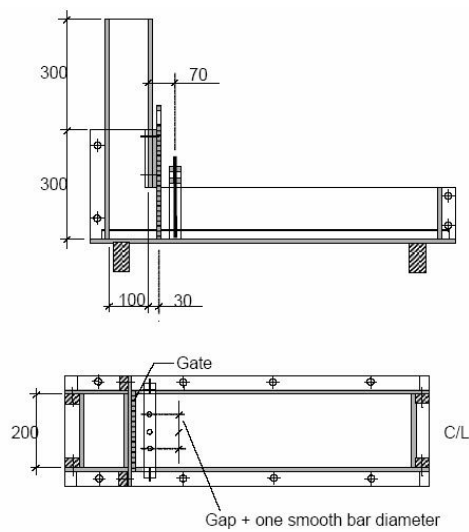
**Fig. 3.6 (a)** Slump Test and T500 mm (s) Measurement Arrangement



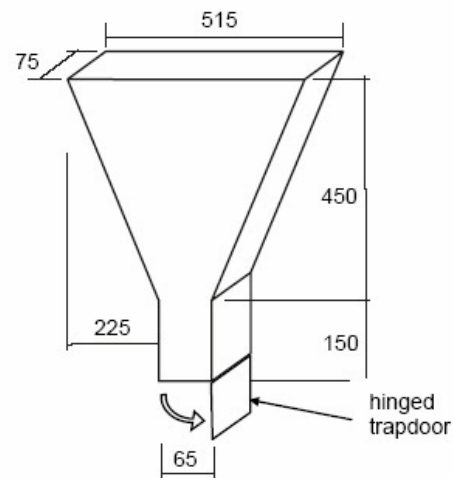
**Fig. 3.6 (b)** General Arrangement of L-Box Test

Although a final consistence adjustment with water is allowed [141], however laboratory observation showed that even a very small water addition after the addition of admixtures can reduce the mix cohesion. A small description of each flow test will now be given.

Slump cone is filled gently and then lifted. T50 cm time is recorded along with total spread when flow seizure is obtained. While testing with narrow end down, the results depend a lot on the skill of the operator especially the height upto which he lifts or if the cone happened to sway laterally would affect the accuracy of results. Simple slump test can give an idea, to an experienced practitioner, about the viscosity, segregation resistance and bleeding etc in addition to deformability. L box-test basically determines the passing ability of SCC and with high deformability,  $h_2/h_1$  ratio approaching unity with reduced T60 cm time should be expected. The exact lifting of the gate in one go upto the required level is needed and influences the time.



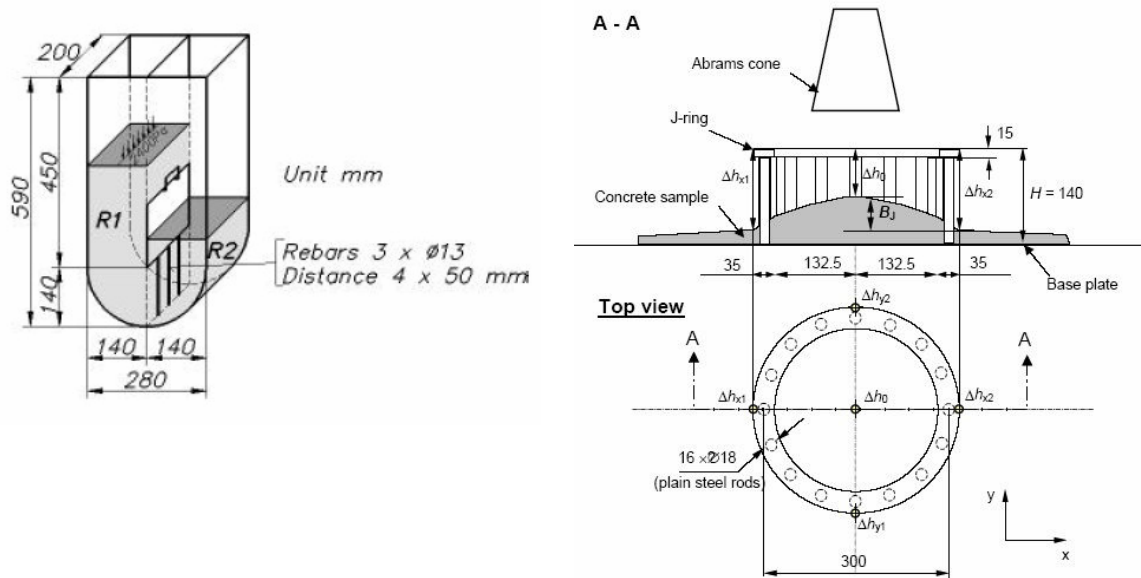
**Fig. 3.6 (c)** Elevation and Sectional View of L-Box Test Arrangement



**Fig. 3.6 (d)** General Arrangement of V-Funnel Test

After filling the V-Funnel, the bottom gate is opened and stop watch is started simultaneously. Seizure of flow can be correctly recorded by stopping the stop-watch when light at the bottom of funnel is seen while looking down from the top. V-Funnel time is considered to be a function of systems viscosity. Higher viscosity means higher funnel time.

U-box test is also a function of passing ability of a SCC mix through congested reinforcement. J-ring or blocking ring test can test passing ability, segregation resistance and filling ability. Lesser is the difference between slump spread and J-ring spread better it is. If difference is more, it would indicate non-continuous packing, low deformation and segregation resistance.



**Fig. 3.6 (e)** General Arrangement of U-Box **Fig. 3.6 (f)** Details of Blocking Ring Apparatus Test

Fig 3.7 shows the air content measuring apparatus. The SCC sample is gently put into the container (bottom half of the air content meter) upto top by leaving a gap of around 1-2 mm between top of the concrete and the top of container. There should be no aggregate particle or paste at the rim junction of top and bottom of the apparatus to provide an air-tight connection between the two halves of the apparatus. After filling the container, the meter is mounted on it and the apparatus is wobbled without impact so as to release any air. Then water is added through side apertures as shown. After that red side stoppers are clamped by turning them down and air is pumped by using the lever with brown mount.



**Fig. 3.7** Air Content Measurement

Correction is done by using top black button (right) and tabbing the glass plate till the needle reads zero. Then green measurement button (left) is pushed and per cent air content is displayed. Air content has to be continuously monitored for all the batches and recorded. It can give an idea about the change of grading, aggregate surface moisture conditions, pumping effects and also



about the adequacy of admixture dispensation at plants for various batches of a placement. A variation in air content should be carefully interpreted.

### 3.4.6 Other Considerations

Fine sand is a useful component in optimizing the particle size distribution and increases the stability and flowability of the SCC mix. Chinese method of making SCC as proposed by Su et al[3] is based on the concept that voids present in loose aggregates are filled with paste and that the packing of aggregates is maximized by using more sand and less gravel .

The void part of loose aggregates generally amounts to about 42-48%. Upon application of mixing in SCC, increased compaction reduces the voids to about 32-41% [151]. It is mentioned that the final density of the mix depends upon the sand/gravel ratio also and not solely on densities of sand or gravel alone. The void fraction of the compacted aggregate and its apparent packing density are directly related to the aggregate specific particle density and particle shape. The void fraction of the various percentile ratios of sand/coarse aggregate is reduced upon compaction/ vibration to 75-80% of its original loose void fraction.

It is reported in the literature that fine sand (0-1 mm) attains a minimum void fraction (of 0.23) when the percentage sand/coarse aggregate ratio is 40%, medium sand (0-2 mm) attains this void fraction (of 0.235) at 50% and coarse sand (0-4 mm) attains this void fraction (of 0.23) at 60% [151]. This is the reason that most of SCC formulations reported in this thesis were based on G4 grading having 50:25:25 mass per cent of 0-2 mm, 2-8 mm and 8-16 mm size fraction of aggregates respectively.

In the modern competitive and quality oriented concrete applications, the use of blended cements has become normal because using a single type of cement can not assure quality and durability. For example OPC is known for bad chloride penetration while CEM III is considered the best for it while the same CEM III could be the worst for frost and carbonation resistance. Blended cements are used on quality sensitive projects.

Ternary-blended cements based on OPC, slag cement and pozzolans have been the subject of investigations since 1950. Studies conducted in France resulted in the commercial production of ternary cements since 1953 and in some parts of Australia ternary and even quaternary cements have been intermittently available since 1966 [152]. According to several researchers [153-155] ternary blends made of Portland cement, silica fume, and fly-ash offer significant advantages over binary blends and even greater enhancements over straight Portland cement.

When ternary and quaternary blended cements containing both SF and FA are being used in many countries, there seems to be no reason for not using FA in combination with other pozzolanic SRM's like SF and RHA in OPC concrete in Germany as disliked elsewhere [17]. The alternative could be to use a single type of cement and add SF, FA or RHA (or their suitable combinations) during mixing resulting in binary and ternary binder systems. The reported research in this thesis also suggests the beneficial effects of binary and ternary blends of different binder systems and it is hoped that FA and RHA in suitable proportions could soon become essential ingredients of HPC/SCC produced at least in the developed world.

## 4 RESULTS

In this chapter the results of various tests performed on HP SCP, SCM and HP SCC systems will be presented.

### 4.1 Tests on HP SCP Systems

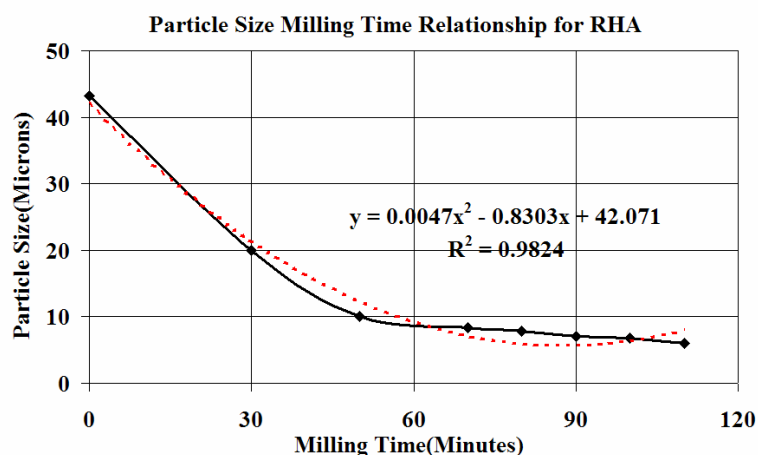
To start with paste systems, physical and chemical analysis of powders used was carried out and the results are presented in Table 3.3.

The cements used in the study of HP SCP systems were from Schwenk Germany. RHA was black in color and was found amorphous after XRD examination. It was imported from USA. RHAP was found to be crystalline and was imported from Pakistan. It had a pale white color. SF was as produced locally made and was grey in color.

#### 4.1.2 RHA Characterization

##### 4.1.2.1 Particle Size

The imported RHA was received in several nicely sealed plastic buckets. The particle size of RHA in all buckets was checked and found to vary drastically with d50 varying between 4-44 microns. It was then decided to subject the coarse ash to milling process so as to bring the resulting ash size down to about 6-7 microns in order to be able to pack the binder phase. Finally the ash in all buckets was mixed together and then used. Figure 4.1 shows the relation between the particle size and milling time. It can be seen that beyond 50 minutes of milling the particle size does not decrease significantly. The relationship is a nice second degree curve.

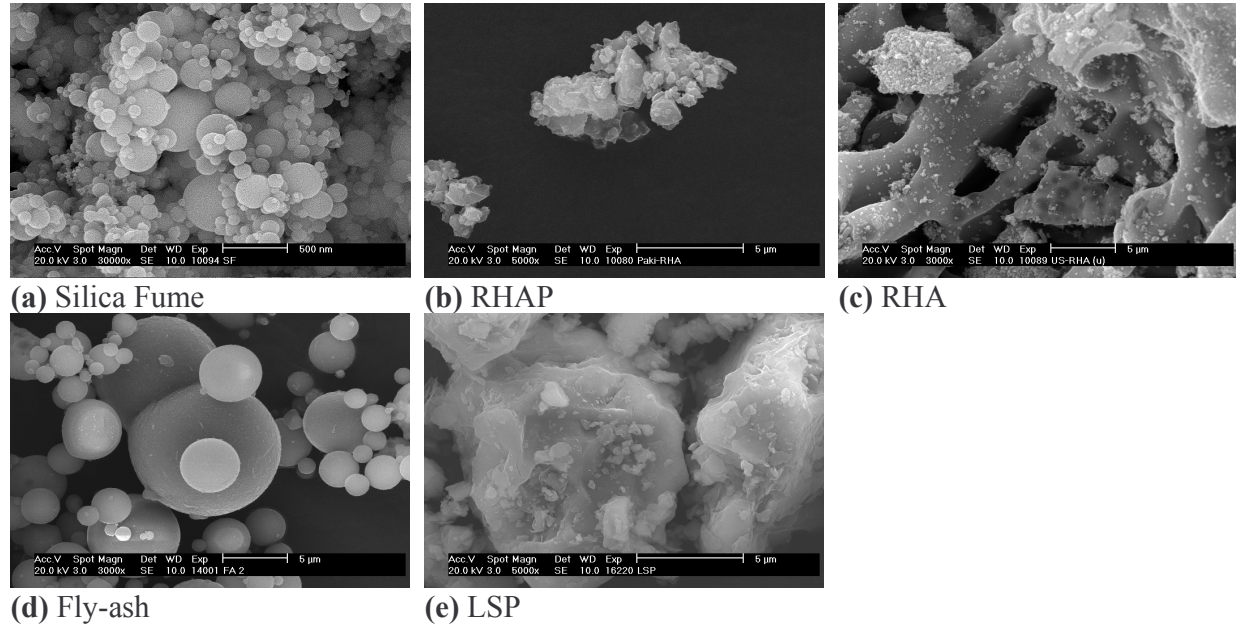


**Fig. 4.1** A Typical RHA Particle Size-Milling Time Response With The Trend-Line Relation

##### 4.1.2.2 Particle Shape of SRM's

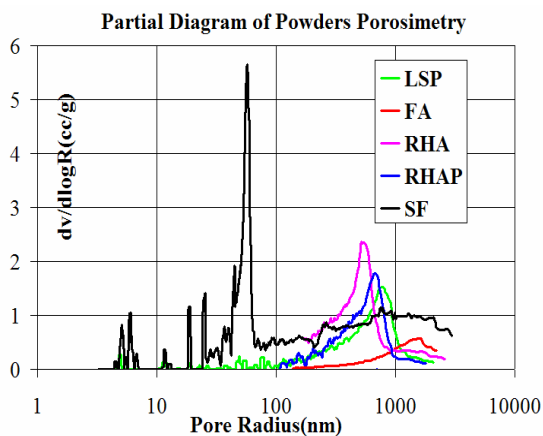
It is very important to know the shape, size and morphological characteristics of the SRM particles used in any investigation on HP SCCS in order to understand and explain some of the

results on flow, strength, microstructure and shrinkage. Figure 4.2 gives the SEM presentation of the SRM particles.

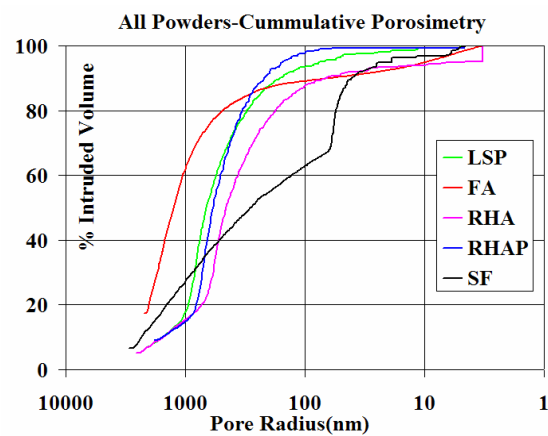


**Fig. 4.2** Shows the SEM Pictures of Various SRM Particles Used in The Study

It must be kept in mind that it is not only the cement grains upon which SP is adsorbed/granted but the powders also adsorb significant SP depending on their size, shape, morphology and internal voids or fissures. MIP studies were therefore done on powders. Fig 4.3(a) and (b) present the powder porosimetry results.



**Fig. 4.3 (a)** Partial SRM's Porosimetry Curve



**Fig. 4.3 (b)** Cumulative SRM's Porosimetry Curve

In Fig 4.3 (a) the partial MIP diagram for various SRM's is shown. SF seems to have very small size of internal pores with high mercury intruded volume. The maximum pore size of FA is the largest. It is thought that a combination of high pore size of powder accompanied by low

mercury intruded volume will need small SP content for the target flow as almost all SP will be available in solution for dispersion purposes. Based on SEM studies, some of FA particles were found hollow /sheared and had small circular voids in their walls. It is therefore natural to expect that FA would require minimum SP content because whatever is added remains available in solution for dispersion of cement grains. From Fig 4.3 (b) it can be seen that intruded mercury volume rises gently and upto 65% of mercury intrudes between size range of 2000-80 nm in SF powder. Then there is an abrupt change possibly indicating bottle neck type of pores in SF. Apart from SF, mercury intrusion for the remaining SRM's (LSP, RHA, and RHAP) starts at much higher pore sizes.

### 4.1.3 Water Demands and Setting Times

This is one of the very important steps which are often neglected in reported research works. If water demand of system is not known w.r.t mixing water content then response of HP SCCS can not be properly explained. Fig 4.4 shows the increase of WD of HP SCP systems with increase in SF content (w.r.t cement mass). CEM I and CEM III gave almost identical water demands while CEM II had lower WD due to its higher particle size. Water demands and setting times of various cements with powders are given Tables 1-4 of Annexure-A.

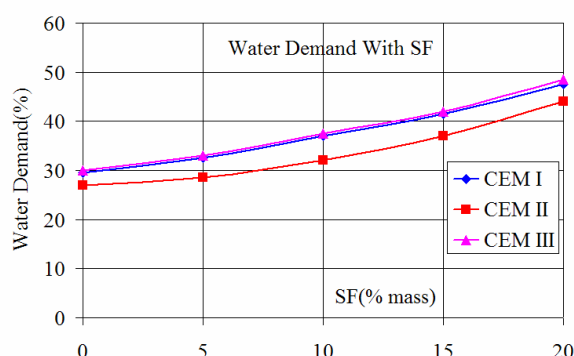


Fig. 4.4 Water Demands of Cements With SF

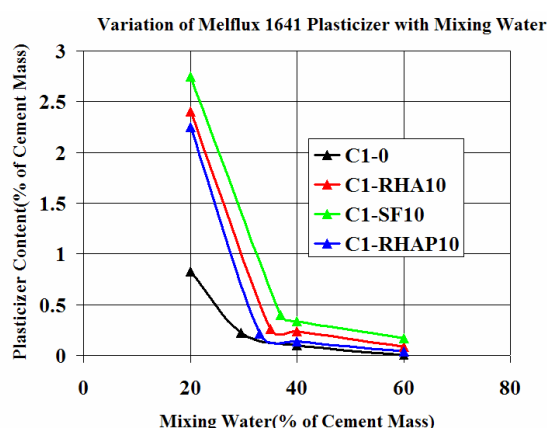


Fig. 4.5 Variation of Plasticizer Quantity With The Amount of Mixing Water

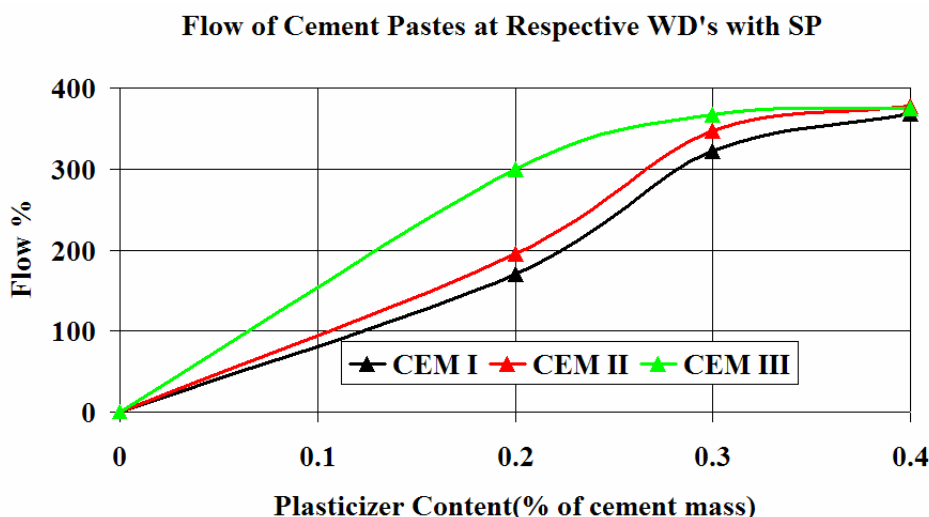
### 4.1.4 Flow of HP SCP Systems

Fig. 4.5 gives relationship between SP quantity required for 30 cm spread and the mixing water content of some selected HP SCP systems. The mixing water contents for these HP SCP systems were 20%, WD, 40% and 60% (w.r.t cement mass). Trial mixes using Hobart Toni Technik mixer were made and tested for flow and SP content, required for target flow of 30 cm spread, was determined and has been shown in fig 4.5.

Fig 4.5 is very interesting in the sense that it demonstrates that at WD, HP SCP systems require low SP contents for meeting target flow, which falls within the manufacturer specified limits. The other thing which can be noticed is that when even a small SRM content (10% of cement mass) is added to cement at 20% mixing water content (w.r.t cement mass), the SP requirement shoots up to give target flow. Such a high SP content is uneconomical and has a pronounced side effect in terms of delayed setting of such cementitious systems. It may also

adversely effect properties like flow retention, strength, pore structure and shrinkage. It is clear that mixing water less than the WD of system is uneconomical, unrealistic and also gives rise to slump retention problems in HPC systems. It can be seen in the same figure that the SP content decrease between WD and 40 % water (which is often specified as the upper limit for a HPC system) is not very significant because of very little difference between the two water contents. It is therefore suggested that HPC or SCC systems should have the mixing water content equal to WD of system which is the divorcing water content below which system is uneconomical and gives rise to unwanted effects while a water content more than WD would adversely affect the strength and durability. The SP content required to meet the target flow at water content greater than WD (for the target flow) is the greatest for SF and then come RHA and RHAP in order.

By gradually increasing the SP content at given mixing water content, a typical S-shaped flow-SP content response can be obtained as shown in Fig 4.6. It is obvious from fig .4.6 that after the saturation point, which appears to be near 0.4% of SP, an increase in the plasticizer content would not increase the flow very significantly. It is also clear that the saturation point of this powder type PCE SP is almost the same for the cements used and can be regarded as the maximum limit of usefulness of a SP. It may also be approximately determined by plotting flow-SP interactive plot. The precise determination of saturation point for a given superplasticized cementitious system involves complex procedures. It is also noted that the SP content within the target flow (200% or 30 cm spread of mini-cone) at this mixing water content is not a function of fineness of cement considered in terms of specific surface areas, but it appears to be more closely related to the total Portland cement clinker content. More is the clinker content less would be the flow for a given SP content. The surface areas of cements increase from CEM I to CEM II to CEM III (see Table 3.2).



**Fig. 4.6** Plasticizer-Flow Response of Neat Cement Pastes at Their Water Demands

#### 4.1.5 Strength of HP SCP Systems

It was observed that RHA containing HP SCP systems developed higher compressive strengths at later ages (3 days and beyond) and this is in conformity with the results obtained elsewhere [41,42] but opposite to those reported in [68,156,157]. These mineral admixtures were taken at 10% of the mass of cement as suggested in the literature [134,158], a mass per cent



suggested to make them thermally stable also upto 300°C [159]. The specimens were tested for strength in SSD condition at the ages of 1, 3, 7 and 28 days and are given in Tables 6-9 of Annexure A. Water absorption tests at 3, 7 and 28 days were also made. Table 10 of Annexure-A gives theoretical paste densities and powder contents of various systems. 28 days flexural and compressive strengths of CEM I 42.5R and CEM III/B have been quantified by treating the neat paste samples as controls. In general, the 28 days compressive strength is increased with pozzolans additions despite dilution of cement in both cements except with CEM I at 20% mixing water (w.r.t mass of cement) the strength reduction takes place due to very high SP content for the pastes containing mineral admixtures. High SP content also entraps significant amount of air, all of which is not able to escape during self-compaction. This creates voids and hence a decrease in strength and possibly more shrinkage (due to early water consumption) compared with control neat HP SCP systems. The flexural strength at various mixing water contents with CEM III is generally decreased for pozzolanic additions. Table 4.1 gives the strength results of various formulations.

**Table 4.1** Strength Quantification of SCP Systems with SRM's at Three Mixing Water Contents

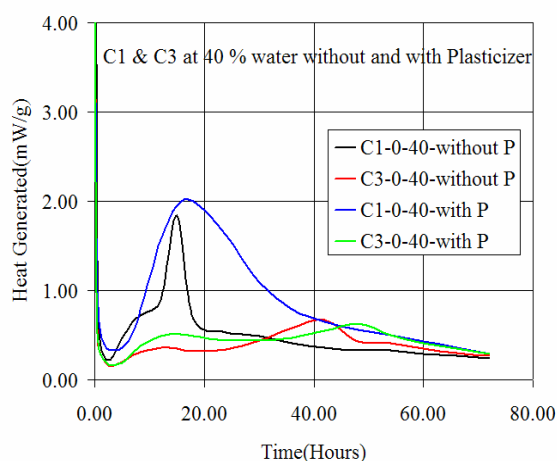
HP SCP System	28 days strength, MPa, CEM I		Changes with Pozzolan, MPa		28 days strength, MPa, CEM III		Changes with Pozzolan, MPa	
	Flexure	Compr- ession	Flexure	Compr- ession	Flexure	Compr- ession	Flexure	Compre- ssion
<b>C-0-20</b>	16.96	133.04	<b>control</b>	<b>control</b>	18.02	104.3	<b>control</b>	<b>control</b>
<b>C-SF10-20</b>	17.78	123.7	<b>+0.82</b>	<b>- 9.34</b>	18.71	113.5	<b>+0.69</b>	<b>+9.2</b>
<b>C-RHA10-20</b>	18.43	124.0	<b>+1.47</b>	<b>-9.04</b>	15.77	116.6	<b>-2.25</b>	<b>+12.3</b>
<b>C-0-40</b>	9.19	77.76	<b>control</b>	<b>control</b>	10.0	65.43	<b>control</b>	<b>control</b>
<b>C-SF10-40</b>	10.29	92.96	<b>+1.1</b>	<b>+15.2</b>	9.95	74.38	<b>-0.05</b>	<b>+8.95</b>
<b>C-RHA10-40</b>	9.76	92.89	<b>-0.53</b>	<b>+15.13</b>	10.66	79.83	<b>+0.66</b>	<b>+5.45</b>
<b>C-0-60</b>	6.15	40.36	<b>control</b>	<b>control</b>	8.0	31.96	<b>control</b>	<b>control</b>
<b>C-SF10-60</b>	6.59	53.13	<b>+0.44</b>	<b>+12.77</b>	8.2	49.03	<b>+0.2</b>	<b>+17.07</b>
<b>C-RHA10-60</b>	7.76	54.16	<b>+1.61</b>	<b>+13.8</b>	5.93	48.44	<b>-2.07</b>	<b>+16.48</b>

#### 4.1.6 Calorimetry

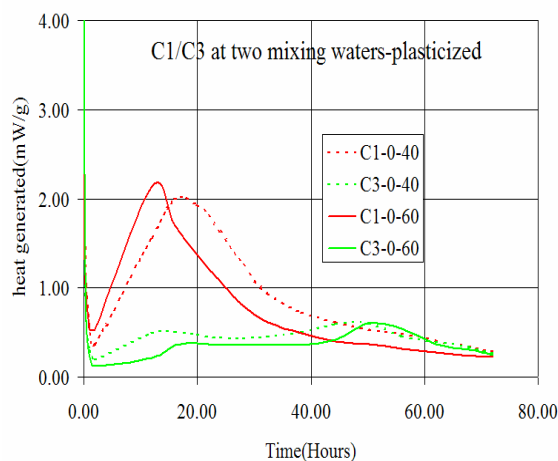
In this technique the heat liberated over time due to hydration reactions is measured with reference to dummy gage. The peaks of liberated heat are then considered reactions and hence reaction kinetics are known. By adding SP equal to that required for producing 200% flow at WD, 40% and 60% mixing waters, the magnitude of heat peaks is slightly increased and their occurrence is delayed for both CEM I and CEM III. This delay is greater for CEM III pastes. The time of occurrence of peaks at WD's and 40% mixing water remains almost the same for both cements as there is not much difference between the two stated water contents. Differential scanning calorimetry by the author showed these points. Moreover the presence of SP also delays the heat peaks observed in the calorimetry of cement pastes (compared with those without it) and the amount of heat liberated depends on the cement content, its type and w/c ratio. Using CEM I with SP needed for 30 cm mini-cone slump spread, increased the heat liberated (compared with control) while with CEM III it got slightly reduced at the same w/c ratios because of further delayed hydration and a low clinker content. At higher w/c ratios in HP SCP systems, the liberated heat was also reduced possibly due to dilution effects. Small sample size



and hand mixing of water, which can be non-uniform at small mixing water contents, can be the possible reasons. 72 hours differential conduction calorimetry was done on the samples with and without superplasticizers/mineral admixtures at various mixing water contents to know the reaction kinetics of SF and RHA in cement pastes. Opposite to these findings which pertain to self-compacting pastes only, Zhang [160] reported that RHA concrete reached maximum temperature earlier than the control and SF containing concrete. This may be due to a resultant lower effective w/c ratio in their RHA concrete compared to control normal concrete. In self-compacting cementitious systems having a target flow, this effect is changed due to presence of SP. As the first peak occurs immediately after the addition of mixing water, it is normally the occurrence of second and third peaks which are considered for comparison purposes. The magnitude of heats released at second and third peaks within a system generally decreased with increasing water content (less cement contents-dilution effect) showing that amount of heat liberated depends more on cement content rather than water content. Generally this is true for mixing water greater than the WD of the system. Comparing the same systems (similar cements and mixing waters) with SF and RHA, the magnitude of heats released by SF system is more than RHA system at the second and third peaks and they occur earlier compared with RHA systems indicating a possible stronger and earlier pozzolanic reaction of SF compared with RHA. It should be kept in mind that systems containing 10% SF/RHA were diluted. Figures 4.7 to 4.9 represent reaction kinetics of various paste systems. Non-representative sample, hand mixing of water in dry constituents and improper sealing of the containers, if present, can change the results. It is important to realize that as only a small sample size is required, the preparation of sample itself can have a significant effect on the response of materials. Therefore this procedure at best can be treated as a qualitative supplementary approach to explain some of the results.



**Fig. 4.7 (a)** Effect of Plasticizer For Two Cements

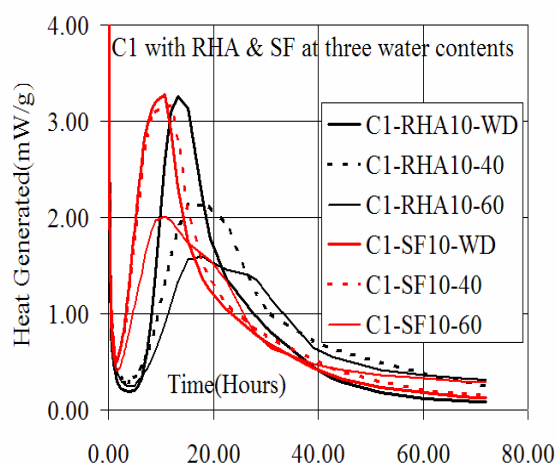


**Fig. 4.7 (b)** Effect of Water Contents

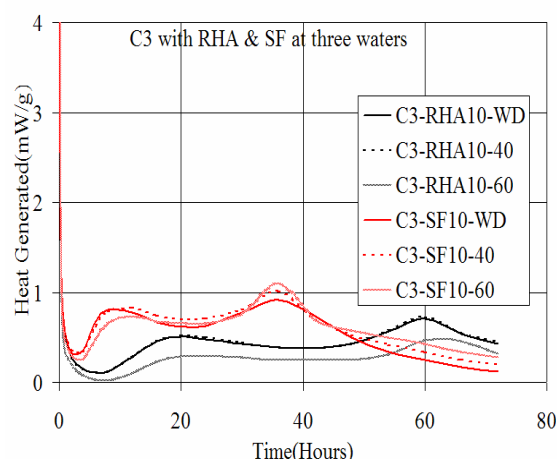
Fig 4.7 (a) shows calorimetry results for CEM I and CEM III at 40% mixing water with and without SP required for target flow. It can be seen that the SP addition makes the water to be uniformly available to all cement particles thus showing a slightly higher heat released at a slight delay. Same comments are almost valid for CEM III. Fig 4.7(b) shows calorimetry results of two plasticized cement pastes at two mixing waters. CEM I at 60 % mixing water does not need any SP to meet the target flow so that at 40% mixing water the delay because of SP, in comparison to that at 60% water, is visible. Moreover a slightly higher heat recorded at 60% water can be

attributed to many factors. For CEM III, lesser heat is released at 60% water because of dilution effect.

In Fig 4.8, calorimetry of HP SCP systems with two pozzolanic powders has been shown with three mixing water contents for 72 hours duration. All systems had same Hagermann's mini-slump flow of 30 cm adjusted by SP. It can be seen that SF with CEM I liberates more heat than RHA at the three mixing water contents showing faster hydration and quicker setting. Same phenomenon is obvious in a slightly better way with CEM III wherein it can be seen that SF liberates much more heat during first 40 hours after that it cools off fast and ends up giving lesser heat than RHA at 72 hours. It also shows an earlier setting than corresponding RHA formulations. With CEM III it is usually the third peak which gives higher liberated heat than the second peak and this must be considered while prescribing curing schemes. It is mentioned that calorimeter automatically registers heat values after every one minute resulting in a huge total file size. However the plotted curves are based on truncated data. The shape and ordinates of curves remain the same.

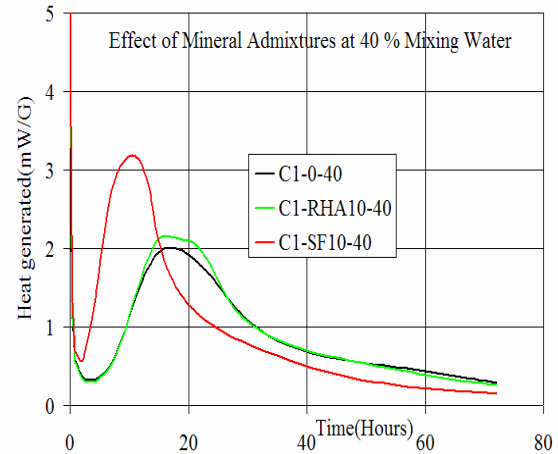
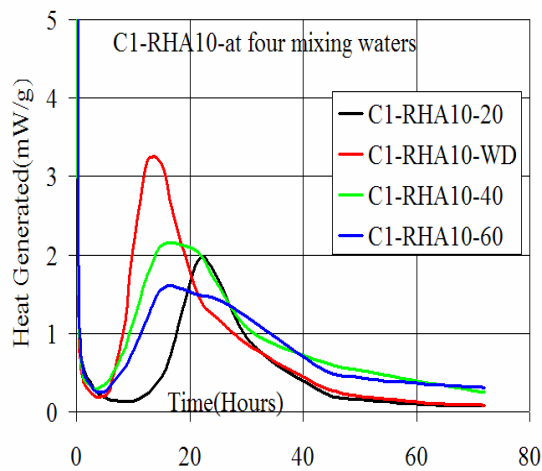


**Fig. 4.8 (a)** CEM I With Two Powders



**Fig. 4.8 (b)** CEM III With Two Powders

Fig 4.9 (a) represents self-compacting paste systems having same flow levels achieved through variation in SP contents for CEM I with 10% RHA(cement mass per cent) at four mixing waters. At 20% mixing water, the peak occurs at 21.5 hours and heat liberated is lesser than those at WD and 40% mixing water, although this system(20% water) had the maximum cement content. It means that there was not enough water for all the cement particles to get hydrated and a part of cement was just acting as filler. At WD, there is optimum water for the cement grains hydration so the maximum heat is liberated at 13 hours. It means that if mixing water is equal to the water demand, all cement particles are able to hydrate and cement is used efficiently. So it can be said that if in HP SCP systems the mixing water is less than the WD, setting would be delayed due to excessive SP content and all cement particles are not hydrated. When mixing water is more than the systems WD, the peaks are delayed (compared with that at WD) accompanied by lesser heat generation. It is due to the fact that as mixing water content is increased, the amount of cement becomes lesser. It implies that it is both the amount of cement as well as that of water which determines the heat liberated with the optimum conditions occurring at WD.

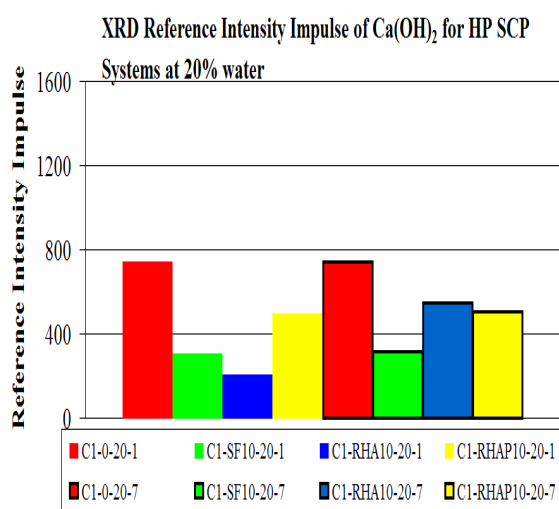


**Fig. 4.9 (a)** C1-RHA10-at Four Mixing Waters **Fig. 4.9 (b)** Effect of Admixtures in CEM I

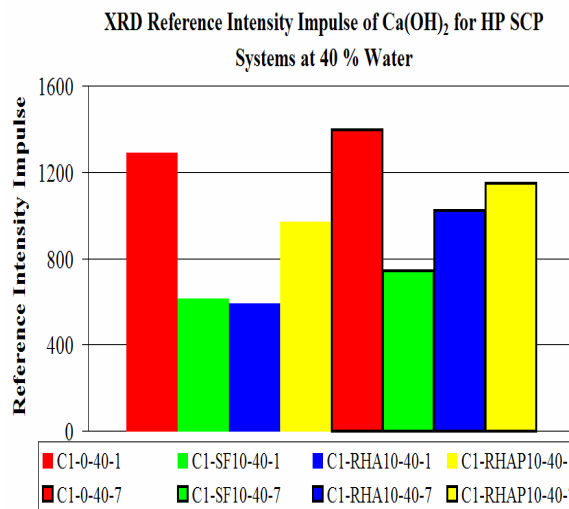
Fig 4.9 (b) shows typical calorimetry curves of plain plasticized cement and with 10% (by cement mass) RHA and SF at 40% mixing water content (more than WD of the system). The cement content with 10% RHA and SF both would be lesser than that in the neat cement paste system. It can be seen that at this mixing water, despite lower cement content, RHA and specially SF addition increases the heat generated. SF also shows reduced setting time than even neat cement paste at the same mixing water despite the dilution effect. Moreover if the maximum heat generated is looked upon as an indication of setting process, addition of SF hastens the setting process of this diluted HP SCP system. At this water content as the SP required for the target flow was comparatively small so RHA and plain cement showed almost overlapping calorimetric curves.

#### 4.1.7 XRD OF HP SCP SYSTEMS

Fig 4.10 presents the XRD reference intensity impulse for  $\text{Ca}(\text{OH})_2$  in various paste systems corresponding to  $2\theta$  value of  $34^\circ$  for  $\text{CuK}\alpha$  radiation within 4-70 degree sweep. The Diffractometer was Philips PW 3710 series. Fig 4.10(a) presents the results of XRD investigation of HP SCP systems at 20% mixing water at 1 and 7 days of age while fig 4.10(b) gives the data at 40% mixing water content (w.r.t cement mass) at the same ages.



**Fig. 4.10 (a)** XRD Results for  $\text{Ca}(\text{OH})_2$  in HP SCP Systems at 20% Mixing Water



**Fig. 4.10 (b)** XRD Results for  $\text{Ca}(\text{OH})_2$  in HP SCP Systems at 40% Mixing Water

The explanation of a typical bar shown above, say C1-SF10-20-1, should mean that this paste system is with CEM I with 10 % (of cement mass) SF at 20 % (of the cement mass) mixing water at the age of 1 day. It will be shown in later articles that  $\text{Ca}(\text{OH})_2$  content and the reference intensity impulse are linearly related. It can be seen from Fig 4.10(a) and (b) that  $\text{Ca}(\text{OH})_2$  content increases with increase in mixing water content for plain cement pastes of similar ages. It also seems to increase slightly in its content with age (between 1 and 7 days) for a typical formulation. For SF, the increase is the minimum within first seven days showing its pozzolanic activity. Crystalline RHAP also does not show significant increase in the quantity of CH beyond 1 day of age at 20% water. In amorphous RHA, there appears to be an increase in CH content showing a rather late start of pozzolanic activity. Figures 15-17 of Annexure-A show the water absorption of SCP systems and figures 1-3 of Annexure-B show water absorption of SCM systems. At both the mixing water contents and at the age of one day, RHA formulation shows less CH than SF formulation. It is not due to its higher pozzolanic activity but it can be attributed to the delayed setting of RHA formulation compared with similar SF formulation. In general  $\text{Ca}(\text{OH})_2$  content gets reduced compared with neat cement pastes, by the addition of mineral admixtures (SF, RHA and RHAP) between first seven days and beyond. The maximum reduction is brought about by the SF followed by amorphous RHA. In general the crystalline RHA gives the least reduction in  $\text{Ca}(\text{OH})_2$  content, at later ages, in comparison to other two mineral admixtures. This is due to its least pozzolanic activity amongst the three mineral admixtures used and is reflected in 28 days strength results. This point will further help in the strength quantification and explanation of other experimental results. The maximum  $\text{Ca}(\text{OH})_2$  content is obtained for the neat pastes of Portland cement. It is generally believed, though not always true, that more is the  $\text{Ca}(\text{OH})_2$  content, lesser will be the strength of Portland cement based composites because of lower strength of  $\text{Ca}(\text{OH})_2$ . This is the reason that only those mineral admixtures increase strength which “eat-up” the  $\text{Ca}(\text{OH})_2$  by forming additional C-S-H and through pore refinement effect. As can be seen in SEM studies, the CH crystals form in the pores or empty spaces only. With an increase in mixing water content the empty pore spaces become increasingly available. The reduction of  $\text{Ca}(\text{OH})_2$  in the pore solution increases the chances of corrosion which should always be weighed against the benefits due to pore

refinement of pozzolanic powders. These benefits, however, generally outclass the disadvantages brought about by reduction in alkali content. From pH studies it was established that RHA increased the alkalinity due to the availability of its alkaline ions like CaO, MgO, Na<sub>2</sub>O and K<sub>2</sub>O in the solution. Three mechanisms are active simultaneously when pozzolanic additions to cement are made and these include reduction in CH content by a reaction of SiO<sub>2</sub> of pozzolan with it, increase in alkalinity of solution due to alkali ions of RHA and the pore refinement. The overall result of these three effects is that the chance of reinforcement corrosion in case of RHA and SF is not on cards and many researchers have proved this point. It should be remembered that at 40% mixing water content, the cement content will be less than that at 20% water for such RHA HP SCP systems (1366 kg/m<sup>3</sup> at 20% mixing water and 1009 kg/m<sup>3</sup> at 40% mixing water for CEM I 42.5R). When the mixing water is 20%, which is less than the WD of the plain cement, the insufficient amount of water is available in the mix and all cement grains do not get hydrated while at 40% mixing water, more water (than the actual demand of the system) is available in the mix so that all cement grains are able to fully get hydrated resulting in higher Ca(OH)<sub>2</sub> content despite low cement content. Presence of more quantity of CH in 40% mixing water than at 20% water for a given mix and age proves that it is the available space, water content and the cement content which are important for CH crystal growth. This further explains the expansion of plain cement pastes at 40% mixing water under covered conditions and is described in the next article.

#### 4.1.8 Shrinkage Response of HP SCP Systems

##### 4.1.8.1 Effects of SP on Shrinkage of HP SCP Systems

In fresh state, the addition of SP increases the flow at given mixing water content or reduces the mixing water content at increased SP content. In HPC/SCC the most important parameter after the flow is early volume stability which has been studied for typical HP SCP systems to show the effect of SP in covered and uncovered conditions. In fluidized concrete, the SP facilitates escape of entrapped air. Typically 1-3% air is lost out of a total of 5-8% of total entrained air. Setting is also retarded due to high SP dose [20] and the extent of retardation depends on the type and dosage of SP. SP gives enhanced effect when added a few minutes after the mixing water has been added to the concrete [20].

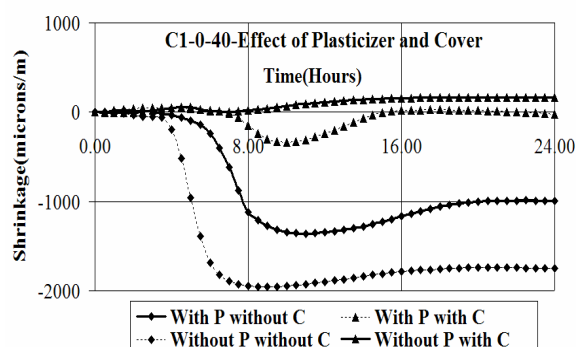


Fig. 4.11 Effect of Plasticizer in Uncovered Conditions for Two Cements

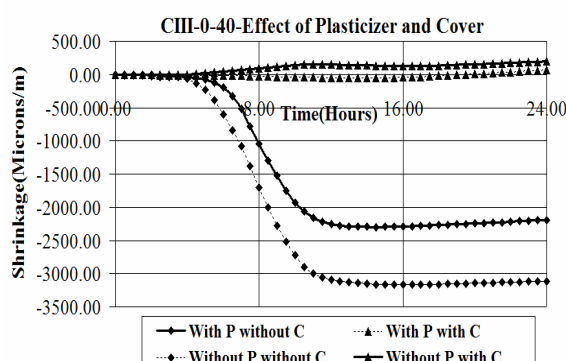


Fig. 4.12 Effect of Plasticizer in Covered Conditions for Two Cements



By doing so SP would be adsorbed to a lesser extent on aluminate phases which might have already undergone some hydration and there will be enough SP in the solution to promote dispersion of the silicate phases and to lower the viscosity of the system. Figures 4.11 and 4.12 demonstrate the effect of superplasticizer on the shrinkage response of HP SCP systems in two exposure conditions. Literature cites that compared with the control mortars, the hardened HRWRA mortars (with dosages 0.3 and 0.75%) had lower overall porosity, higher compressive strength due to improvement in the interfacial zone relative to the corresponding bulk paste [21]. Effect of SP on the early volume stability of two cements at 40% mixing water in covered/sealed and uncovered/unsealed conditions is illustrated in Figs 4.11 and 4.12.

The SP added was of the powder type Melflux 1641 F manufactured by Deggusa Germany. The positive effect on early volume stability in terms of shrinkage reduction is shown by both the cements in uncovered conditions.

In Fig 4.11 shrinkage response of CEM I paste containing 40% water w.r.t cement mass is shown. In the legend, “with P with C” should be read as “with plasticizer and with cover”. The effect of plasticizer and cover can be noted by comparing the relevant curves.

It can be seen that addition of plasticizer reduces early shrinkage in uncovered condition for both cements possibly due to decrease in surface tension by SP. It is stated elsewhere that in fluidized cementitious systems SP facilitates easy escape of 1-3% of entrapped air as mentioned earlier. In covered condition HP SCP system without SP shows greater expansion than that with SP. Covering the plasticized paste produces less shrinkage and sometimes a slight expansion at the end of 24 hours measurement. A little shrinkage recovery is clearly seen in all curves after about 8 hours possibly due to three parallel operating mechanisms consisting of 100% relative humidity, thermal expansion due to heat of hydration and the formation of expansive species such as  $\text{Ca(OH)}_2$  and ettringite crystals with more shrinkage occurring later at a slower rate. Same comments are offered for CEM III formulations shown in Fig. 4.12 with the difference that it showed more shrinkage in uncovered condition and more expansion in covered conditions (due to the presence of higher effective free water) and the shrinkage recovery at approximately 8 hours is not visible due to its lower clinker content/ heat of hydration. Literature suggests surface area of cement, total alkalis,  $\text{C}_3\text{A}$  and  $\text{SO}_3$  contents of cement as major sources of shrinkage. This explanation is contained in the literature which can be consulted for citations of points mentioned here [114].

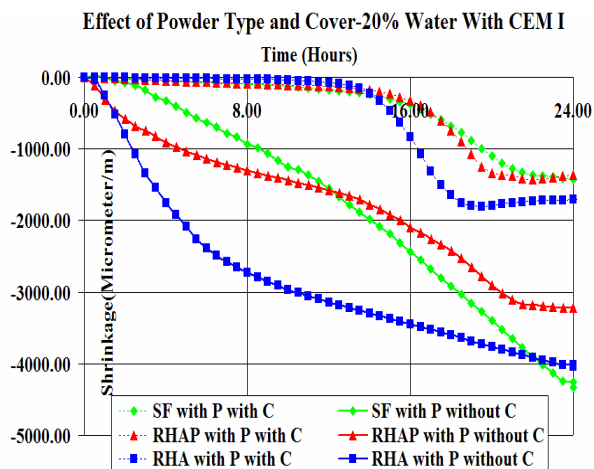
#### 4.1.8.2 Effects of SRM's

A slight shrinkage recovery was observed during 8.37-10.32 hours after mixing with water in a typical C1-0-20 system in uncovered conditions (Fig. not shown here). The same thing happened at 40% mixing water which has already been explained while describing the effects of SP addition. While for covered condition this time range was 6.27-8 hours (Fig. 4.11). This can also be attributed to the same internal crystal growth and thermal effects. This onset of shrinkage recovery (internal swelling due to  $\text{Ca(OH)}_2$  crystal growth and thermal effects) seems to depend on the available amount of mixing water. CEM III in uncovered/unsealed conditions gives higher total early shrinkage, because of higher effective free water and higher evaporating water gradient due to finer pore structure than CEM I paste but when covered this shrinkage is arrested to a great extent and the formulations end up giving a slight expansion at 24 hours of measurement. Again the 100% RH and small amounts of  $\text{Ca(OH)}_2$  crystals are believed to be the reasons. It was also found that for CEM I and CEM III pastes at target flow levels achieved by

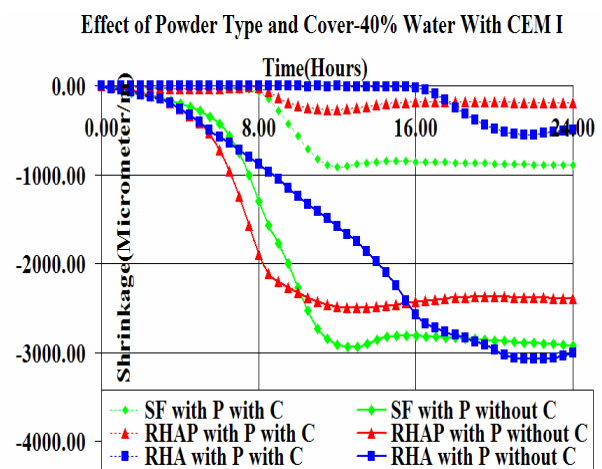


plasticizer, the first 24 hour shrinkage increases with the inclusion of both SF and RHA in uncovered cement pastes, possibly due to consumption of water by those mineral admixtures. However, if the mixing water content was more than the water demand of the system then their inclusion decreased the first 24 hours linear shrinkage possibly due to dilution of cement content.

In Fig 4.13 three types of SRM's have been used with CEM I 42.5R at 20% mixing water content. They had 200% flow (30 cm mini cone spread) obtained by using powder type superplasticizers. Because of very low mixing water, a very high amount of SP was used for flow target for formulations containing pozzolanic materials like amorphous RHA and SF. This resulted in an appreciable delay in setting time especially with RHA, and of SF also to some extent, which can be seen in the shrinkage curves of these powders in uncovered conditions. At this mixing water with CEM I, SF gives higher 24 hours early shrinkage than RHA possibly due to faster consumption of water which is simultaneously lost in evaporation. In covered condition almost all SRM's seem to have obtained setting though earlier than uncovered condition because the loss of water was prevented and this relatively increased availability of water which brought about the earlier setting. Crystalline RHAP gave lesser shrinkage compared with amorphous RHA in both covering conditions despite faster setting. It also had lesser SP content to achieve the same flow level. If the mixing water was more than the WD of the system (like 40%), both the rice husk ashes gave very reduced shrinkages in covered conditions compared with SF for such HP SCP systems as shown in Fig 4.14. Shrinkage values have been reduced (compared with Fig 4.13) due to dilution effect. It proves that it is not the amount of water alone but it is the amount of both cement and water that matters the most for increased shrinkages.

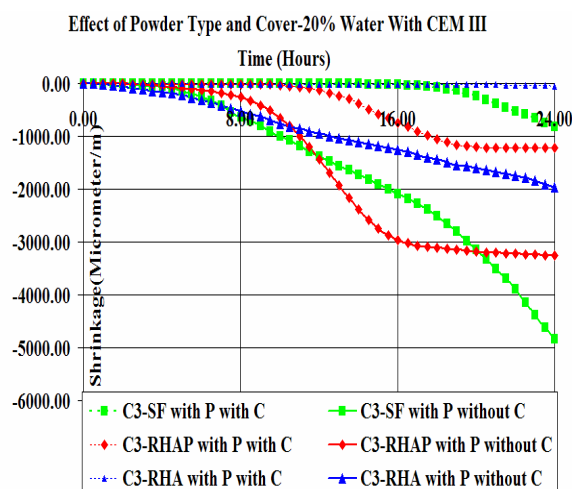


**Fig. 4.13** Effect of Powder Type and Cover with CEM I at 20% Mixing Water

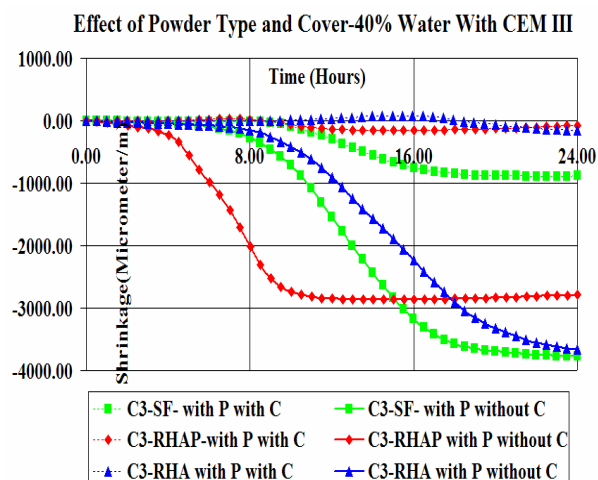


**Fig. 4.14** Effect of Powder Type and Cover with CEM I at 20% Mixing Water

It can be seen that all the SRM's obtained their setting in both exposure conditions which is obvious from their inflection points. In uncovered conditions, setting was achieved first by crystalline RHAP followed by SF and then RHA. Same sequence appears in covered conditions regarding onset of setting.



**Fig. 4.15 (a)** Effect of Powder Type and Cover with CEM III at 20% Mixing Water



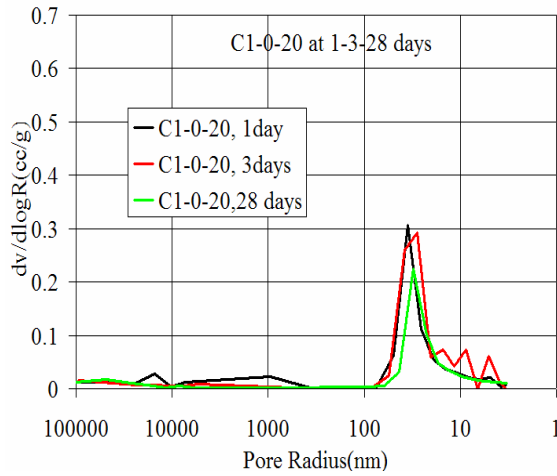
**Fig. 4.15 (b)** Effect of Powder Types and Cover with CEM III at 40% Mixing Water

In Fig 4.15 (a), it can be seen again that both RHA and SF do not show a clear setting behavior at this mixing water content with CEM III in both uncovered and covered conditions and therefore are understandable. It is due to the combined effect of very high SP dosages and CEM III itself being late setting due to lower (only 30%) cement clinker content. However crystalline RHAP was able to achieve setting in both exposure conditions. At 40% mixing water with CEM III (Fig 4.15(b) ), the ashes show a minimal shrinkage at the end of 24 hours of measurement in covered condition meaning that such materials can be utilized in situations where curing compounds would be applied to the placed cementitious systems. In uncovered conditions crystalline RHAP sets faster and shows lesser shrinkage than amorphous RHA and SF containing paste systems.

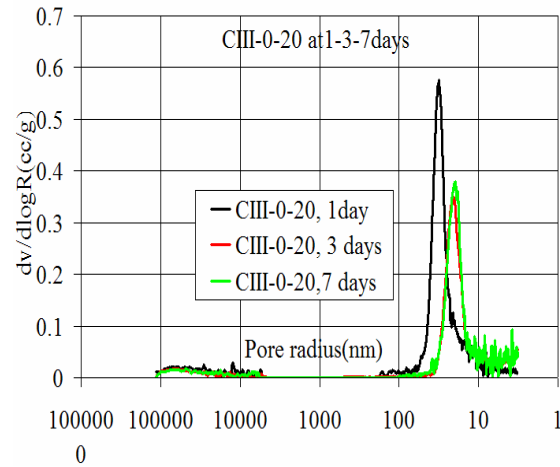
Swelling (or reduction in shrinkage) can be expected in the cases of fully saturated air (as in covered/sealed conditions) [114] and availability of a reasonable amount of water. Accumulation or slow dissipation of generated heat coupled with internal crystal growth are the factors responsible for this phenomenon. All these suggested mechanisms may be operative in parallel. The 24 hour value of shrinkage depends on evaporation rate or specimen surface exposure conditions, type of cement and its contents, mixing water, admixtures contents, temperature, relative humidity and internal crystals growth. Free linear shrinkage studies are useful for the qualitative assessment of various SRM's. Controlling or minimizing the shrinkage at the paste level may ensure satisfactory performance of resulting mortars and concretes. As the studied pastes had a  $w/c < 0.45$ , considerable self-desiccation resulting in chemical shrinkage is expected particularly for uncovered specimens [86].

#### 4.1.9 MIP of HP SCP Systems

The literature reports that the porosity in the interfacial zone of RHA composite would be higher than that of SF composite [68] and this study confirms it indirectly in terms of maximum pore diameter obtained from the partial porosimetry curves.

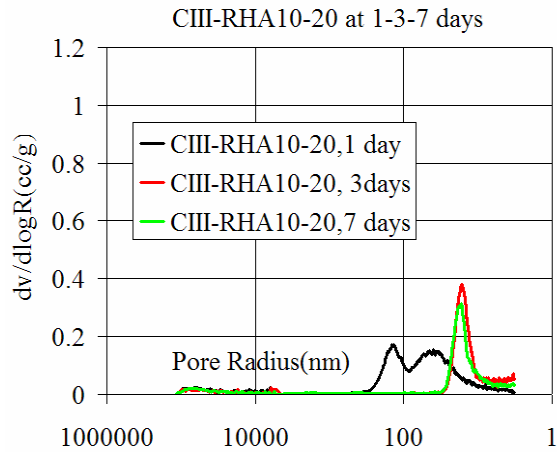


**Fig. 4.16 (a)** MIP Results of CEM I Paste With 20 % Mixing Water at Three Ages

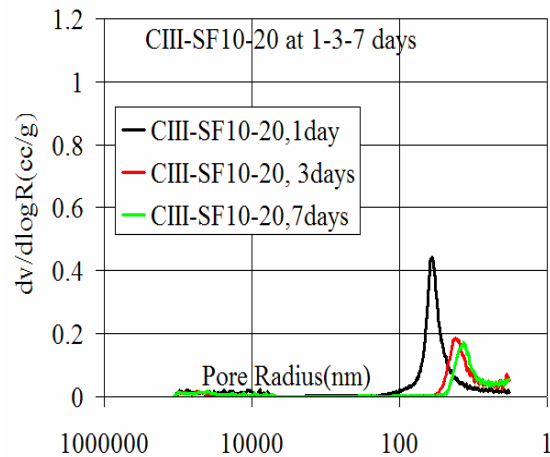


**Fig. 4.16 (b)** MIP Results of CEM III Paste With 20% Mixing Water at Three Ages

Fig 4.16 (a) and (b) show the MIP results of neat cement pastes of CEM I and CEM III respectively at 20 % mixing water. A relatively higher intruded volume of mercury for CEM III at 1 day age shows higher porosity due to delayed setting at this mixing water content. The pore sizes shift to the narrow end of the range with age. It can be seen from Fig. 4.16(a) that beyond 3 days of age there is very little improvement in the pore structure refinement. Therefore with the remaining samples mostly MIP study was done upto 7 days of age.



**Fig. 4.17 (a)** MIP Results of CEM III With 10% RHA and 20 % Mixing Water at Three Ages



**Fig. 4.17 (b)** MIP Results of CEM III with 10% SF and 20% Mixing Water at Three Ages

Fig 4.17 (a) shows that RHA gives a bi-modal MIP intrusion curve at the age of 1 day. This is due to a much delayed hydration of this type of HP SCP system which needs a high SP dose to meet target flow at this mixing water. A bi-modal curve can be interpreted as of having two pore groups of different sizes. However after the start of water curing at the age of 1 day, the curve shape becomes normal and a significant pore refinement takes place between the age of one and three days. There is not much of improvement in pore structure refinement beyond three or at the

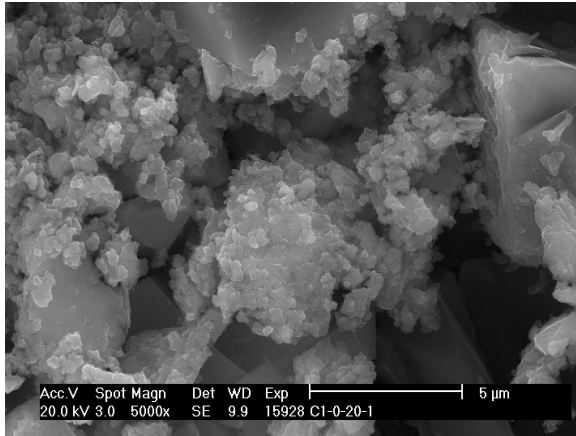
most 7 days of age. Fig 4.17(b) shows partial curves at three ages with SF formulations. Though pore size is higher at 1 day but it is uniformly distributed throughout the matrix as could be evidenced from strength results. However between 1 to 7 days of age, SF improves the pore refinement slightly better than RHA. At 1 day and due to faster setting of SF paste compared with RHA paste, high intruded mercury volume can be attributed to morphology of SF and to well connected finer pore system. Figs 1 and 2 in Annexure-A give MIP results for neat CEM III paste at 40 and 60% water wherein a pore refinement effect is also clearly visible.

Fig 3 and 4 in the same annexure clearly show that inclusion of RHA and SF in cement paste shifts the pore size towards the narrow end of range. This is called “pore refinement effect” and is responsible for higher strength and improved durability characteristics obtained by using these pozzolanic SRM's.

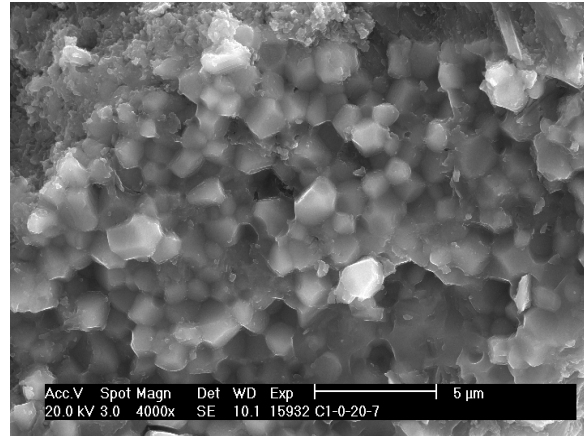
Although pore refinement effect due to pozzolanic SRM's can also be seen in Figs 5 and 6 of Annexure-A, however, the pore sizes are comparatively bigger than those of Figs 3 and 4 of the same annexure showing that an increase in the mixing water content produces bigger pore sizes which result in high fluid transport and a compromised durability of the resulting cementitious system. Moreover in RHA systems, more mercury penetrates indicating a sort of continuous but finer pore structure. This continuous porosity gives higher water absorptions shown in Figs 15-17 of Annexure-A. At higher mixing waters and beyond 1 day age, SF shows lesser intruded volume showing either comparatively less number of pores, or pores with lesser maximum size or both compared to RHA. Table 11 of Annexure-A gives the maximum pore radius obtained from partial diagrams for various HP SCP systems.

#### 4.1.10 HP SCP Microstructure by SEM

Selected specimens were studied by SEM technique to have a closer look at the microstructure and crystal growth which could lead to some explanations on shrinkage and strength etc. During shrinkage studies on neat cement pastes at 40% mixing water; some expansion was noted in the covered conditions during 24 hours measurement. The reason was looked into by SEM. The machine used was FEI XL 30 Environmental Scanning Electron Microscope with Field Emission Gun (ESEM FEG). It was capable of giving spot chemical analysis with the help of EDAX (energy dispersive X-ray analyzer). This machine could be used in two modes including high vacuum and ESEM. Three signals are possible and include SE (secondary electrons), BSE (back scattered electrons) and EDAX (Energy dispersive X-ray analysis). CI-0-20 HP SCP system was seen for its microstructure at the age of one and seven days and is shown in Figures 4.18 and 4.19 respectively. At the age of one day large crystals of CH can be clearly seen with a rather open microstructure as all cement particles would not hydrate at this mixing water content. These CH crystals are believed to be the source of expansion observed in the cementitious systems. At the age of seven days the microstructure improves and crystal size is changed as shown in Fig 4.19.



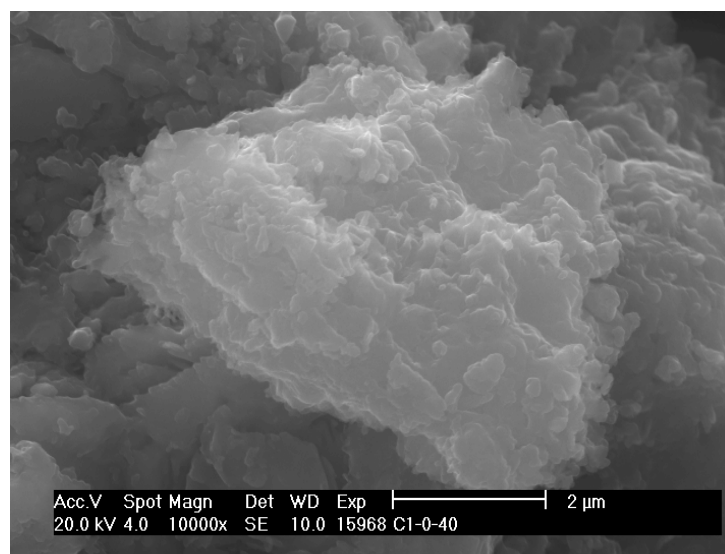
**Fig. 4.18** SEM for C1-0-20 HP SCP System at The Age of 1 Day



**Fig. 4.19** SEM for C1-0-20 HP SCP System at The Age of 7 Days

During the first 24 hours, the specimens were placed in moist air with relative humidity of 90%+. After that water curing was done till the test age in SSD condition. Thereafter these were oven dried at 105°C for 24 hours before making samples for SEM investigations. Significant  $\text{Ca(OH)}_2$  is expected to build-up during first 24 hours.

In neat cement pastes substantial amounts of  $\text{Ca(OH)}_2$  are formed during the initial hours after mixing and the formation rate continues upto seven days and even beyond at a relatively decreasing rate. In the above figures well defined crystals of  $\text{Ca(OH)}_2$  are visible in the neat HP SCP system. At different locations of a sample, surface morphology has been different. Fig 4.20 shows neat cement paste at 40% mixing water content at 1 day of age. Large  $\text{Ca(OH)}_2$  crystals are seen. These crystals reduce shrinkage in uncovered sample while in covered sample they produce expansion in the presence of other favorable conditions. It is clear that in comparison to 20% mixing water, more calcium hydroxide crystals grow in empty pore spaces, originally occupied by water, at 40% mixing water. The amount and size of  $\text{Ca(OH)}_2$  crystals heavily depends upon the amount of mixing water content and the empty space available.



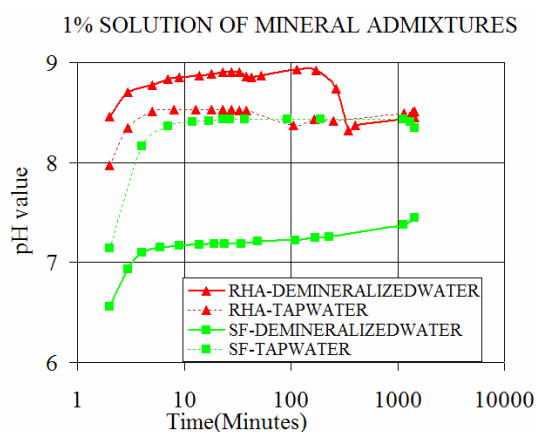
**Fig 4.20** SEM for C1-0-40 HP SCP System at the Age of 24 Hours



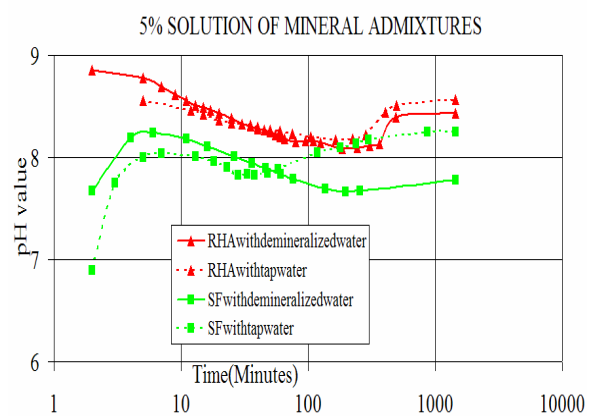
Therefore all cement particles have an equal chance of getting required water for hydration especially in the presence of SP at 40% mixing water. This increases the  $\text{Ca(OH)}_2$  content. More SEM details of paste systems containing pozzolanic powders showing the morphology and microstructure are shown in Figs 7-14 of Annexure-A which are in line with these statements. In Figs 7 and 8 (of Annexure-A), crystal growth at 20% water at 7 days is visible while at 1 day hydration progress is very slow at this water due to very high SP content. In Figures 9 and 10(of Annexure-A) neat pastes at 40% water at the ages of 1 and 7 days are shown. Due to adequate water, a different structure is seen with different morphology. In Figs 11 and 12 (of Annexure-A), RHA formulations at 20% water content are shown at the age of 1 day and 7 days respectively. These show CH and possibly ettringite crystals at some spots of the sample. Figures 13 and 14 of the same Annexure are for SF formulations at the similar mixing water content. A relatively denser microstructure with different type of crystal growth and morphology is seen.

#### 4.1.11 pH Measurement of Pozzolanic SRM Solutions

Before using SF and RHA in the cementitious systems, the changes brought about by them in the solution in terms of pH should be known. Therefore pH measurements were carried out for SF and RHA mineral solutions with demineralized and tap water having initial pH of 6.26 and 8.29 respectively. One minute of manual stirring of water and pozzolanic SRM's was done in an open glass cylinder before starting a 24 hours of pH monitoring with the help of Mettler Toledo-MP 220 pH meter without continuous agitation and in an laboratory environment with possible environment related  $\text{CO}_2$  changes in order to approximate the mixing conditions at site. Literature [39] contains similar measurements but in a closed environment and with continuous stirring. Such conditions are difficult to be realized in actual constructions where concrete using SF/RHA would need placement soon after mixing. The measurements showed that SF slightly reduced pH of the tap water while RHA marginally increased it at the end of 24 hour measurement.



**Fig. 4.21 (a)** Variation of pH of Pozzolanic Mineral Solution at 1% Concentration



**Fig. 4.21 (b)** Variation of pH of Pozzolanic Mineral Solution at 5% Concentration

Before the start of measurement, the pH meter was calibrated against three standard solutions having pH values of 4.01, 6.86 and 9.18.

Readings were taken till late evenings during these experiments and then early mornings next day. RHA/SF was seen settled at the bottom towards the end of measurements. The tap water



supplied in Freiberg has a pH value in the range of 8.2-8.5. The tap water pH was measured at 8.29 while that of demineralized water was 6.26. This simple test would give an idea about the alkalinity or otherwise imparted by the pozzolanic powders used in this investigation. Fig 4.21 (a) and (b) give pH variations of pozzolanic SRM solution at two different concentrations. In Fig 4.21(a) RHA solution with demineralized water gives higher pH value during first 3-4 hours compared with tap water solution and the trend slightly changes at the end of 24 hours of measurement. For Fig 4.21(b) same comments are offered to RHA solution while SF solution showed a reversed trend with tap water with pH being higher at the end of 24 hours measurement and like that of RHA solution. Generally speaking, RHA increases the pH of both tap and demineralized water w.r.t their starting values and the increase being more pronounced for the latter one. This is due to the presence of alkali ions of CaO, MgO, Na<sub>2</sub>O and K<sub>2</sub>O in RHA. This helps offset the decrease in pH value of the pore solution of cementitious systems due to pozzolanic reaction between silica of RHA and calcium hydroxide. SF also increases pH of both waters but to a lesser extent than RHA. RHA provided higher pH than SF solutions. Considering this point and the pore refinement effect as visible in MIP results, it looks possible that ASR would get reduced with these pozzolanic SRM's as reported in the literature [82, 83]. Increase of initial solution concentration does not seem to change the final results significantly. At 5% concentration of SF solution with tap water slightly reduces the pH when compared with starting value.

#### 4.1.12 Laboratory Investigations of Rheology of RHA Paste

It became obvious that RHA mixes had high internal friction and high viscosity as observed during mixing of HP SCP/SCM systems in Hobart type mixer. It was therefore decided to make a test on HP SCP systems incorporating RHA using Haake RS Rheo-stress Rheometer with serrated parallel plates PP 35 Ti with 1 mm gap. Samples were prepared using powder type PCE SP for giving the target flow level of 200% or 30 cm spread on Hagermann's mini slump cone. The total mixing time was 4 minutes. Yield point measurement could be made from deformation-shear stress response on a log-log scale (Fig 4.22 b). The time or flow curve would generally measure the viscosity as a function of time while shear rate is kept constant (Fig. 4.22a). The cement used was Schwenk CEM I 42.5R. Some of the results are shown in fig 4.22.

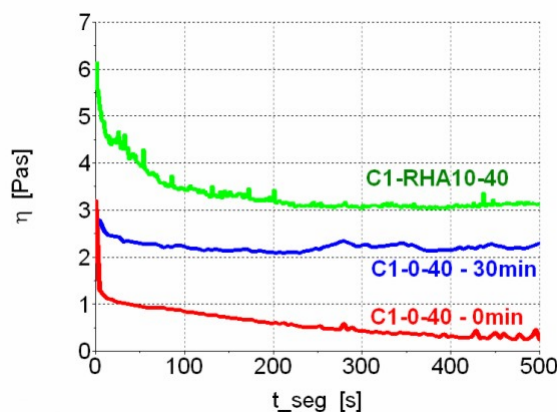


Fig. 4.22 (a) Viscosity-Time Response of Cement Paste With and Without RHA

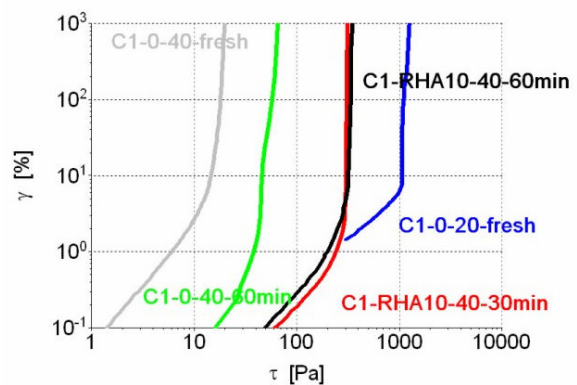


Fig. 4.22 (b) Shear Rate-Viscosity Response of Cement Paste With and Without RHA

By adding 10% RHA (w.r.t cement mass), yield stress increased by about 20 times. Moreover RHA pastes measured at 30 and 60 minutes show a very little increase in yield stress and corresponding deformation (fig. 4.22(b)). This is due to the fact that RHA increases the setting process very drastically in self-compacting cementitious systems.

Fig 4.22(a) shows viscosity-time response of cement paste with and without RHA. Addition of RHA by 10% of cement mass at 40% mixing water increases the viscosity by about 4-6 times although it had less cement content due to replacement. After about 300 seconds viscosity becomes almost constant. A neat cement paste at the same mixing water shows less viscosity although it has more cement in it. The increase in viscosity from fresh state to about 30 minutes later clearly shows the thixotropic behavior of cementitious systems.

Fig 4.22(b) shows shear rate-viscosity response of cement paste with and without RHA. Yield stress of C1-0-20 fresh cement paste seems to be around 1000 Pa and once it is activated, constant deformation at this rate takes place. Comparing this with C1-0-40 fresh paste response with an approximate yield stress of 10 Pa shows that by increasing the mixing water content from 20 to 40%, the yield stress of fresh cement paste decreases by about 100 times. However the deformation at which this yield stress occurs remains almost the same for two neat cement paste mixes.

## 4.2 TESTS ON HP SCM SYSTEMS

### 4.2.1 General

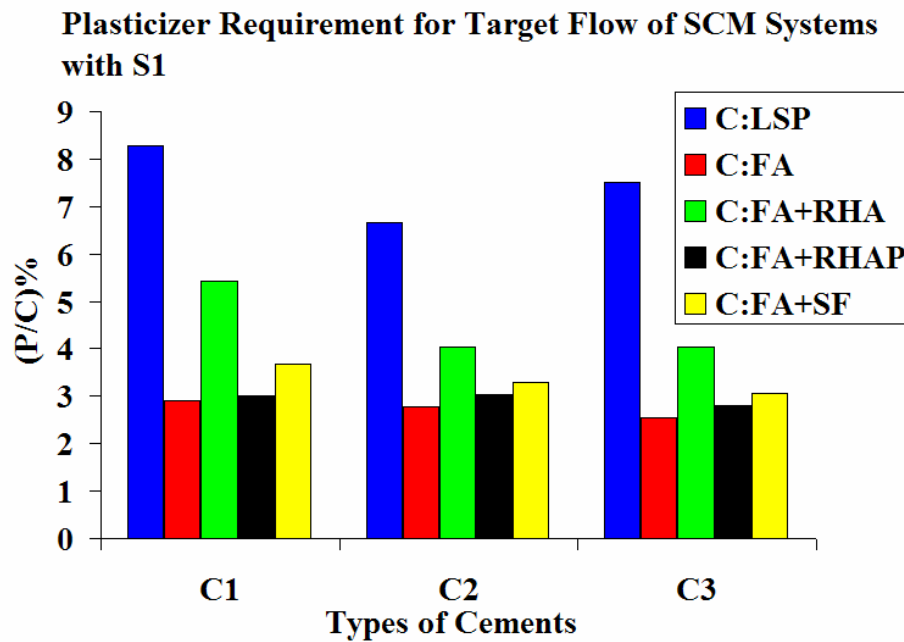
After studying HP SCP systems, the second phase of research continued on HP SCM systems. The following tests were performed on HP SCM systems and these would be taken up in the text that follows.

- Flow
- Strength
- XRD study
- Shrinkage response
- MIP study
- SEM study
- Thermal analysis

### 4.2.2 Flow and SP Requirements of HP SCM Systems

The flow target was fixed at  $31 \pm 2$  cm and was achieved by using Melflux 2500 L 30% SP. The aggregate grading is very important as it affects flow/strength and microstructure of HP SCM systems. Therefore the grading curves of the sands used in this study are shown in Fig 3.3. Sand S1 consisted of particles of 0-2 mm size fraction while blended sand S2 consisted of 80% 0-2 mm and 20% 2-4 mm size fraction of particles. Sand S1 (0-2 mm size) had a passing percent of about 75 at 1 mm sieve while S2 had about 60% passing at the same sieve. S1 looks to be better for stability of HP SCCS.

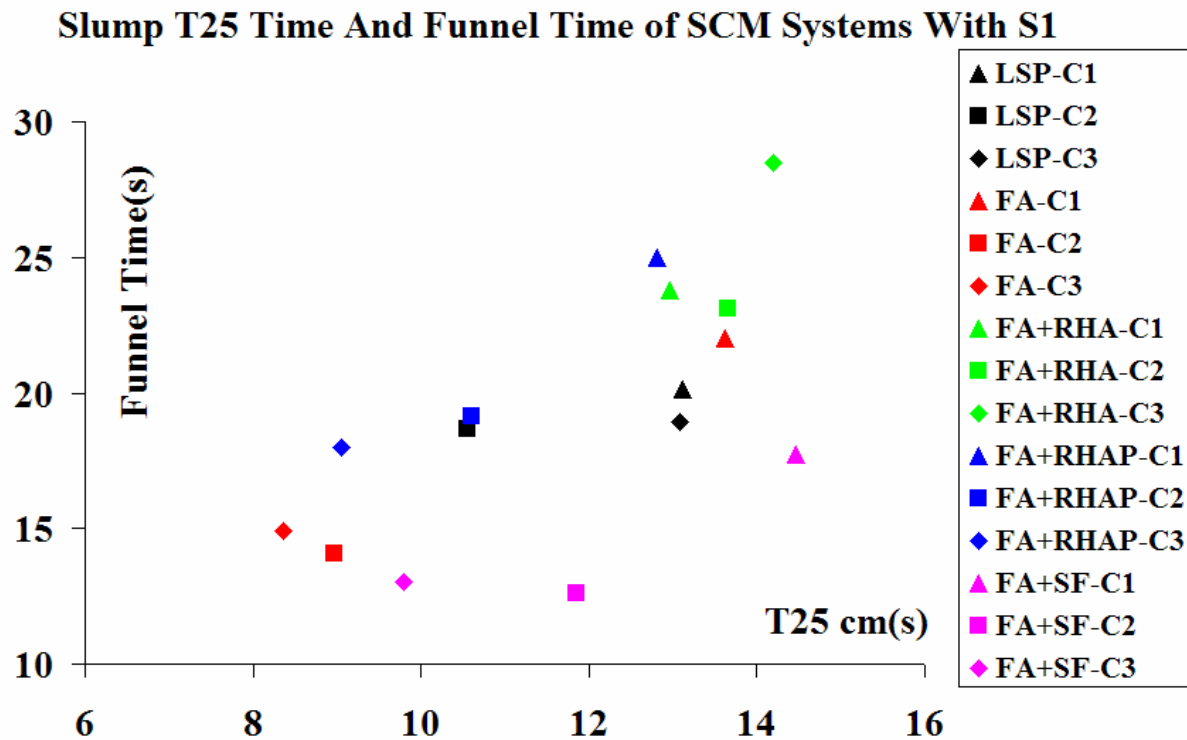
Five types of SRM's or their combinations were used in the study. It has already been mentioned that SP demand also depends on the size, shape, surface morphology and internal porosity of SRM particles. Fig 4.23 shows that FA requires minimum SP while LSP requires maximum SP for obtaining the required flow. Both SRM types have been used extensively by the researchers for reducing water demand of self-compacting cementitious systems in addition to improving their flow response. The particle size of LSP is very fine so it would even pack the spaces between cement grains but because of its highly abrasive, irregular and broken surface and high particle porosity it requires higher SP content to give a target flow. This highlights the importance of particle shape on the flow response and SP demand. From powder porosimetry it is evident that LSP had relatively higher maximum pore sizes. So SP content adsorbed into such pores is no longer available for cement particle dispersion. These two factors are responsible for high SP demand of LSP. Adding 20% RHA in FA increases the SP content because of irregular and internally porous particles of RHA. The amorphous RHA requires higher SP to give the same target flow than the crystalline one because amorphous RHA has higher internal porosity. Adding SF in FA (by 20% mass of FA) increases the SP demand due to numerous very fine particles of SF. These diagrams (figures 4.2, 4.3 and 4.23) seen together tell volumes about the importance of particle, shape and surface morphology regarding interpretation of flow of the HP SCM systems. Both LSP and FA+RHA systems have higher SP demand than the maximum specified dose by the manufacturer (which is 3 % of cement mass based on total SP mass and 1% of the mass of total solids content of SP). Despite requiring highest SP for the target flow, LSP formulations did not show very retarded setting.



**Fig. 4.23** Plasticizer Requirement for SCM Systems Using Various SRM's

It can be stated here that for given mix proportions, w/c and w/p ratio, the SP content needed for the target flow also depends on size, shape, morphology and internal porosity of SRM's.

Keeping in mind the particle shapes and SRM's porosimetry results, the relative viscosity in terms of V-funnel time and slump spread T25 cm time can be understood for different formulations. It is mentioned here that based on information and observation, the mixing regime is very important for reducing the SP content required for a given flow and for SP activation. Figure 4.24 is a plot between V-funnel time and T25 cm slump spread time. Both of these parameters are described to be a function of system's viscosity.

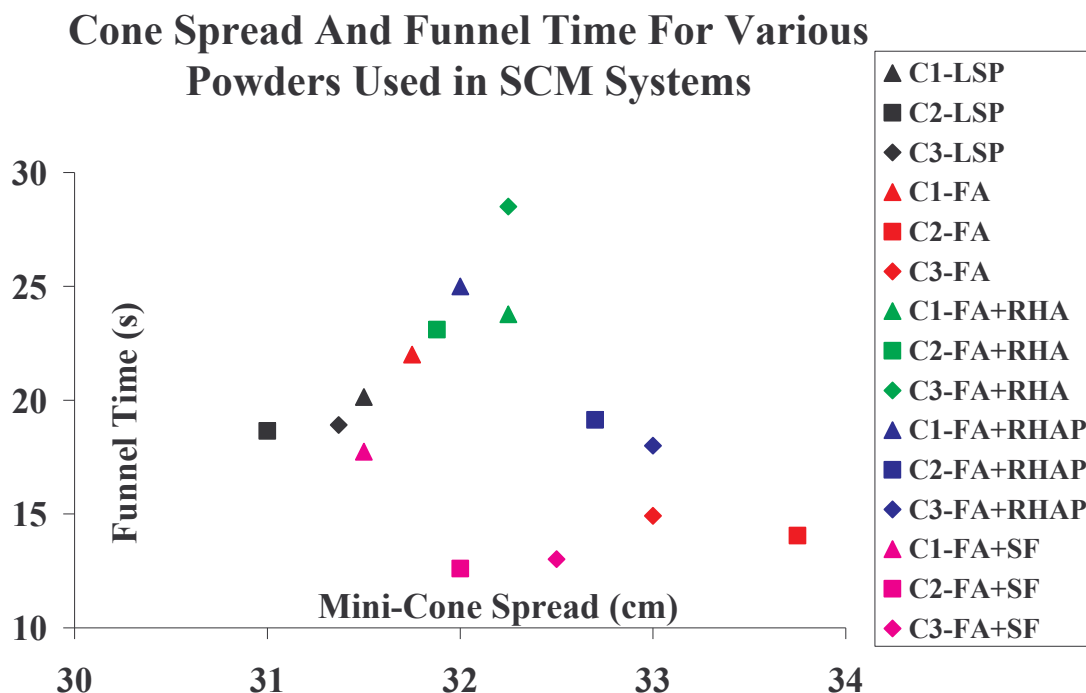


**Fig. 4.24** V-Funnel Time and T25 cm Time of The Mini-Slump Cone Relationship for SCM Systems

It can be seen in Fig 4.24 that.

- 80% FA+20% RHA combination generally gives the highest funnel time due to irregular RHA particles which have internal porosity as well.
- Generally CEM I formulations give higher viscosity (in terms of V-funnel time) than CEM II and CEM III formulations.
- CEM II formulations generally give the lowest funnel times
- FA+SF (80:20) formulation gives the lowest viscosity and yield stress. It is due to compatibility of their shapes and highly variable sizes which improve their internal packing and result in reduced internal friction during flow.

Fig 4.25 is a relation between V-funnel time and total spread of different HP SCM systems. It suggests that when SF is added in FA (by 20% mass of FA) yield stress decreases. This is because of the fact that both FA and SF have spherical particle shapes of varying sizes and they get easily adjusted while flowing through a constantly decreasing section. Moreover at equal flow target level, 20% SF in 80% FA reduces the total spread (compared with 100% FA) indicating an expected increase in yield stress when SF is added to FA.



**Fig. 4.25** Funnel Time and Mini Slump Cone Spread Relations of SCM Systems

FA alone gives maximum spread at the lowest SP content. Considering spread as a function of yield of the system, it can be stated that FA containing HP SCM system has the minimum yield stress while LSP shows the maximum yield stress (compared to FA system) despite the fact that its SP content is also the highest for the target flow. It can again be explained in the light of particle shape, surface morphology and the earlier comments about SRM's. Moreover, for the FA system, the effective water content, for given mixing water, becomes more which is also responsible for dropping the yield stress of the system in addition to its particle characteristics.

It is stated here that the selected target mini-cone spread could be considered high in the absence of viscosity agent as a spread of around 26-28 cm qualifies a mortar system to be classified as self-compacting. Because of low water-powder ratio, no separation of water at the rims of the mini-cone slump spreads (which is indicative of possible bleeding) was found. However upon testing the hardened specimens it was found that static stability of such systems after placement could have been slightly reduced. The surface settlement of freshly placed concrete reflects the degree of consolidation in fresh state that is associated with bleeding and air loss [148]. It is concluded that the flow of SCM system especially through continuously reducing sections depends very heavily on the shape, surface morphology and internal porosity of the SRM particles. Spherical particles of various sizes get easily adjusted during flow through such sections by just rolling over each other without much internal friction.



### 4.2.3 Strength of HP SCM Systems and Their Quantification

The strength results of these formulations had 95% statistical acceptance level. LSP is relatively inert [141] and it is proposed by the author to consider it as a base line material for simple quantification of strength increments obtained with other reactive powders. The structural and construction engineers are interested only in the strength enhancements associated with powders and not in the assessment of the contributions of physical and chemical factors towards the total strength of a system. For pozzolanic SRM's used with the three cements, the increase in compressive strength above base line LSP is the minimum for FA+ 20% crystalline RHAP system showing it to possess a little pozzolanic activity. A progressive increase in compressive strength of SCM containing ternary binder systems of FA+ RHA (amorphous) and FA+SF SRM's (80:20 by mass) is shown in Table 4.2.

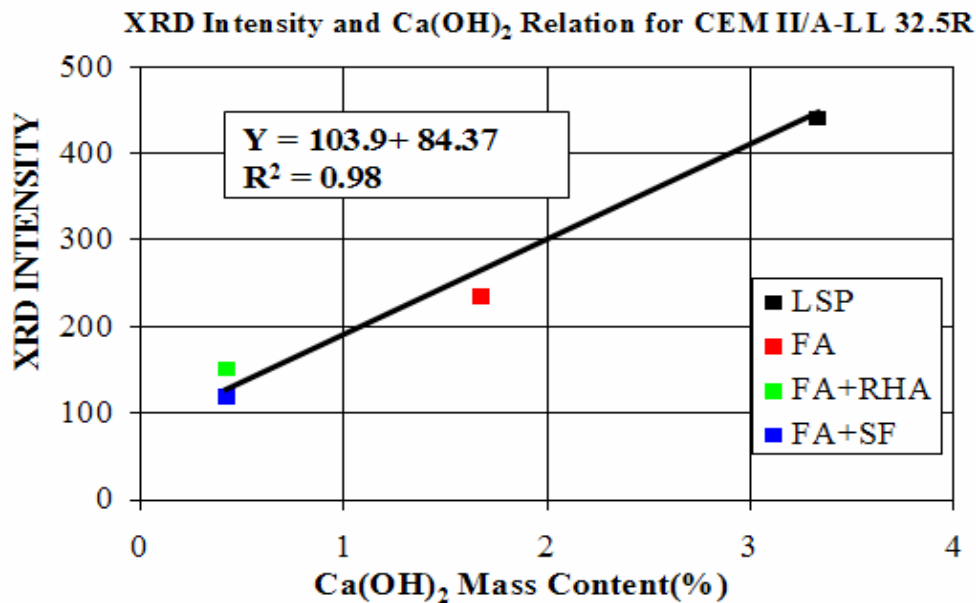
**Table 4.2: 28-Day Strength Quantification of Various SCM Systems With CEM I and CEM II. Values are in MPa.**

Powder	CEM I				CEM II			
	Flexure	Increase	Compre- ssion	Increase	Flexure	Increase	Compre- - ssion	Increase
<b>LSP</b>	9.95	Base line	77.14	Base line	8.92	Base line	65.67	Base line
<b>FA</b>	11.86	+1.91	117.38	<b>+40.24</b>	9.77	+0.85	100.9	<b>+35.23</b>
<b>80% FA+ 20%RHA</b>	12.69	+2.74	125.3	<b>+48.16</b>	13.09	+4.17	112.26	<b>+46.59</b>
<b>80%FA+20 %RHAP</b>	12.75	+2.8	115.3	<b>+38.16</b>	11.35	+2.43	97.8	<b>+32.13</b>
<b>80% FA+ 20%SF</b>	17.24	+7.29	131.22	<b>+54</b>	14.28	+5.36	119.68	<b>+54</b>

The cement content with CEM I and sand S1 was 541, 522, 521, 523 and 522 kg/m<sup>3</sup> respectively for HP SCM systems made with LSP, FA, FA+RHA, FA+RHAP and FA+SF. A slight difference in cement content is due to the differences in respective SRM densities. HP SCM's made with CEM III showed exactly similar trend in strength increase for respective formulations. The exact values are given in Table 5 of Annexure-B. The compressive strength increases were +36.86, +43.46, +31.46 and +39.36 for FA, FA+RHA, FA+RHAP and FA+SF formulations respectively. The data obtained with all cements and the powders used in HP SCM systems suggest the validity of proposed simple strength quantification procedure for HP SCM systems.

### 4.2.4 XRD and Thermal Analysis

These tests were carried out on the powdered specimens at a given age for a given formulation with a view to find some correlation. A good correlation between amount of CH as indicated by TG coupled with the theoretical formula and the XRD reference intensity peak for CH was established and is shown in Fig 4.26.

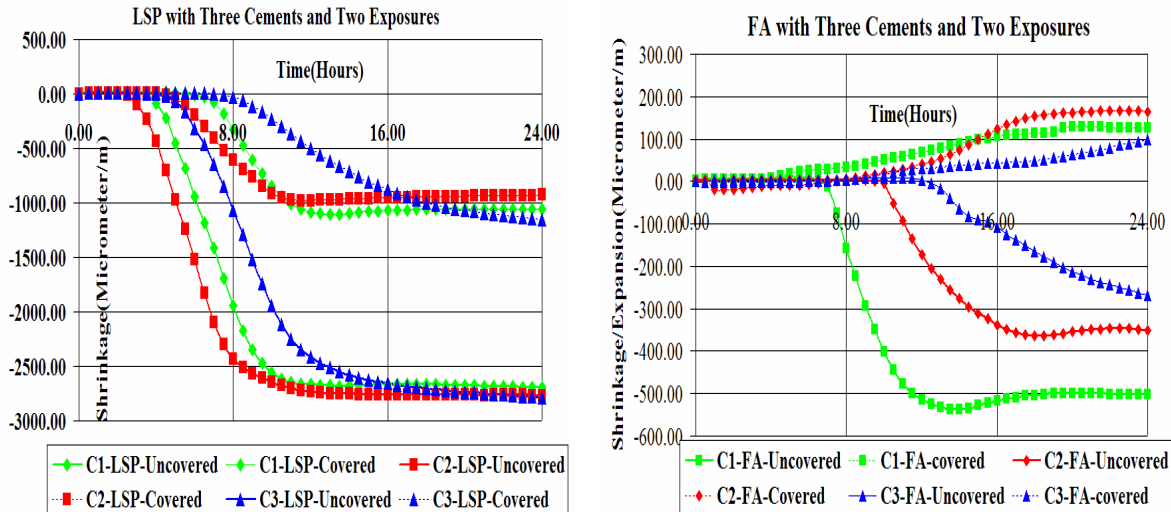


**Fig. 4.26** Relation Between XRD Reference Intensity and CH Quantity in HP SCM Systems Using Different SRM's

#### 4.2.5 Early Shrinkage Study of HP SCM Systems

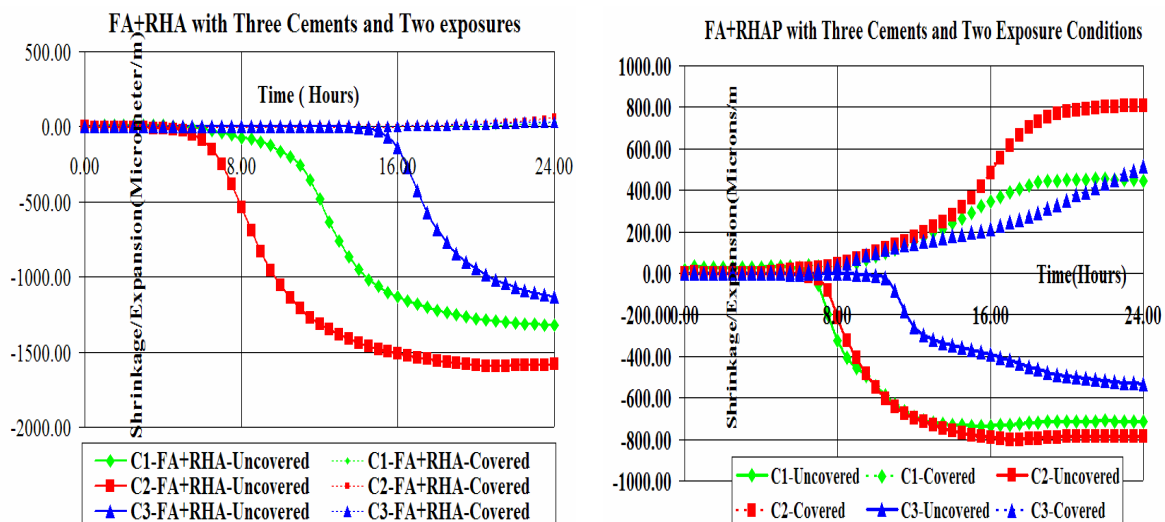
The shrinkage measuring equipment has already been shown in Figure 3.2 illustrating different exposure conditions. It should be noted that about 20% shrinkage was further reduced when the covering plastic sheet was further topped by an insulation sheet affixed in position with the help of adhesive tape to prevent condensation of water on the underside of the plastic sheet. This condensation takes place because of the fact that the temperature outside the plastic sheet is lower (Laboratory temperature) while temperature inside the sample in channel is higher. This temperature gradient between the sample and environment is responsible for higher shrinkage. If this temperature gradient is reduced shrinkage is also reduced (by about 20% in this study) or vice-versa. The expansion would also increase by the same amount in the relevant cases. Therefore after having established this factor subsequent shrinkage measurements were made in two exposure conditions only. Fig 4.27(left) shows the early linear shrinkage measurement of LSP with three cements and two exposures. LSP shows highest value of early shrinkage in uncovered conditions as well as in the covered conditions with the type of cement having very negligible effect on the 24 hour total shrinkage value. This highest shrinkage is attributed to the highest water uptake by LSP particles resulting in a relatively faster Vicat setting assumed in the vicinity of inflection points on these curves. Other parameters like highest SP content for the flow target, entrapping and releasing more air during self-compaction process might have some effect also. On the right of the same figure, is FA powder in SCM system. This system gives the lowest shrinkage with all cements in uncovered conditions possibly due to delayed setting. In covered conditions all cements gave expansion due to higher effective water content in the FA formulation encouraging the creation of expansive species including calcium hydroxide. Thermal effects might have also played some role. FA acts like calcium sink and removes calcium ions from pore solution. This depresses calcium ions concentration during the early hours and delays

the CH and CSH nucleation and the crystallization causing retardation in hydration [114]. The carbon content in FA would also have retarding effect.



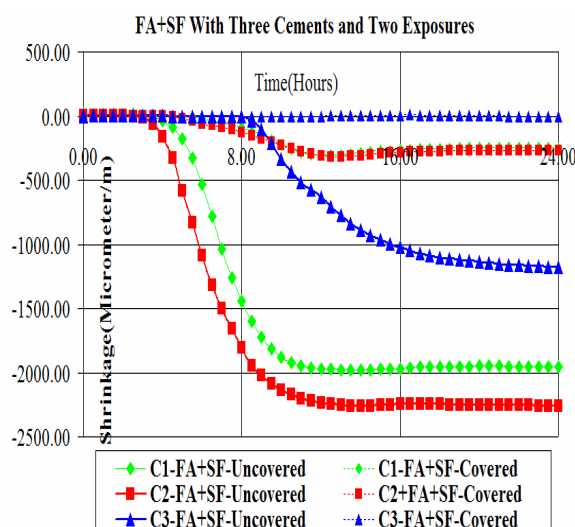
**Fig. 4.27(left).** LSP With Three Cements and Two Exposures and FA With Three Cements and Two Exposures **(right)**

In Fig 4.28(left) FA+RHA (20% by FA mass) formulation response is shown. Addition of 20% RHA in FA increases the shrinkage in uncovered condition (compared with FA system). Simultaneous reduction in CH crystals content due to its pozzolanic reaction with silica rich RHA could also be present in parallel with water uptake by RHA particles. In covered conditions expansion is increased (shrinkage is reduced due to water absorbed inside internal pores of RHA and thus lesser effective water remains available in the system). Growth of hydrates and thermal gradient could be other reasons.



**Fig. 4.28(left).** FA+RHA With Three Cements and Two Exposures and FA+RHAP With Three Cements and Two Exposures **(right)**

Fig 4.28 (right) is another interesting case with 20% crystalline RHAP in FA. This HP SCM system gave almost similar shrinkage and expansion in uncovered and covered conditions respectively with all cements. Crystalline RHAP further increases the effective water, for given mixing water content (due to its relatively lower WD and lower pozzolanic activity compared with RHA) coupled with typical delayed FA setting. In uncovered conditions it increases shrinkage slightly (compared with FA system) due to reduced FA and hence lesser delay in setting. In covered conditions 100% RH, thermal effects and expansive species are the reasons for expansion with all cements.



**Fig. 4.29** FA+SF with Three Cements and Two Exposures

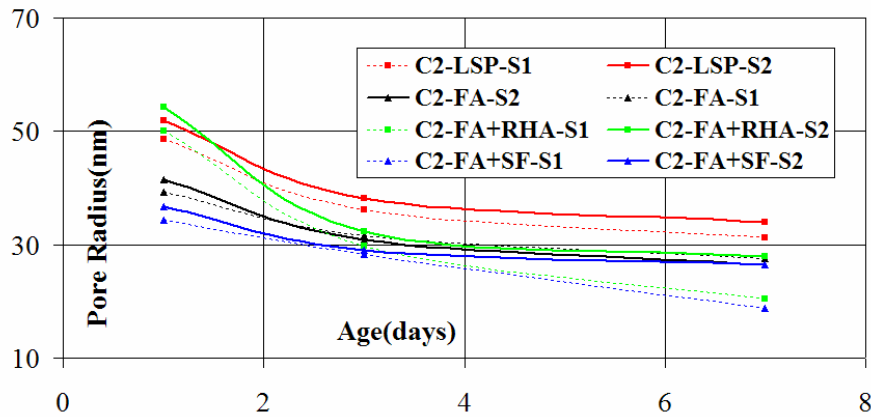
Fig 4.29 shows FA+SF (SF equal to 20% by mass of FA) formulation with increased uncovered shrinkage (than FA+RHA combination) due to faster setting and consumption of water during hydration. SF is known to speed up the setting/hydration process releasing heat faster (as evidenced during calorimetry) and hence giving higher early shrinkage. In covered conditions the evaporation is prevented so both CEM I and CEM II gave almost overlapping reduced shrinkage response while CEM III had lower clinker content and slower hydration/ less heat of hydration. It registered almost negligible volume change in this condition due to reasons stated earlier.

#### 4.2.6 Microstructure of HP SCM Systems by MIP

Fig 4.30 gives the effect of sand coarseness on the maximum pore size for a given formulation. Two sands S1 (100% 0-2 mm size) and S2 (blended sand-80% 0-2 mm and 20% 2-4 mm size) were used with CEM II and four SRM's (LSP, FA, FA+RHA and FA+SF). Porosimetry was done at 1, 3 and 7 days of age. In fact replacing 20% finer sand with a coarser one (keeping mixing water content constant) results in a slight increase of maximum pore size with all four powders as shown in Fig 4.30 and this is in line with literature [56]. This is due to the fact that the effective water content available in mix becomes higher for S2 compared with S1 resulting in bigger maximum pore size. FA+RHA (80:20 mass per cent) formulation shows biggest voids at the age of one day. It should be remembered that these two ashes have high

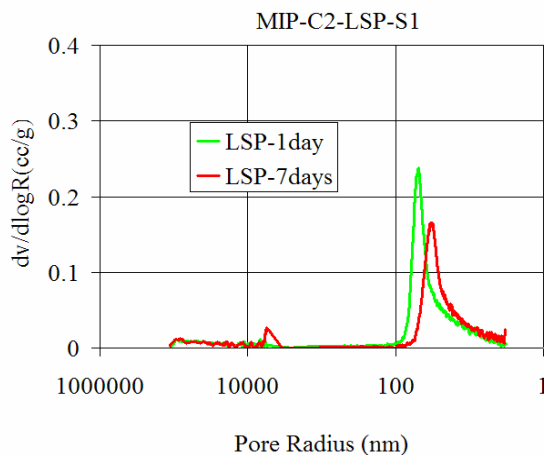
carbon contents which in the presence of high SP quantity retard the setting process to a significant degree resulting in high maximum pore sizes at this age. But at the age of 3 and 7 days, RHA and SF formulations gave the lowest pore sizes and were competitive. The effect of a slightly higher pore size with coarser sand S2 should be offset by higher modulus of the composite resulting in slight strength increase. LSP formulations with almost all cements gave higher maximum pore sizes while FA+SF gave the lowest. RHA and SF as FA blends seem to reduce porosity at the age 7 days and beyond and are comparable.

**Effect of Sand Type on Age-Pore Size Relation of HP SCCS With Various Powders**

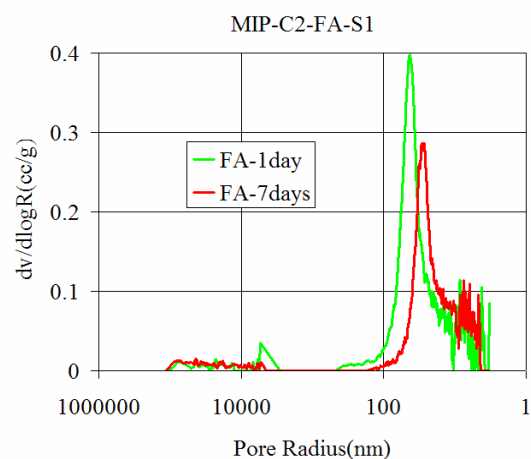


**Fig. 4.30** Effect of Sand Type on Age-Pore Size Relation of HP SCM With Various SRM's

Figures 4.31(a) to (e) give MIP results on LSP, FA, FA+RHA, FA+RHAP and FA+SF SRM's. It is obvious that the maximum pore size decreases with age and also with inclusion of RHA and SF in FA containing SCM's and the pore size distributions shift to smaller end of the pore range. RHA and SF were each taken as 20% of FA mass. Fig 4.31 shows some typical pore size and intruded mercury volume response of powders with CEM II. RHA and SF seem to reduce porosity at the age of 7 days and beyond.

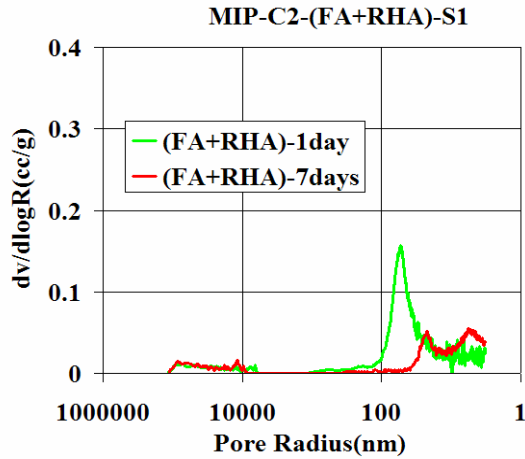


**Fig. 4.31 (a)** MIP Results of C2-LSP-S1 at Two Ages

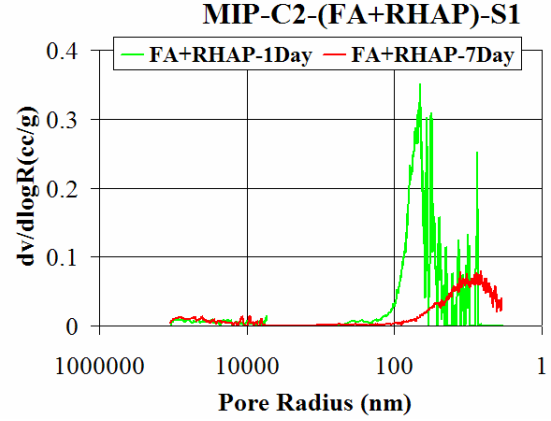


**Fig. 4.31 (b)** MIP Results of C2-FA -S1 at Two Ages

It is obvious that the maximum pore size decreases with age and also with inclusion of RHA and SF in FA containing SCM's and the pore size distributions shift towards smaller end of the pore range. Fig 4.31(a) shows higher maximum pore sizes for LSP (31.4 microns at 7 days) while for FA (Fig 4.31(b)) the maximum pore size is reduced (27 microns at 7 days) but the intruded volume is high possibly due to continuous pore system.

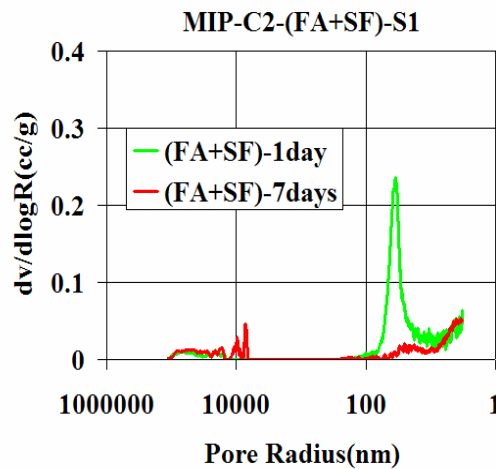


**Fig. 4.31 (c)** MIP Results of C2-FA+RHA-S1 at Two Ages



**Fig. 4.31 (d)** MIP Results of C2-FA+RHAP-S1 at Two Ages

In Fig 4.31 (c ) containing FA+RHA shows a bi-modal trend at the age of 7 days indicating two different pore group sizes, however intruded volume is less at one day age (compared with FA+SF SCM system) and maximum pore size is 5.24 microns at 7 day age. Fig 4.31(d) shows that by adding RHAP in FA the maximum pore size of 13.6 microns after 7 days of age is obtained. FA+SF formulation (Fig 4.31 e) shows 3.32 microns size at 7 days. Therefore pore refinement effect of all pozzolanic materials is obvious and it increases w.r.t the degree of pozzolanic activity of the powders and with age of course. This is responsible for the strength increases as shown in the Table 4.2. Table 4.3 gives the summary of results of maximum pore size for various SRM's used in HP SCM formulations with CEM II.



**Fig. 4.31 (e)** MIP Results of C2-FA+SF-S1 at Two Ages

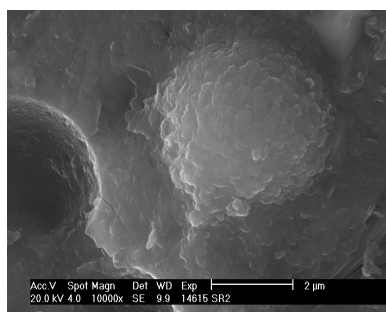


**Table 4.3** MIP Pore Size Characteristics of HP SCM Formulations with CEM II

Formulation of SCM	Max. Pore size (nm)		Range of Pore-Sizes (nm)	
	1 day	7 day	1 day	7 day
<b>LSP</b>	49.29	31.4	3.4-88	3.35-71
<b>FA</b>	42.87	27	3.36-267	4-99
<b>FA+RHAP</b>	46.33	13.6	6.97-318	3.54-81.8
<b>FA+RHA</b>	51.4	5.24	3.42-631	3.2-78
<b>FA+SF</b>	34.29	3.32	3.3-79	2-30

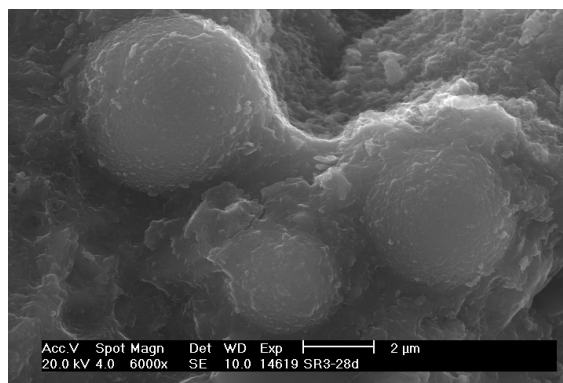
#### 4.2.7 Microstructure of HP SCM Systems by SEM

Fig 4.32 (a) presents a SEM picture of CII-FA-S1 SCM system at 28 days. Another picture representing the microstructure of this SCM system is also given in Fig. 4 of Annexure-B which shows developed CH crystals indicating delayed pozzolanic activity. Fig 4.32(a) is quite interesting and shows the perfect “nucleation” phenomena of FA particles very clearly and growth of products of hydration can be seen on a FA particle. On the left side of this picture, an air void is also noticeable.

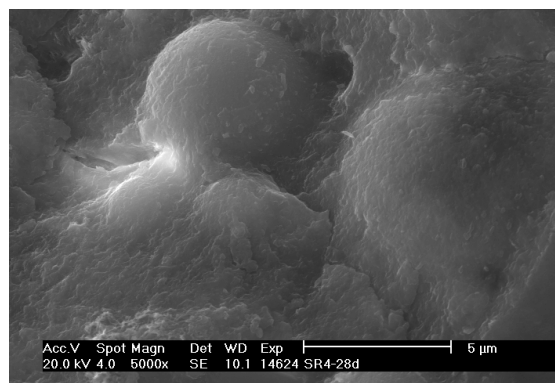


**Fig. 4.32 (a)** SEM of C2-FA-S1 at 28 Days Age  
Showing Perfect Nucleation on FA Particle

This phenomenon along with filler effect is responsible for improved strength of FA containing SCM systems. Closer to the particle is a hollow circular void which might have been created by entrapped air, a part of which subsequently escaped during self-compaction/hardening process. Fig 4.32(b) shows the SEM picture of FA+RHA SCM system made in CEM II at the age of 28 days. The microstructure is quite dense and the hydration products are not only covering the FA particles but they are also seen within the particles. This improves the strength further and results in micro-structure improvements. Fig 5 in Annexure-B also shows the growth of some ettringite crystals in an empty pore. Fig 4.32 (c) shows SEM of FA+SF SCM system made in CEM II. A great similarity in the microstructure and morphology of the surface with that of Fig 4.32(b) is visible. It may mean that the mechanisms of hydration and especially the products of hydration created by RHA and SF are very similar. Therefore if microstructure is same, almost same strength and pore sizes can be expected. Fig 6 of Annexure B shows the growth of ettringite crystals. Again one is surprised to see the similarity between the crystal sizes; structure and morphology produced by RHA and SF in FA systems (see figures 5 and 6 of Annexure-B for comparison).



**Fig. 4.32 (b)** SEM of C2-FA+RHA-S1 at 28 Days Age



**Fig. 4.32 (c)** SEM of C2-FA+SF-S1-at 28 Days Age

The size, shape and morphology of hydration products and crystals are changed when a different SRM is used in SCM systems. Generally the porosity in ITZ of RHA composite is slightly higher than that of SF composite and higher compressive strength of RHA concrete compared with that of control is due to the reduced porosity, reduced CH and reduced dimensions of ITZ between the paste and aggregate [68]. The RHA Concrete has been reported to have excellent resistance to chloride ion penetration and to freezing and thawing [160] and it is only due to improved ITZ/microstructure.

Comparison between the SEM microstructure of amorphous and crystalline blends of FA (FA+RHA and FA+RHAP) can be made by inspecting figs 7-9 of annexure-B with all three cements at the age of 28 days. Tables 8 and 9 of Annexure-B give reference intensity for CH for various SRM formulations. The FA+RHA systems have the following plus point over FA+RHAP systems.

- HP SCM systems using FA+RHA show denser microstructure, formation of even more hydration products over the SRM particles and lesser number of pores/CH crystals are seen. The maximum pore sizes are also reduced.

All this indicates a superior pozzolanic activity of RHA compared with RHAP resulting in higher “pore refinement effect” and hence the strength.

#### 4.2.8 Water Absorption of SCCS

Water absorption of HP SCP and HP SCM systems was determined in SSD condition at the age of 3, 7 and 28 days. In Annexure-A, Figures 15-17 show the water absorption response of HP SCP systems with CEM III at 20%, 40% and 60% mixing water content (w.r.t the cement mass). In general, water absorption increases with the water curing period and with increase in mixing water contents. In these figures neat cement paste systems show lowest water absorption while RHA formulations show highest water absorption although the inclusion of such mineral and pozzolanic admixtures reduces the maximum pore size compared with neat pastes. It means that the water absorption is not connected to the maximum pore size but it seems to be connected to the type of porosity. The porosity seems to become finer but relatively more connected for systems with pozzolanic powders than the neat paste systems.

Similarly Figures 1-3 in Annexure-B show water absorption of HP SCM systems with three cements at constant w/c and w/p ratios. Here again one can see that addition of 20% RHA in FA shows the highest water absorption. The second highest is LSP while FA alone seems to give the least water absorption. Addition of RHA in HP SCP and HP SCM systems increases the water absorption though maximum pore size is reduced. The only possibility for this to happen is the type of porosity, which seem to be connected with long but finer pores.

### 4.3 TESTS ON HP SCC SYSTEMS

#### 4.3.1 Gradings and Flow

Various SCC mixes were designed for different target slump spreads after careful study of the literature already reported. Moreover mixes were also tested at local ready made concrete manufacturing plant and then these were successfully placed in a local tunnel of teaching and research mine of Freiberg, Germany. Table 1 of Annexure-C shows the ingredients of some of the mixes designed for various target spreads. Table 2 and 3 of the same Annexure give the flow properties of same mixes. The target slump spreads for G4 and G2 formulations were  $66 \pm 1$  and  $70 \pm 1$  cm respectively. It is possible that if the target slump of G4 grading was in the vicinity of 70 cm spread, it could have been obtained by using higher P/S ratio and the funnel times would not have had that big a difference and the grading effects would have been then truly reflected. It appears that for G4 formulation a slight increase in P/S ratio drops the V- Funnel time considerably. It has been experienced that in general high sand content within the similar total aggregate content might need higher P/S ratio for a target spread due to higher surface area. The bleeding and segregation problems for a moderate and reasonable P/S ratio are more significant for low sand mixes. Figure 4.33 shows the relation between admixtures ratio (P/S) and V-Funnel time of SCC mixes with CEM II for G2 and G4 gradings.

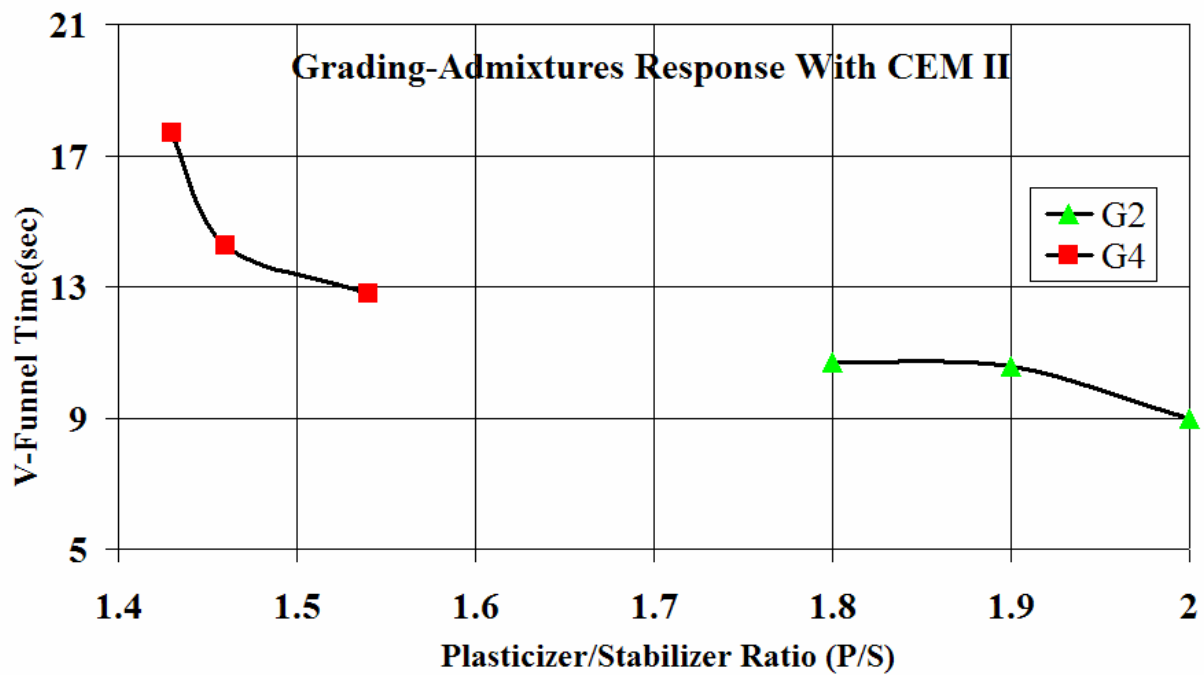
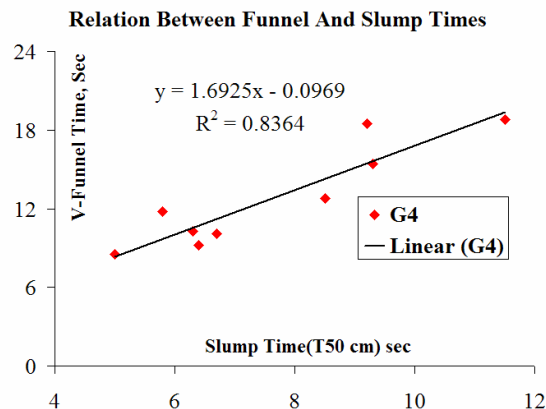


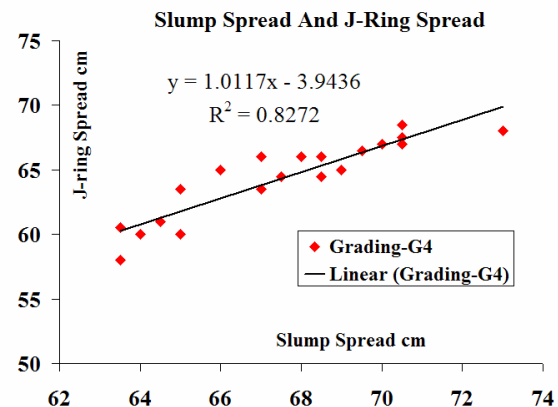
Fig. 4.33 V-Funnel Time and P/S Ratio Relation For Two Aggregate Gradings

As stated earlier, V-Funnel time is indicative of the viscosity of the system while the spread gives an indication of the yield of the system.

Fig. 4.34 gives the relation between T50 cm slump time and V-Funnel time both being a function of viscosity of the SCC mixes. Out of nine mixes, three had a flow range of 65-68 cm while remaining had a flow range of 69-72 cm with G4 grading. Of course their P/S ratio was different with greater ratio for the higher slump spreads. Inspecting the figure it becomes apparent that both times enjoy a reasonable straight line relationship even with difference in cement types. It can therefore be inferred that T50 cm time is also an indirect measure of viscosity of the SCC systems.



**Fig. 4.34** Relation Between T50 cm Slump Time and V-funnel Time



**Fig. 4.35** Relation Between Slump and J-Ring spreads of Some of SCC Mixes

Although a funnel time of 6-11 seconds is considered essential for SCC, yet literature suggests a time between 10-20 seconds may still be good for practice [161]. A slump spread is always more than J-ring spread because in the later, the presence of intermittent peripheral obstructions at 50 cm diameter offers resistance. Fig 4.35 shows relation between slump test and J-ring results of some SCC mixes of G4 grading with different cements. The relation has also been fitted by a straight line in which y is the J-ring spread in cm and x is the slump spread in cm. It can be seen in Figure 4.35 that J-ring spreads and slump spreads had a reasonably straight-line relation. The difference would have been probably further reduced with round coarse aggregates and by using only one type of cement. It also appears that variations in P/S ratio do not bear a significant effect on this response.

#### 4.3.1.1 Differences in Flow Response

A careful study of the literature would reveal that most of the published results on various aspects of SCC are based on laboratory studies. Based on experience it has been observed that a similar SCC formulation may give a very different flow response when tested at plants or at site placements. The differences are due to the degree of activation of SP, environmental factors including temperature and relative humidity and a rather inaccurate estimation of aggregate surface moisture at ready mixed concrete manufacturing plants. Table 4.4 outlines the differences in the response of similar formulations when tested in the laboratory and then at plant and site.

**Table 4.4: A Typical Difference in Flow Parameters as Measured in Laboratory, Plant and Tunnel Site** (mixture: CEM II /A-LL 32.5 R= 380 kg/m<sup>3</sup>, FA 1=147 kg/m<sup>3</sup>, w/c=0.45, w/cm=0.32, total aggregate content with G4 was 1625.3 kg/m<sup>3</sup>. M1 and M2 were two different measurements on the same day).

Tests	Location				
	Plant	Tunnel	Laboratory	Tunnel M1	Tunnel M2
SP/VEA	2.5/1.05	2.5/1.05	2/1.3	2/1.3	2/1.3
Slump: T50 cm in s, spread in mm	7 690	3.8 735	8.5 650	1.9 785	2.5 750
V-Funnel, time in s	13.4	6.43	12.8	4	5.3
L-box, h2/h1 T60 cm In s	0.85,14.3	1,2.94	0.93,11	1,2	1,2.78
J-Ring, T50 cm in s, spread in cm	10.9,66	4.5,71.5	14.8,60	2.9,77.5	4.7,73
Air %	1.4	0.60	2.7	-	-
Concrete Temp, C°	22	24	24	21	-
Water temperature in °C, Air temperature C°	16,23	-, 10	20.5,-	-, -	-, -

It is obvious that the flow characteristics of a similar formulation were different when measured at these locations. The main difference was due to the environmental factors mentioned in article 4.3.3.1 and to the inaccurate aggregate surface moisture estimation and its correction. It is therefore advisable to test the laboratory prescribed formulation at the plant before placement as is also recommended elsewhere [141].

#### 4.3.2 Water Demand of SCC Mix

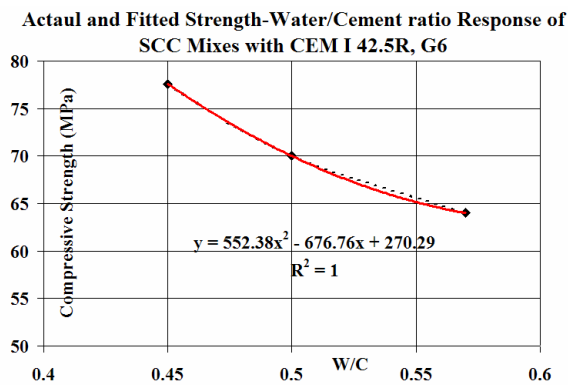
It has already been emphasized that all HP SCCS systems should be made with mixing water equal to the water demand of the system. An excellent method was developed by Marquardt et al [144,145]. The apparatus used was sophisticated and it measured the power consumption of the motor while continuously adding water to the powders. The water addition was stopped at the maximum power consumption and then SP was added. The WD of aggregates > 2mm was determined by centrifuging the saturated aggregates. It has been claimed that the WD so determined was closer to the SSD conditions. However a simple procedure has been proposed which is based on the concept that the water demand of SCC formulation is the sum of individual water demands of the powders and aggregate components. The selection of powder/filler is always based on best engineering judgment keeping in view the reduction in WD, flow, strength, volume stability and place-ability. Therefore the SRM's to be used can be selected in terms of mass per cent of cement. Thereafter these can be mixed and Vicat WD can be noted for the powders. For different size fraction of aggregates, ASTM procedure to calculate SSD water absorption can be applied and WD of various size fractions in terms of per cent can be determined. Then adding up the WD of powders and aggregates as per calculation of Table



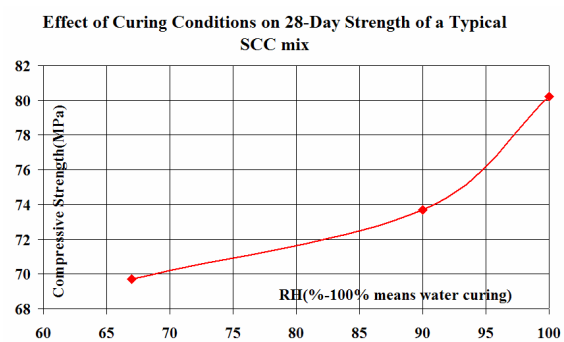
3.7, the total WD of SCC system can be noted. This procedure offers a rather simple solution to a complex issue and can be used at site also.

### 4.3.3 Strength of HP SCC

Structural and construction engineers are interested in two main parameters of SCC in addition to its volume stability. These two parameters include flow and strength. Therefore the selected formulations cast in laboratory, at plant and then at site were tested for strength. In Fig 4.36 the strength of SCC is plotted against W/C ratio of the formulations cast in the laboratory for G6 grading. It is obvious that strength heavily depends on the W/C ratio. The average 28 day compressive strength of the tested formulations was 0.216 MPa, 0.175 MPa and 0.239 MPa per kg of cement for CEM I 42.5 R, CEM II /A-LL 32.5 R and CEM II/B-M 32.5 R respectively as against 0.14 MPa/kg of cement reported elsewhere [3] which may be due to their lower cement content.



**Fig. 4.36** Compressive Strength Versus W/C Ratio of SCC- Actual and Fitted Curves After 28 Days



**Fig. 4.37** Effect of Curing Conditions on The Compressive Strength of a Typical SCC Mix

#### 4.3.3.1 Differences in Strength Response

The next parameter was to find the differences in the strength of similar SCC mixes which had been cast at different locations. In the laboratory the samples, after casting, were placed in an environment with 90% + humidity and temperature was around 27°C. After one day these were demoulded and were put in water upto 7 days of age after which these were moist air cured at 67% relative humidity within laboratory temperature. Within the tunnel site location, the temperature during summer months was close to 11-13°C while relative humidity was around 90% .This factor was responsible for the strength response differences as given in Table 4.5.

**Table 4.5** Strength Results of Different Tunnel Placements With Different Curing Conditions

Mix	Curing Condition	7 Day Strength, in MPa		28 Day Strength, in MPa		90 Day Strength, in MPa	
		Flexural Strength	Compressive Strength	Flexural Strength	Compressive Strength	Flexural Strength	Compressive Strength
1	Tunnel	-	54	7.9	62	9.3	78
	Laboratory	-	54	7.5	80	7.2	101
2	Tunnel	-	53	9.9	64	10.1	78
	Laboratory	8	54	8.7	74	8.9	95

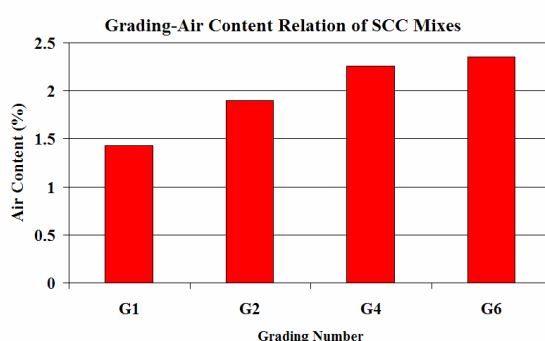
Compressive strength in laboratory at 28 days and 90 days is more. It may be possibly due to higher curing temperature and initial 7 days of water curing. In the tunnel after casting, the specimens were left in open. However surprisingly the flexural strength is higher for the tunnel cured samples. It may be due to continued higher relative humidity in the tunnel environment. After observing all the available data, it can be said that a little variation in P/S ratio does not change the strength significantly in actual conditions if all the other parameters and ingredients remain the same. Moreover an increase of 5 % (of the total aggregate content) in sand content does not reduce the strength significantly if the total aggregate content is kept constant. The strength is more influenced by w/c ratio.

#### 4.3.3.2 Effect of Curing Conditions on Strength of SCC

Fig 4.37 shows the effect of curing conditions on the strength of a typical SCC formulation tested in the laboratory. It can be seen that as relative humidity during curing improves, the strength also improves correspondingly. This test was done to know if SCC placement is left as such, in a tunnel for example, then how the strength is affected in comparison to other humid environments. 100% relative humidity in Figure 4.37 means water curing. A difference of about 10 MPa (around 14%) is noticeable between water cured SCC and that cured according to DIN standards. Table 4 of Annexure-C gives the compressive strength record of some typical SCC mixes. It is clear that all mixes gave a reasonable extra strength margin in comparison with the target strength.

#### 4.3.3.3 Air Content of SCC Gradings

Various aggregate gradings were used in making SCC. The details of mixes are shown in Tables 1-3 of Annexure-C. The average air content for different gradings is shown in Fig 4.38. It appears that by increasing sand content, with constant total aggregate content, the entrapped air content increases and is as expected.



**Fig. 4.38** Effect of Aggregate Grading on Air Content of SCC Mixes

## 5 DISCUSSION

This thesis contains the results pertaining to three types of HP SCCS. Therefore the discussion that follows encompasses the salient features of all of these systems.

### 5.1 Flow of SCCS

For HP SCCS with given ingredients, the SP demand for a given target flow depends on the shape, size, morphology, internal porosity and degree of pozzolanic activity of the SRM's. Previously it was thought that only cement particles adsorb SP while other fillers do not, which is incorrect.

The quantity of mixing water is important for properties of cementitious systems in fresh and hardened state. From fig 4.5 it is very clear that the SCCS should have mixing water content very close to the water demand of the system in order to reduce the quantity of SP required for the target flow resulting in both economy and durability. It is important to describe here that if mixing water content is less than WD of the system, very high SP doses are required to obtain the target flow which disturbs the economy and produces significant delays in setting. In such case, the surface of all cement and powder particles is not adequately wet making the SP grafts on powder particles difficult. In this situation all cement particles do not get hydrated and a part of cement acts as filler only. On the other hand if mixing water is more than the water demand of the system then durability would be at stake due to higher maximum pore size of HP SCCS which usually encourages easier fluid transport within the hardened mass and durability related issues like corrosion and/or carbonation can result faster. Both of these effects are undesirable in construction industry. Therefore in the opinion of the author it would be the ideal situation if self-compacting systems should be made at the mixing water equal to WD of the system. Determination of WD of a cementitious system is important and at times difficult starting step. Many researchers have suggested procedures using sophisticated equipment which may not be available at sites. An alternate simple concept/procedure suggested by the author [125] can be used at sites also.

LSP has been used by many researchers in SCCS. However in this reported work on HP SCM systems, the SP demand to meet a target flow was found to be the highest for LSP formulations while it was the lowest for FA formulations. The reasons for high SP demand of LSP were irregular particle shape, rough morphology and internal uptake of SP in the narrow and at times bottle neck type of pores which even during high shear mixing do not allow the intruded SP to come out and be available for the dispersion. As stated earlier SP demand decreased from CEM I to CEM II to CEM III for the similar flow target in HP SCP systems and seemed to depend on the clinker content of cement as stated in article 4.1.4. The same comment holds for 21 HP SCM formulations made with three cements with two exceptions which included only LSP with CEM II/A-LL 32.5R with two sands resulting in lower SP content than CEM III.

#### 5.1.1 Time of Addition of SP

In self-compacting systems, the time of addition of SP is very important along with the degree of wetness of SRM surfaces. As per literature and author's experience, SP should preferably be added to SRM's which have been previously wetted with about 80% of the total mixing water content, after say 1-2 minutes of mixing. During that time the aluminate phases

would have reacted to some extent and resultantly a smaller quantity of SP can produce desired flow. Adding SP in two batches has also been reported effective. However for workability retention, SP addition in a single dose is more effective [140] and was observed in all systems. A delayed SP addition (after addition of water) increases the workability [76] and was adopted for SCM systems. Moreover at high shear rates SP seems to be activated within relatively short time and with a relatively lesser amount of SP. For SCC systems, the activation of SP in laboratory can either be ensured by higher mixing time (say 4-5 minutes) or by keeping the sample undisturbed, after initial mixing of two minutes, for about 10 minutes and then giving a final mixing of 1 minute. Second option was closer to our practical applications.

### 5.1.2 Factors Affecting the Flow of SCCS

High packing density, low w/c and low porosity are the typical characteristics of HPC/SCC. In the present research this objective has been obtained by using continuous aggregate grading and by packing the binder phase which reduces the amount of water and lowers the entrapped air as well. The lower is the void volume, lower will be paste or cement component resulting in lower porosity and hence lower shrinkage [164].

With reference to Table 5 of Annexure-A, addition of 10% SF and RHA in HP SCP system increased the SP demand of CEM I paste from 0.097% to 0.34% and 0.24% respectively at 40% mixing water for the target flow. SF required more SP than RHA due to increased surface area, slow shear rate and larger mercury volume got intruded in its smaller pores. It proved that a part of SP goes into narrow spherical and complex pores of SF and is no more available for dispersion. However when SF is compared with RHA in SCM systems (Fig 4.23), situation was reversed and SF required less SP than RHA formulations. It may be because of the higher shear rate and duration of Eirich mixer which results in lesser SP to be intrudable in spherical SF particles in the presence of high centrifugal forces. At higher shear rates, irregular internally porous RHA particles require more SP to overcome increased internal friction. It means that the amount of SP needed for a target flow of SCCS depends upon

- Time and sequence of addition and degree of surface wetness of powders
- Surface area of powders-(more is surface area higher is SP demand)
- Nature of powder pores-(small spherical and longer /or bottle neck pores need more SP)
- Particle shape, size and surface morphology( irregular shape with rough surface texture and uneven surface topology needs more SP to overcome internal friction between particles during flow)
- Shear rate and duration - (high shear rate and duration can reduce SP demand of spherical powder particles due to high centrifugal forces which seem to be more effective on spherical shape of particles).High shear rate reduced the SP required for SF to obtain the target flow compared with RHA when both were substituted at 20% of FA mass in SCM systems.

## 5.2 Strength of HP SCCS

Strength of HP SCP and HP SCM systems is given in Tables 4.1 and 4.2 respectively. In HP SCP systems with CEM III, 28 day compressive strength increases with the inclusion of pozzolanic SRM's at all mixing waters despite dilution while it decreases at 20% water content

with CEM I possibly because of higher SP content, coarser pore structure of resulting composite and faster consumption of water through hydration and/or evaporation[112]. The faster consumption of water during the first 24 hours when curing takes place in moist air at relative humidity less than 100% creates air voids which reduce the subsequent strength. In general the strength increase in HP SCP systems is due to combined filler and pore refinement effect.

In HP SCM systems, LSP gives least strength due to higher maximum pore size and poor packing which decreases progressively for pozzolanic FA and its 20% by mass blends of RHAP, RHA and SF. Considering this strength increase, as evidenced in Table 4.2 and maximum pore sizes as contained in Table 4.3, it can be stated that strength of HP SCM systems is generally defined and governed by the combination of maximum pore size and by the degree of pozzolanic activity. Higher maximum pore sizes and lower pozzolanic activity gives lower strength. In summary it is concluded that suitable binary and ternary binder pozzolanic SRM's or their combinations increase flow, strength and durability due to their shape and pore-refinement effect [123] respectively.

### 5.3 Microstructure of HP SCCS

Microstructure of HP SCCS was studied by MIP and SEM techniques. Table 11 of Annexure-A gives the maximum pore radius obtained from the partial diagrams of various HP SCP systems. The following points have been noted.

- Inclusion of pozzolanic SRM's in HP SCP systems decreases the maximum pore sizes of the composite despite dilution effect and due to pore refinement effect. The reduction in pore sizes depends on the degree of pozzolanic activity of SRM.
- Between 3 and 7 days, the rate of decrease in the maximum pore radius is not very significant and this further diminishes between 7 and 28 days.
- Increase in w/c ratio increases the maximum pore size very drastically
- In general CEM I formulations gave higher maximum pore sizes than CEM III formulations.
- CEM III at the age of 1 day gives higher pore sizes due to its delayed setting (lower clinker content plus higher SP content) but thereafter it gives finer pore sizes.

In general mortars give higher maximum pore sizes than paste systems. However comparing the maximum pore radius at 7 days, of HP SCP and HP SCM formulations, this looks almost the same though these systems, strictly speaking, are not comparable as one system possesses aggregate and other does not. It appears that the presence of additional pozzolanic SRM's improves the ITZ of HP SCM which gave almost comparable maximum pore size. Moreover binary and ternary binders seem to produce a finer and denser microstructure.

The results confirm the "pore refinement effect" of the pozzolanic SRM additions which improve the strength as well as durability of HP SCCS. SF and RHA as 20% FA blends (by mass) give comparable pore refinement effect. It further proves the efficiency of binary and ternary binders in HP SCM systems. Higher pore sizes of CEM III at the age of 1 day are due to the fact that this cement has only 30% Portland cement clinker content and also needs very high SP doses for the target flow. Both these effects are additive and resulted in delayed hydration giving bigger pores at the age of one day. However at later ages trend got reversed. Pore refinement effect seems to be strongly dependent on the degree of pozzolanic activity and this



effect is maximum for FA+SF combination and decreases towards FA+RHA, FA , FA+RHAP and LSP respective in the order stated. MIP studies on SCM systems showed that

- LSP formulations gave the maximum size of pores at all ages.
- FA+SF in 80:20 mass per cent gave the lowest pore sizes
- FA+RHA and FA+SF systems showed almost comparable maximum pore sizes at the age of three day and beyond.
- Replacing finer sand with blended coarser sand, for constant mixing water content, slightly increases the maximum pore size due to an increase in the effective water content.

The highest pore size of LSP formulations is due to their highly irregular surface, internal porosity, poor packing and very high SP demand. Coarser sand gives slightly bigger maximum pore size because the effective water for given mixing water increases because of its lesser surface area for a given volume. Higher water content generally results in higher maximum pore sizes. The hydration mechanisms of binary and ternary binder systems are quite complex and have not been fully understood. However addition of pozzolanic SRM's is responsible for the pore-refinement effect which has also been observed in SEM pictures of the respective formulations. A strong 'nucleation' effect was seen and verified for the FA formulations (Fig 4.32(a)). RHA and SF seem to give rise to almost similar hydration products as seen in Figures 4.32 (b & c) suggesting a possible and more or less similar hydration mechanism of these two pozzolanic powders. Moreover in the empty pores, similar type of crystal growth for both RHA/SF formulations has been seen and is shown in Figs 5-6 of Annexure-B which further supplements this observation. RHAP and RHA have been compared in terms of flow, strength, microstructure and early volume stability. Consider Figures 7 to 9 in Annexure-B to compare the SEM microstructure of FA+RHA's (both amorphous and crystalline) with three cements at the age of 28 days. With reference to Table 11 of Annexure-A CEM I formulations generally gave higher pore sizes than those with CEM III. Keeping this mind and comparing responses in Figs 7(a) to 9(a) with 7(b) to 9(b) of Annexure-B, it becomes evident that FA+RHAP formulations with all three cements produce rather different type of hydration products and morphology than those of FA+ RHA formulations due to reduced pozzolanic activity and slightly higher maximum pore size resulting in lower strengths for FA+RHAP formulations. CH and other crystals can also be seen only with FA+RHAP formulations (see Figs 7(b) to 9(b) of Annexure-B) which further supplement this statement. This argument is finally proved from the XRD and thermal analysis data which shows higher CH content as appearing in Table 7 of Annexure-B for FA+RHAP formulation than FA+RHA. FA+RHAP shows higher maximum pore size also and more mercury intrudes in it as observed in partial MIP diagrams compared with FA+RHA containing HP SCM systems indicating that FA+RHAP produces a sort of connected pore system while for FA+RHA the pore system may also be continuous but size is smaller. It is not only the maximum pore size which is important but the type of porosity (open or connected) is also equally important to describe the response of HP SCCS formulation.

#### 5.4 Dimensional Stability of HP SCCS

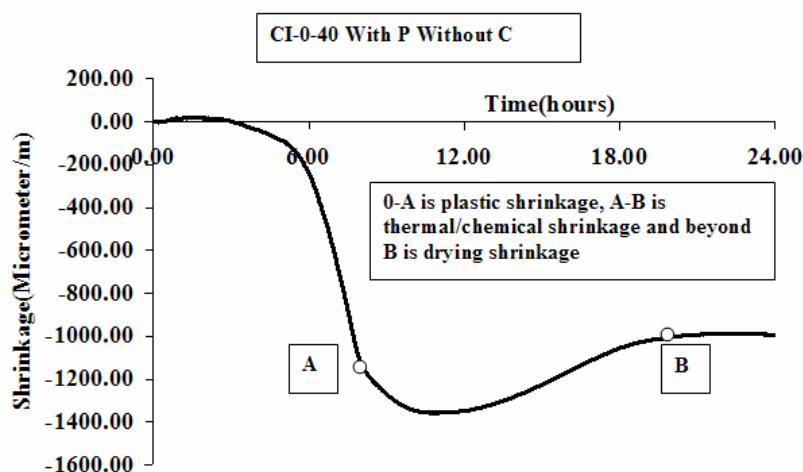
Results of first 24 hours linear shrinkage measurement on various SCCS have been shown and explained already in the form of graphs. The following points have emerged.



- SP seems to reduce the early shrinkage in uncovered condition for HP SCP systems and gives a slightly delayed setting. At times it ends up giving a small expansion after 24 hours of measurement in covered conditions at suitable mixing water contents.
- Covering a formulation reduces the shrinkage and increases the expansion as the case may be.
- For a given formulation, early dimensional stability of HP SCCS depends on the type, shape and internal porosity of the SRM's used and upon the exposure conditions.
- Higher is the degree of pozzolanic activity greater will be the shrinkage in uncovered conditions. Early shrinkage/expansion seems to also depend on thermal gradient between the environment and sample as evidenced in a side investigation. Higher is this gradient; higher would be the shrinkage in uncovered condition. The times of occurrence of maximum heat and maximum shrinkage were also found to be very close.
- Cement content is the main source of shrinkage. At higher w/c ratios, the shrinkage of a similar formulation decreases due to dilution effect.
- Normally the ashes (RHAP+FA, FA, and FA+RHA) contained in HP SCM systems produce expansion in covered condition to varying degrees and in the mentioned descending order.
- LSP shows maximum linear shrinkage in both uncovered and covered conditions.

Based on results of this study it seems that early linear shrinkage behavior of HP SCCS is governed by several simultaneous and overlapping mechanisms. During the first stage, right after mixing, the paste or mortar tends to shrink due to water loss occurring either through evaporation (classical plastic shrinkage) and/or through water up-take by porous, inert, pozzolanic or latent hydraulic fine particles. As a consequence thereof, significant shrinkage during this stage can be observed in uncovered conditions. In covered conditions pure pastes show almost no shrinkage. The nature of the particles added will determine the amount of shrinkage/expansion in both conditions. The second stage can be observed when the material sets through hydration. Towards the end of setting the initial pronounced shrinkage is arrested and the curves become flat or show even a slight expansion. Flat curves are observed with limestone powder (see Fig 4.27-left). If a slight expansion is observed in uncovered condition, its onset corresponds to the maxima in the heat flow measurements. It was also observed therein that the maximum shrinkage in uncovered conditions occurred at/near the maximum temperature. Therefore the expansion can be explained to a large extent by thermal expansion originating from the heat of hydration. Some researchers also claim expansion through the formation of hydrates. The exact amount to be attributed to each mechanism needs to be quantified by further studies if deemed necessary. The third stage is the classical drying shrinkage of a porous solid material. Its magnitude can somehow be related to pore size distributions. Here also further studies need to be conducted for quantitative results using similar powders.

A typical schematic Fig 5.1 shows that the apparatus used was quite sensitive and was able to capture the plastic shrinkage well before the setting of plasticized paste system. It clearly shows plastic shrinkage (0 to A), setting (A to B) and expansion due to temperature and hydrates formation resulting in shrinkage recovery and beyond B is the typical drying shrinkage. The minimum recordable strain was 1.25 microns per meter.



**Fig 5.1** A Typical Schematic Shrinkage Response Curve of a Cementitious System Showing Various Stages

Crystalline RHAP with FA in 20:80 mass per cent in the paste systems seems to be more effective than amorphous RHA for shrinkage reduction in uncovered condition. In covered conditions it produces expansion due to reasons explained earlier. The shrinkage response of both RHA's was quite different in covered condition in HP SCM systems. While RHAP, as a blend of FA, relatively increased the effective w/c ratio and hence showed higher expansion in covered condition (compared with FA alone). RHA in covered conditions gave decreased shrinkage (compared with FA alone) and an increased shrinkage was obtained in uncovered condition as explained elsewhere [114]. If curing membrane is used immediately after placement to prevent evaporation, FA+RHA and/or FA+SF in 80:20 mass ratio seem to be useful combinations for HP SCM systems w.r.t dimensional stability. The literature [162,163] mentions the existence of two types of CSH, one being termed as low density (LD) and other one as high density (HD). The shrinkable CSH is LD so it can be interpreted that if any formulation has high shrinkage it may have higher LD CSH content. Despite massive literature reported use of LSP in self-compacting systems, LSP has been found to give the maximum early linear shrinkage, the lowest strength and the highest maximum pore size in comparison to other powders used in HP SCM systems in both the exposure conditions. Some experts are of the opinion that  $\text{CaCO}_3$  percent content in LSP controls its performance and dimensional stability. They state that LSP having  $\text{CaCO}_3$  content in the range of 96-98% gives much better response. But the fact remains that it is not only the  $\text{CaCO}_3$  content alone which determines the response of LSP but the ingredients in the left over percentile are also terribly important. In general early linear shrinkage response trends of SF and RHA in HP SCP/SCM systems seem to be comparable at least in terms of values. It has now been established that both linear and volume techniques of shrinkage measurement are valid and give almost identical results [165].

## 5.5 Experiences with SCC

After having tested about 60 laboratory mixes, ten mixes at a semi-automated plant and about equal number of placements in a local tunnel, it is felt that a similar SCC formulation can give different response at these locations due to the following reasons.

- Difference in environmental factors (Temperature and relative humidity)
- Inaccurate aggregate surface moisture estimation and its correction at plant
- Manual admixture dispensation at semi-automated plants

The first two factors vary with climate and aggregate storage conditions and must be kept in mind for the successful placement of SCC formulation. It is suggested that a sand content of 50-55% of the total aggregate mass may be good for successful placements using natural boundary-line elongated aggregates. This point became clear when sand content was gradually increased from 39% to 50% by mass of total aggregate content in laboratory mixes (G1 to G4 grading), which improved the response. It is important to mention here that European Guidelines for Self-Compacting Concrete [141] also allow a maximum of 55% of the sand content w.r.t total aggregate mass content perhaps to take care of such elongated aggregates.

The determination of water demand of SCC system is an essential starting step. So far it has been difficult to determine the water demand of SCC because of the absence of any simple procedure suited to site conditions. Therefore a simplified procedure has been suggested. It is recommended that the total mixing water should not be greater than the water demand of the system for economy and durability.

The difference in batch sizes w.r.t chemical admixtures could also be one of the reasons for response difference between the laboratory and plant mixes. The data shows that a little variation in plasticizer or stabilizer contents does not change the SCC strength significantly if other constituents remain the same. Moreover an increase of 5 % sand (keeping the total aggregate content constant) does not reduce the SCC strength significantly. During experimentation it was also observed that for the same formulation, flow times are reduced with increased cement content keeping the total powder content constant. Moreover for a given grading and SCC mix ingredients, the flow seems to start at a typical P/S ratio beyond which any further increase in P/S ratio does not improve the flow very significantly. 24 hour strength of SCC samples taken at the ground level (above the underground tunnel) had similar strength as those collected from within the tunnel after having been pumped 150 m horizontally and 150 meters vertically for similar curing conditions. It indicates that voids or air content in both concretes would have been unremarkable and pumping caused no significant difference in air content and hence strength. During laboratory study it was observed that high sand SCC mixes(G6-55% sand of the total aggregate content) showed better stability and higher air content compared with G4 grading (50% sand content) due to possible entrapment of more air during mixing(Fig. 4.38).

The estimation of aggregate moisture is an important area in the manufacture of SCC. There are three broad classes of aggregate surface moisture and these include oven dried, saturated surface dry (SSD) and wet conditions. In laboratory oven dried aggregates are usually used while at ready mixed concrete plants the aggregates are stored in large bins open to sky and are transferred to silos before mixing. Such aggregates usually contain water which is greater than water corresponding to SSD condition and of course this would vary depending on the climatic and storage conditions. SSD condition is that at which aggregate neither absorbs water from nor contributes water to concrete mix.

It is therefore important that the total effective water available in the mix is the same for both the laboratory and plant mixes if comparisons are to be made. For comparison purposes and using oven dry aggregates, the effective water in the mix would be the total mixing water minus the water absorption of aggregates corresponding to SSD conditions. In plant made mixes, the

effective water available in the mix would be the total mixing water which includes excessive aggregate moisture ( $>$ SSD condition) and water contributions of SP and VEA.

Aggregates taken from bins were tested for SSD moisture content as per ASTM C 127 and 128. The moisture content of various size fractions tested in the laboratory was found to be lower than that found at plant (for the same size fractions) possibly due to the samples being taken from the lower part of the silos at the ready mixed concrete plant.

Different procedures would give different results for SSD water content of aggregates but all of these would not be far away between themselves. A simple one suiting field conditions may then be selected for the purpose.

## 6 CONCLUSIONS

Based on this research work, the following conclusions can be drawn.

1. Mixing water greater than WD of HP SCCS is detrimental to its strength and durability. The estimation of the water demand of HP SCCS has been a complex procedure requiring laboratory equipment. In this research a simple alternative procedure suiting field conditions also, has been suggested so that all HP SCCS could be easily made at mixing water content equal to the system's demand.

2. LSP has been overwhelmingly used in SCCS by several researchers possibly in the absence of data on its comparative response with other SRM's. In this study LSP along with other pozzolanic SRM's have been used in SCM systems. LSP showed the highest linear early shrinkage, highest maximum pore size, highest SP demand for the target flow and the lowest strength. This investigation has established this point conclusively and it is hoped that construction engineers will use it judiciously.

Some researchers are of the opinion that the  $\text{CaCO}_3$  content of LSP is a decisive factor in determining its overall response. They state that if  $\text{CaCO}_3$  is between 96-98% it can give a very different and useful response. In the opinion of author it is not simply the  $\text{CaCO}_3$  content but more importantly it is the elements in the left over percentage (100-  $\text{CaCO}_3$  % by mass), which influence its response in a very significant way.

3. For a given formulation of HP SCCS, the flow generally depends on the size, shape, morphology and internal porosity of the particles. Aggregates increase the resistance to flow by offering high internal resistance which can be overcome by increasing the paste component and reducing the aggregate content and their sizes. Increasing cement content for constant paste content also decreases flow times.

4. Strength quantification due to any powder in HP SCM system can be done easily by considering the strength obtained with a relatively inert powder material as a base line to serve the purpose of structural and construction engineers. Of course this strength quantification contains the effects of both physical and chemical factors. In case of HP SCP systems, neat formulations can be considered as control for the purpose.

5. The microstructure of HP SCCS is very important from strength and durability point of view. The SEM investigation of FA+RHA and FA+RHAP with three cements has been shown in figs 7-9 of annexure-B. CH contents of both ashes and other SRM's are shown in Table 7 of Annexure-B. In general amorphous RHA in FA gives a denser microstructure as seen by SEM and its hydration products engulf FA particles more uniformly over its entire surface. After 28 days voids are rarely seen in FA+RHA containing HP SCM systems because of pore refinement effect and accumulation of hydration products over the periphery of FA/RHA particles. However for FA+RHAP higher pore sizes along with presence of CH crystals are responsible for lower strength with the three cements used. RHA brings about almost similar microstructural improvements as those of SF. Both crystalline and amorphous RHA as FA blends give different microstructure which is responsible for the difference in their overall response. Amorphous RHA

as FA blend is a better option for microstructural improvements if SF is not economically available.

6. From dimensional stability point of view, FA+ RHA (20% by FA mass) seems to be a good combination for reducing or eliminating the early shrinkage of HP SCCS provided the curing membrane is applied immediately after the finishing operations. If curing membrane would not be applied, then FA+RHAP looks to be a better option. It is further hoped that if crystalline RHAP is added in LSP (20% by LSP mass), the shrinkage of LSP in covered conditions could be arrested to a great extent.

7. Contrary to the general impression, suitable binary and ternary binder blends of FA using RHAP, RHA and SF each taken as 20% mass of FA have proven successful in the overall response improvement of HP SCCS.

RHA has proven to be a very good substitute of SF in HP SCCS in terms of strength, microstructure and early volume stability. It would be particularly beneficial for the rice growing developing countries to use it as SRM in HP SCCS. Rice husk can also be used for energy generation and the resulting ash can be employed as a value added material in cementitious systems as is being practiced in USA and elsewhere. The author hopes that this study will further contribute to the use of RHA in HP SCCS in a meaningful way.



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### B-EDUCATION

**M.Sc Structural Engineering.** University of Surrey, England, U.K. – 1981.

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### C-MEMBERSHIP OF PROFESSIONAL BODIES

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5. Convener, Accreditation Committee Pakistan Engineering Council (1997-2000).
6. Fellow, Institution of Engineers Pakistan, Member Executive Committee (1994-96)
7. Vice-President, Pakistan Engineering Congress 1996 –5 Oct 2003.

### D-PERSONAL HONORS/AWARDS

- Merit Scholarship from Board of Intermediate & Secondary Education Lahore, Pakistan. 1971-75 for B.Sc. Engineering Degree.
- British Government Scholarship for Master’s Degree in Structural Engineering from Surrey, U.K., 1980-81
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**E- EMPLOYMENT**

- |   |   |
|---|---|
| 1. Professor of Civil Engineering<br>University of Engineering & Technology, Lahore           | 13 Dec. 1993 to date                    |
| 2. Associate Professor of Civil Engineering<br>University of Engineering & Technology, Lahore | 18 Feb. 1987 to 12 Dec. 1993            |
| 3. Assistant Professor of Civil Engineering<br>University of Engineering & Technology, Lahore | Jan. 1982 to 17 <sup>th</sup> Feb. 1987 |
| 4. Lecturer of Civil Engineering<br>University of Engineering & Technology, Lahore            | Oct. 1976 to Dec. 1981                  |

**F- CONFERENCES ORGANIZED**

- Secretary ACI-RILEM International Conference on “Advanced Cement Based Materials”- December 2007, Lahore, Pakistan

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- Chairman Organizing Committee, 6<sup>th</sup> International Colloquium on Concrete in Developing Countries”, Jan 4-6, 1997. Jointly sponsored by CSCE, IEP and UET Lahore, Jan 4-6, 1997, Lahore, Pakistan.
- Co-Chairman Technical Committee, 6<sup>th</sup> International Colloquium on Concrete in Developing Countries”, Jan 4-6, 1997, Jointly sponsored by CSCE, IEP, and UET Lahore, Jan 4-6, 1997, Lahore, Pakistan.
- Co-Editor Proceedings, “6<sup>th</sup> International Colloquium on Concrete in Developing Countries”, Jan 4-6, 1997, Jointly sponsored by CSCE, IEP, and UET Lahore, Jan 4-6, 1997, Lahore, Pakistan.

## ANNEXURE-A

**Table 1 Water Demands and Setting Times of Cement Pastes With SF**

Sr No	SF%	CEM I			CEM II			CEM III		
		WD%	IST	FST	WD%	IST	FST	WD%	IST	FST
1	0	29.5	3-10	3-40	27	3-24	3-47	29.5	4-07	4-47
2	5	32.5	3-06	3-32	28.5	3-22	4-02	32.0	4-28	5-12
3	10	37	3-15	3-34	32	3-33	4-00	36.5	5-42	6-07
4	15	41.5	3-30	3-42	37	4-29	4-46	41.5	5-57	6-17
5	20	47.5	4-01	4-10	44	4-45	4-57	47.5	-	-

WD is per cent of cement mass. IST and FST are in hours and minutes.

**Table 2 Water Demands of Cement Paste Systems with RHA**

Water Demand %	CEM I with RHA%			CEM II with RHA%			CEM III with RHA%		
	0	5	10	0	5	10	0	5	10
	29.5	32.5	35	27	28.5	31	29.5	33	36

Note: For 5% RHA IST= 4-14, FST= 5-04, with 10% RHA, IST= 6-17 & FST= More than 7 hours for CEM I

**Table 3 Regression Equations of Water Demands of Paste Systems**

Type of Cement	Mineral Admixture%(x)	Regression Equation for WD	Regression co-eff
CEM I	SF	$28.6+0.9(x)$	0.9868
CEM II	SF	$25.2+0.85(x)$	0.9417
CEM III	SF	$28.3+0.91(x)$	0.9803
CEM I	RHA	$29.583+0.55(x)$	0.9973
CEM II	RHA	$26.833+0.4(x)$	0.9796
CEM III	RHA	$29.5+0.65(x)$	0.998

**Table 4 Regression Relations of Setting Times for Three Cements**

Cement type	IST		FST	
	Regression Equation	Co-eff	Regression Equation	Co-eff
CEM I (C1)	$0.0036x^2-0.0293x+3.1617$	0.9975	$0.0037x^2-0.0508x+3.6728$	0.9858
CEM II (C2)	$0.0039x^2-0.0011x+3.3379$	0.9229	$0.0019x^2+0.0227x+3.7884$	0.9129
CEM III (C3)	$-0.0011x^2+0.1507x+4.0207$	0.9249	$-0.0025x^2+0.1458x+4.7206$	0.9501

Where x is SF per cent mass and varies between  $0 < x < 20$ . Evaluation of above equations will give corresponding setting times in hours and WD's in per cent of cement mass.

**Table 5** Deggusa Superplasticizer Content of Melflux 1641 (per cent of cement mass) For 200% flow (30 cm spread) of Schwenk HP Cement Paste Systems

Type of Cement	Mixing Water %	SF/RHA Admixture %	Plasticizer Type/Contents For 200% Flow
CEM I	WD/SC=29.5	nil	0.22%
CEM I	20	nil	0.825, (0.442-2651)
CEM I	32.5=WD/SC	5% SF	0.38
CEM I	20	5% SF	1.0
CEM I	40	5% SF	0.18
CEM I	60	5% SF	0.055
CEM I	20	10% SF	2.75, (2.0- 2651)
CEM I	WD/SC=37	10% SF	0.4
CEM I	40	10% SF	0.34
CEM I	60	10% SF	0.17
CEM I	40	5%RHA	0.115
CEM I	60	5%RHA	0.019
CEM I	20	5%RHA	0.7(2651)
CEM I	20	10%RHA	1.72(2651)
CEM I	60	10%RHA	0.085, (0.055- 2651)
CEM I	40	10%RHA	0.24, (0.19- 2651)
CEM I	60	nil	Zero per cent
CEM I	40	nil	0.097
CEM I	35=WD/SC	10%RHA	0.26
CEM II	27=WD/SC	nil	0.21
CEM II	20	nil	0.42
CEM II	40	nil	0.06
CEM II	60	nil	zero
CEM II	28.5=WD/SCC	5% SF	0.27
CEM II	32=WD/SC	10% SF	0.35
CEM II	20	5% SF	0.75
CEM II	40	5% SF	0.128
CEM II	60	5% SF	0.06
CEM II	20	10% SF	1.70
CEM II	40	10% SF	0.21
CEM II	60	10% SF	0.11
CEM II	20	5%RHA	0.36(2651)
CEM II	40	5% RHA	0.08
CEM II	60	5%RHA	0.01
CEM II	20	10%RHA	0.58(2651)
CEM II	40	10%RHA	0.13
CEM II	60	10%RHA	0.031
CEM II	31=WD/SC	10%RHA	-
CEM III	29.5=WD/SC	nil	0.17
CEM III	20	nil	0.803, (0.37-2651)
CEM III	40	nil	0.08
CEM III	60	nil	0.007



**Table 5 Continued**

Type of Cement	Mixing Water%	SF/RHA Admixture%	Plasticizer Type/Contents For 200% flow
CEM III	32=WD/SC	5% SF	0.185
CEM III	20	5% SF	0.73
CEM III	40	5% SF	0.17
CEM III	60	5% SF	0.075
CEM III	36.5=WD/SC	10% SF	0.34
CEM III	20	10% SF	1.87, (1.32- 2651)
CEM III	40	10% SF	0.293
CEM III	60	10% SF	0.16
CEM III	33=WD/SC	5% RHA	-
CEM III	20	5% RHA	0.29(2651)
CEM III	40	5% RHA	0.122
CEM III	60	5% RHA	0.05
CEM III	20	10% RHA	1.3(2651)
CEM III	40	10% RHA	0.175
CEM III	60	10% RHA	0.07
CEM III	36=WD/SC	10% RHA	0.23
CEM III	40	nil	0.08
CEM III	60	nil	0.007
CEM I	33=WD	10% RHAP	0.217
CEM I	40	10% RHAP	0.14
CEM I	60	10% RHAP	0.04
CEM I	20	10% RHAP	1.61(2651)
CEM III	34%=WD	10% RHAP	0.15
CEM III	20	10% RHAP	0.65 (2651) 6 min of mixing
CEM III	40	10% RHAP	0.105
CEM III	60	10% RHAP	0.04

**Table 6** Compressive Strength of HP SCP Systems With CEM I at 200% Flow

Type of Paste	Age (Days)			
	1	3	7	28
CI-0-40	42.96	60.92	66.24	77.76
CI-SF10-40	47.07	68.8	80.03	92.96
CI-RHA10-40	34.26	69.88	82.36	92.89
CI-0-60	17.74	26.0	31.48	40.36
CI-SF10-60	22.03	36.96	46.08	53.13
CI-RHA10-60	20.41	31.84	45.6	54.16
CI-0-WD	59.3	77.6	82.53	111.14
CI-SF10-WD	48.69	65.29	79.53	105.9
CI-RHA10- WD	45.87	70.73	85.72	106.43
CI-0-20	80.06	90.0	95.56	133.04
CI-SF10-20	44.86	87.53	114.46	123.7
CI-RHA10-20	5.91	94.63	115	124

**Table 7** Flexural Strength of HP SCP Systems With CEM I at 200% Flow

Type of Paste	Age (Days)			
	1	3	7	28
CI-0-40	5.226	6.90	8.07	9.19
CI-SF10-40	6.03	8.56	9.13	10.29
CI-RHA10-40	5.78	7.82	8.80	9.763
CI-0-60	3.61	5.00	5.74	6.15
CI-SF10-60	4.036	5.976	6.40	6.59
CI-RHA10-60	3.95	5.46	7.57	7.76
CI-0-WD	7.53	11.65	12.61	13.59
CI-SF10-WD	5.87	7.66	9.14	9.84
CI-RHA10- WD	6.04	7.83	9.30	11.05
CI-0-20	9.79	13.50	15.06	16.96
CI-SF10-20	6.013	15.83	16.82	17.78
CI-RHA10-20	nil	14.06	17.87	18.43

**Table 8** Compressive Strength of HP SCP Systems with CEM III at 200% Flow

Type of Paste	Age (Days)			
	1	3	7	28
CIII-0-40	3.172	26.36	48.94	65.43
CIII-SF10-40	3.18	32.55	54.2	74.38
CIII-RHA10-40	1.648	35.32	56.5	79.83
CIII-0-60	0.931	11.12	20.36	31.96
CIII-SF10-60	1.285	15.89	31.6	49.03
CIII-RHA10-60	0.671	13.45	28.0	48.44
CIII-0-20	20.03	78.4	90.9	104.3
CIII-SF10-20	3.196	57.42	88.49	113.5
CIII-RHA10-20	2.33	60.0	89.42	116.60

**Table 9** Flexural Strength of HP SCP Systems With CEM III at 200% Flow

Type of Paste	Age (Days)			
	1	3	7	28
CIII-0-40	0	6.53	8.65	10.0
CIII-SF10-40	0	3.96	6.05	9.95
CIII-RHA10-40	0	6.66	8.56	10.66
CIII-0-60	0	2.88	6.07	8.00
CIII-SF10-60	0	4.56	5.73	8.206
CIII-RHA10-60	0	3.55	5.30	5.93
CIII-0-20	3.98	13.9	15.77	18.02
CIII-SF10-20	0	11.7	14.88	18.71
C11-RHA10-20	0	10	13.70	15.77

**Table 10** Paste Densities (Theoretical) and Powder Contents

Paste	Paste Density kg/ m <sup>3</sup>	Cement kg/m <sup>3</sup>	SF kg/m <sup>3</sup>	RHA kg/m <sup>3</sup>	RHAP kg/m <sup>3</sup>
CI-0-20	2321	1934	-	-	-
CI-SF10-20	2320	1786	178.6	-	-
CI-RHA10-20	2316	1782	-	178.2	-
CI-RHAP10-20	2330	1792	-	-	179.2
CIII-0-20	2236	1864	-	-	-
CIII-SF10-20	2245	1727	172.7	-	-
CIII-RHA10-20	2236	1720	-	172	-
CIII-RHAP10-20	2251	1731	-	-	173.1
CI-0-40	1952	1395	-	-	-
CI-SF10-40	1977	1318	131.8	-	-
CI-RHA10-40	1970	1313	-	131.3	-
CI-RHAP10-40	1979	1320	-	-	131.96
CIII-0-40	1901	1358	-	-	-
CIII-SF10-40	1925	1283	128.3	-	-
CIII-RHA10-40	1921	1281	-	128.1	-
CIII-RHAP10-40	1929	1286	-	-	128.6

**Table 11** Maximum Pore Radius (nm) of Various HP SCP Systems

HP SCP Systems	Age (Days)		
	1	3	7
CI-0-20	35	30.9	30
CI-RHA10-20	40	30	26
CI-RHAP10-20	32	28	27
CI-SF10-20	34	25	21
CIII-0-20	31	21	20
CIII-RHA10-20	34.8	16.6	15
CIII-RHAP10-20	36	18	16
CIII-SF10-20	34	17	14
CI-0-40	76	65	62
CI-RHA10-40	100	50	45
CI-RHAP10-40	102	58	55
CI-SF10-40	52	42	40
CIII-0-40	420	62	50
CIII-RHA10-40	300	40	30
CIII-RHAP10-40	320	42	38
CIII-SF10-40	105	30	20
CI-0-60	520	300	140
CI-RHA10-60	430	80	75
CI-RHAP10-60	500	270	90
CI-SF10-60	240	78	65
CIII-0-60	900	272	72
CIII-RHA10-60	700	200	35
CIII-RHAP10-60	530	260	50
CIII-SF10-60	460	100	25

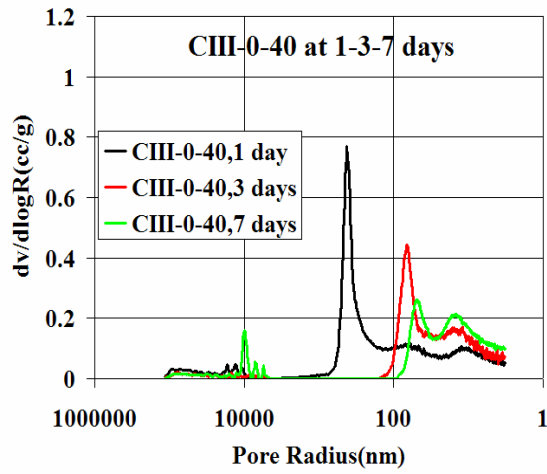


Fig. 1 MIP Results of CEM III Pastes at Three Ages at 40% Water

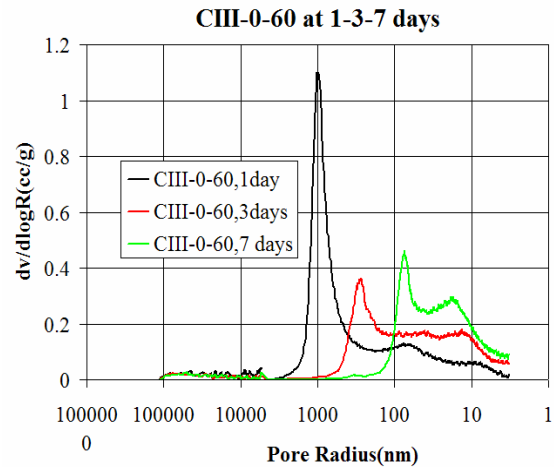


Fig. 2 MIP Results of CEM III Pastes at Three Ages at 60% Water

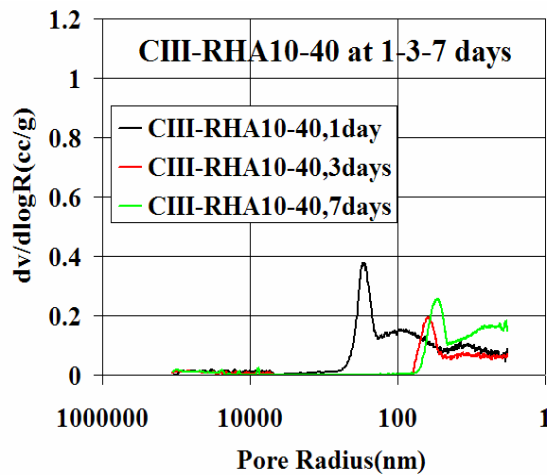


Fig. 3 MIP Results of CEM III With RHA at Three Ages at 40% Water

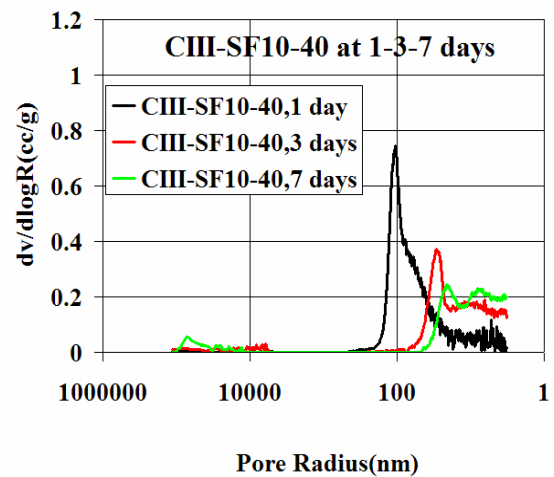
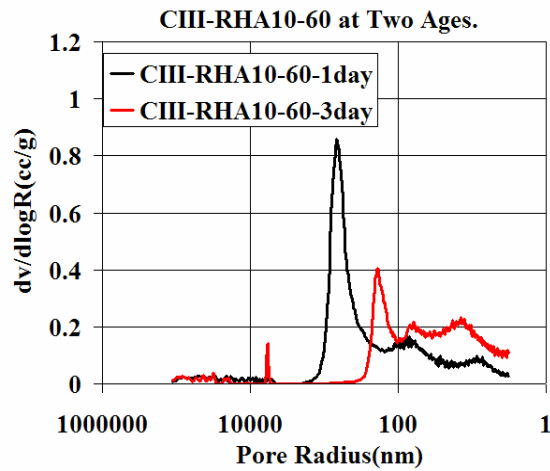
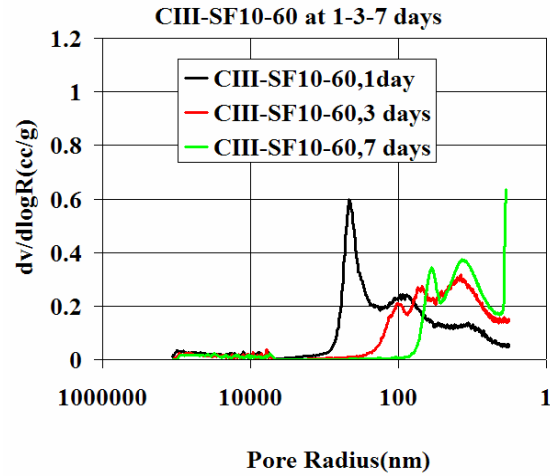


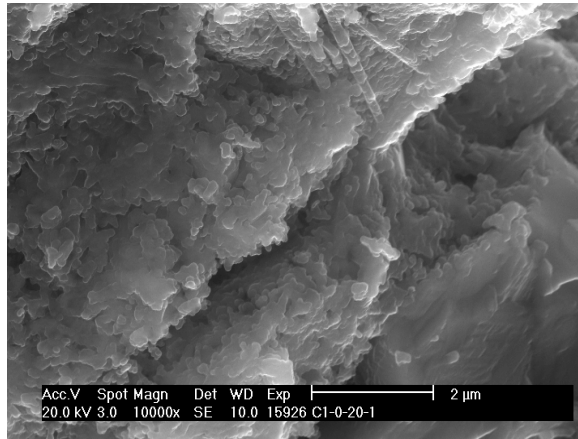
Fig. 4 MIP Results of CEM III With SF at Three Ages at 20% Water



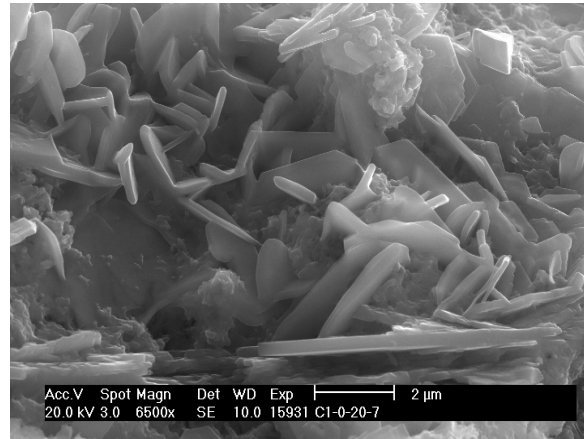
**Fig. 5** MIP Results of CEM III With RHA at Two Ages at 60% Water



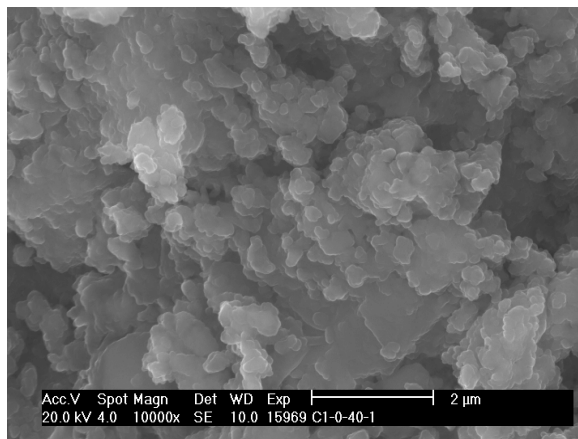
**Fig. 6** MIP Results of CEM III With SF at Three Ages at 60% Water



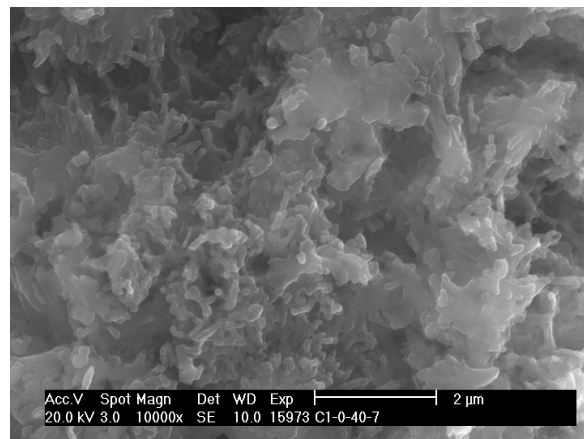
**Fig. 7** SEM for C1-0-20 HP SCP System at The Age of 1 Day



**Fig. 8** SEM for C1-0-20 HP SCP System at The Age of 7 Days



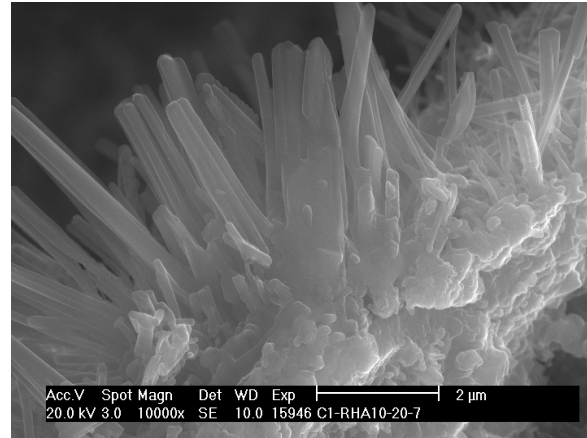
**Fig. 9** SEM for C1-0-40 HP SCP System at The Age of 1 Day



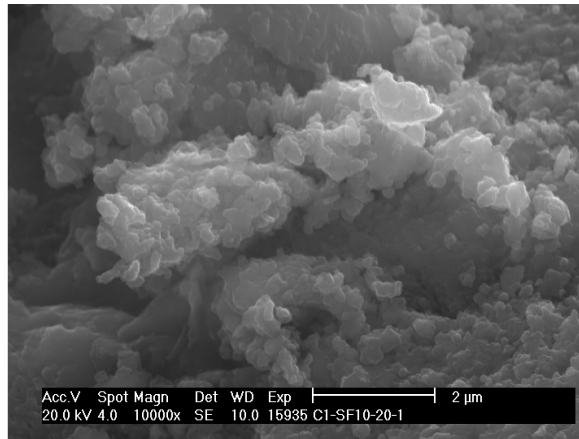
**Fig. 10** SEM for C1-0-40 HP SCP System at The Age of 7 Days



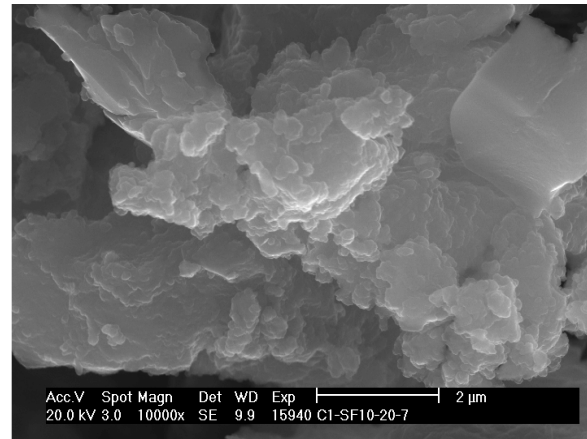
**Fig. 11** SEM for C1-RHA10-20 HP SCP System at the Age of 1 day



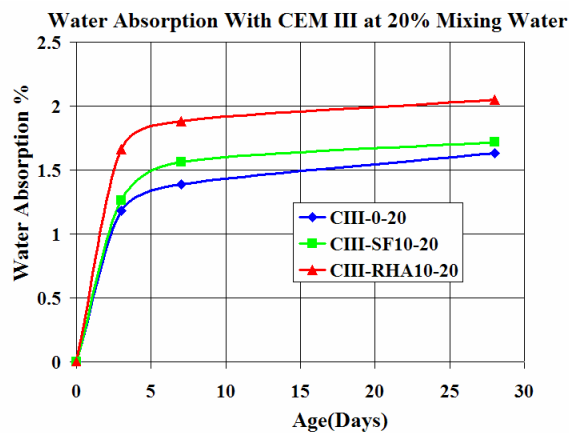
**Fig. 12** SEM for C1-RHA10-20 HP SCP System at The Age of 7 days



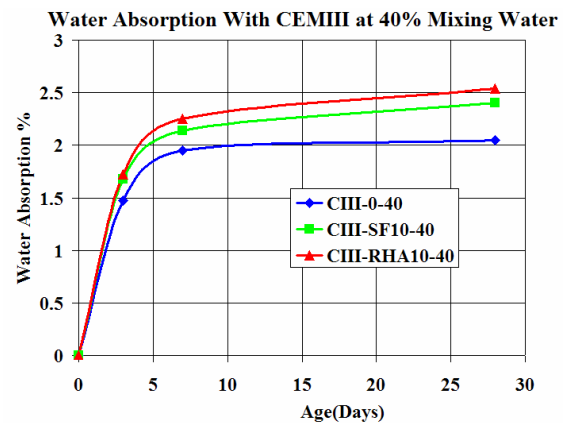
**Fig. 13** SEM for C1-SF10-20 HP SCP System at The Age of 1 Day



**Fig. 14** SEM for C1-SF10-20 HP SCP System at The Age of 7 Days



**Fig. 15** Water Absorption With CEM III at 20% Mixing Water Content



**Fig. 16** Water Absorption With CEM III at 40% Mixing Water Content



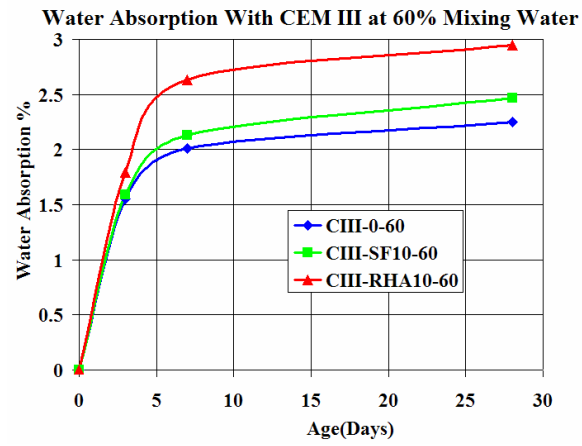


Fig. 17 Water Absorption With CEM III at 60% Mixing Water Content

$$\% \text{ WD of SRM} = \left[ \frac{(\text{Mass of cement} + \text{SRM}) \% \text{ WD of Mixture} - \text{Mass of Cement} \cdot \text{its } \% \text{ WD}}{\text{Mass of SRM}} \right] 100 \quad (1)$$

**ANNEXURE-B****Table 1** Properties of Cements Used

Cement Type	Water Demand (% Cement Mass)	Setting Times (hours)	
		IST	FST
CEM I 42.5 R	31	2.5	3.5
CEM II/A-LL 32.5 R	28	2.0	3.45
CEM III/B 32.5 N-NW/HS/NA	32	3.4	7.5

**Table 2** Flows of HP SCM Systems With CEM I 42.5 R With W/C=0.4 and W/P=0.2

Series	Cement Content kg/m <sup>3</sup>	SCM system	P/C Ratio %	Cone Spread, cm	T25 cm sec	V-Funnel Time, sec
SSSR1	541	1:1:2(C1:LSP:S1)	8.27	31.5	13.12	20.14
SSSR2	522	1:1:2(C1:FA:S1)	2.90	31.75	13.625	22.015
SSSR3	521	1:0.8:0.2:2(C1:FA:RHA:S1)	5.43	32.25	12.97	23.77
SSSR3A	523	1:0.8:0.2:2(C1:FA:RHAP:S1)	3.02	32.0	12.82	25.00
SSSR4	522	1:0.8:0.2:2(C1:FA:SF:S1)-	3.68	31.5	14.46	17.74

**Table 3** Flows of HP SCM systems With CEM II/A-LL 32.5R With W/C=0.4 and W/P=0.2

Series	Cement Content kg/m <sup>3</sup>	SCM system	P/C Ratio %	Cone Spread, cm	T25 cm, sec	V-Funnel Time, sec
SR1	539	1:1:2(C2:LSP:S1)	6.66	31	10.55	18.65
SR2	520	1:1:2(C2:FA:S1)	2.78	33.75	8.96	14.05
SR3	520	1:0.8:0.2:2(C2:FA:RHA:S1)	4.05	31.88	13.65	23.1
SR3A	521	1:0.8:0.2:2(C2:FA:RHAP:S1)	3.03	32.75	10.61	19.13
SR4	521	1:0.8:0.2:2(C2:FA:SF:S1)	3.28	32	11.85	12.6
SR5	539	1:1:2 (C2:LSP:S2)	9.27	31.8	12.39	16.525
SR6	520	1:1:2 (C2:FA:S2)	2.53	33.75	10.05	15.2
SR7	520	1:0.8:0.2:2 (C2:FA:RHA:S2)	3.29	32.25	13.91	25
SR8	520	1:0.8:0.2:2 (C2:FA:SF:S2)	2.78	32	13	14

**Table 4** Flows of HP SCM Systems With CEM III /B 32.5 N-NW/HS/NA 5R With W/C=0.4 and W/P=0.2

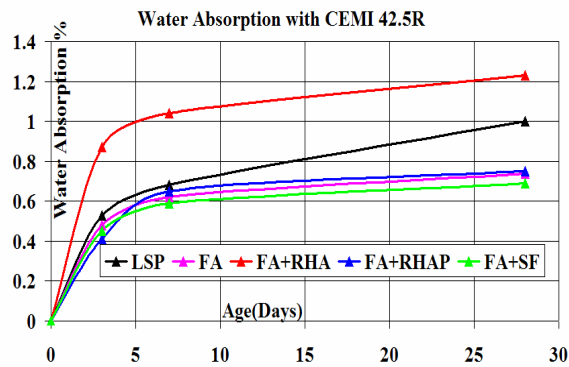
Series	Cement Content kg/m <sup>3</sup>	SCM system	P/C Ratio %	Cone Spread, cm	T25 cm, sec	V-Funnel Time, sec
SSR1	535	1:1:2(C3:LSP:S1)	7.5	31.37	13.08	18.91
SSR2	517	1:1:2(C3:FA:S1)	2.54	33	8.36	14.92
SSR3	516	1:0.8:0.2:2(C3:FA:RHA:S1)	4.05	32.25	14.2	28.5
SSR3A	518	1:0.8:0.2:2(C3:FA:RHAP:S1)	2.795	33.0	9.05	18.00
SSR4	517	1:0.8:0.2:2(C3:FA:SF:S1)	3.054	32.5	9.8	13.02
SSR5	535	1:1:2 (C3:LSP:S2)	9.82	31.9	11.75	16.43
SSR6	516	1:1:2 ( C3:FA:S2)	2.29	33	8.53	16.2
SSR7	516	1:0.8:0.2:2 (C3:FA:RHA:S2)	3.21	32	15.9	31.79
SSR8	517	1:0.8:0.2:2 (C3:FA:SF:S2)	2.54	32.4	9.56	13.025

**Table 5** 28 Day Strength Quantification of SCM Systems Using Various SRM's With CEM III

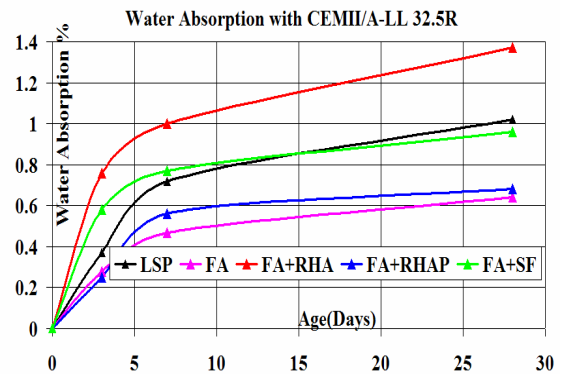
Powder	Flexure,(MPa)	Increase, (MPa)	Compression, (MPa)	Increase,(MPa)
LSP	10.56	Base Line	63.14	Base Line
FA	12.29	+1.73	100.0	+36.86
80%FA+20%RHA	12.58	+2.02	106.6	+43.46
80%FA+20%RHAP	13.33	+2.77	94.6	+31.46
80%FA+20%SF	12.59	+2.03	102.5	+39.36

**Table 6** First 24-Hour Linear Shrinkage Values of HP SCM Systems

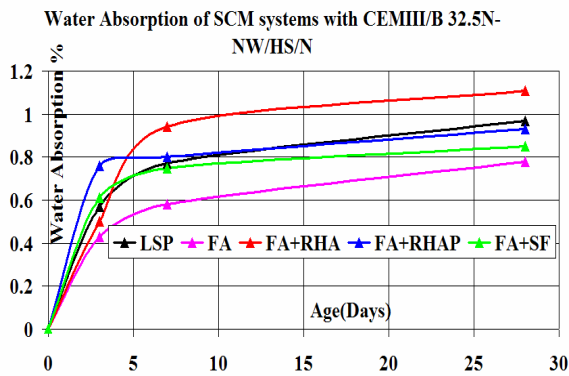
Formulation of HP SCM	Shrinkage/Expansion (µm/m) for Exposure Condition for S1		
	Open to Lab Environment	Covered with Plastic Sheet	Covered with Plastic Sheet and Insulation
C1-LSP	-2694.29	-1058.87	-880
C1-FA	-503.6	+126.03	+148.92
C1-FA+RHA	-1324.08	+38.05	+34.82
C1-FA+SF	-1954.62	-246.87	-206.28
C2-LSP	-2764.77	-927	Not measured
C2-FA	-352.6	+165.2	-do-
C2-FA+RHA	-1581.27	+64	-do-
C2-FA+SF	-2259	-269.58	-do-
C3-LSP	-2787.87	-1149.7	-do-
C3-FA	-268	+98	-do-
C3-FA+RHA	-1131.38	+33.36	-do-
C3-FA+SF	-1176	-6.17	-do-



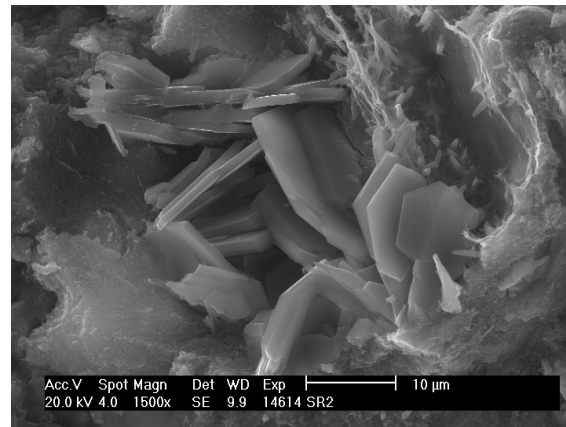
**Fig. 1** Water Absorption of SCM Systems Using Different SRM's With CEM I



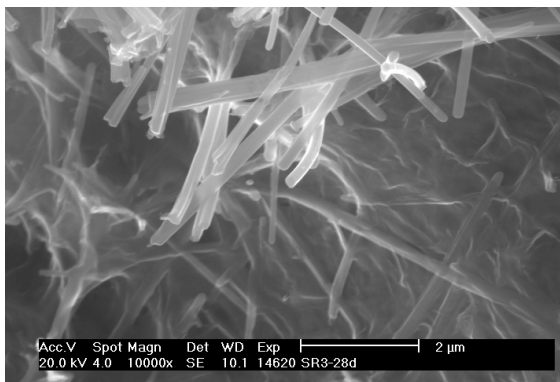
**Fig. 2** Water Absorption of SCM Systems Using Different SRM's With CEM II



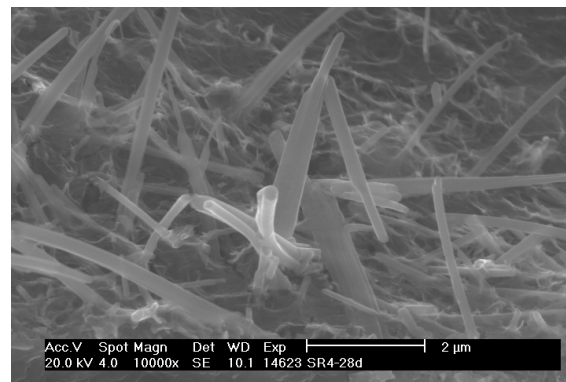
**Fig. 3** Water Absorption of SCM Systems Using Different SRM's With CEM III



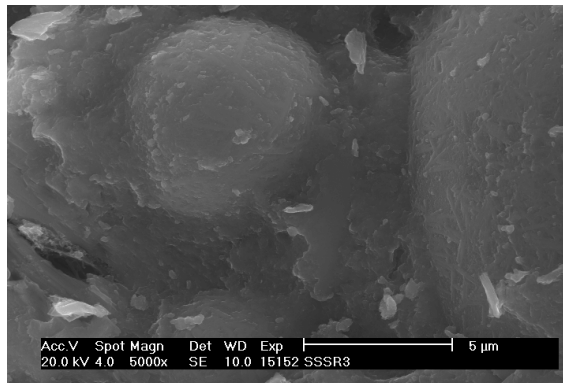
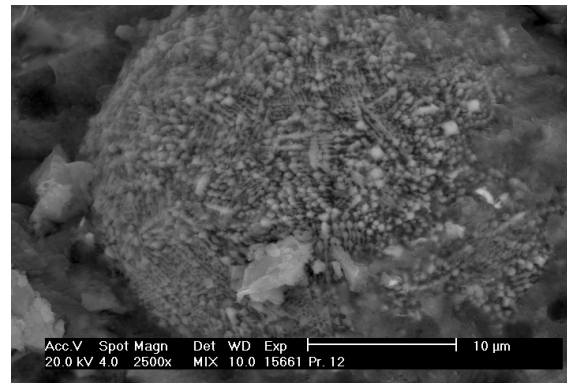
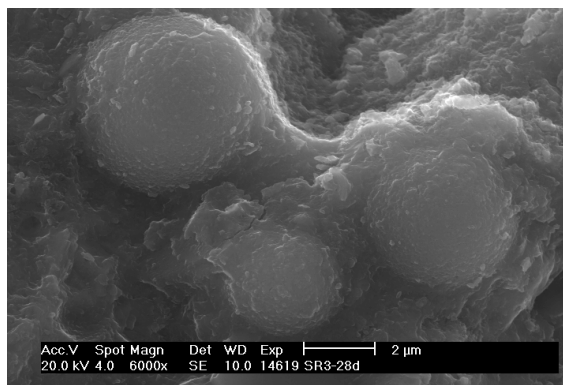
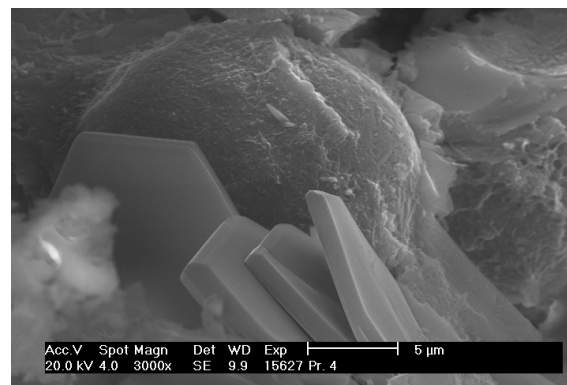
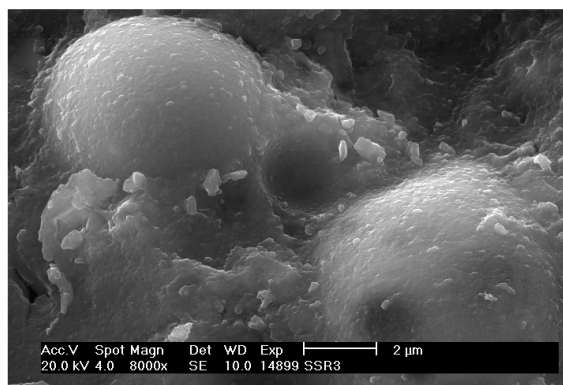
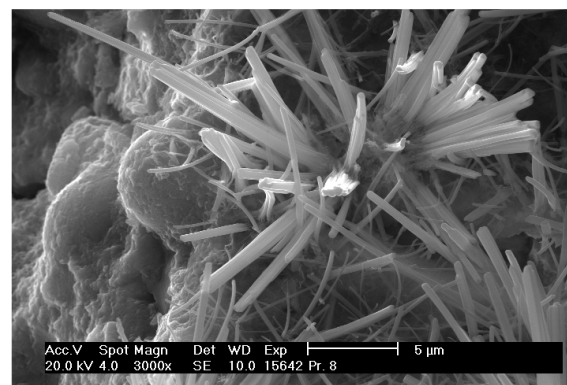
**Fig. 4** SEM of C2-FA-S1 at 28 Days Age



**Fig. 5** SEM of C2-FA+RHA-S1-28 Days



**Fig. 6** SEM of C2-FA+SF-S1-28 Days

**Fig. 7(a)** CEM I-FA+RHA-28 Days, x5000**Fig. 7(b)** CEM I-FA+RHAP-28 Days, x2500**Fig. 8(a)** CEM II-FA+RHA-28 Days, x6000**Fig. 8 (b)** CEM II-FA+RHAP-28 Days, x3000**Fig. 9(a)** CEM III-FA+RHA-28 days, x8000**Fig. 9(b)** CEM III-FA+RHAP-28 days, x3000

**Table 7** Ca (OH)<sub>2</sub> Quantity Based on Thermal Analysis and Theoretical Approach

Formulations	Ca(OH) <sub>2</sub> Quantity (Mass %) at The Age of (Days)		
	1 day	7 day	28 day
CEM II-LSP-S1	2.9	3.3	3.33
CEM I-LSP-S1	-	-	3.32
CEM I-FA-S1	-	-	1.58
CEM II-FA-S1	1.66	2.1	1.677
CEM II-FA+RHA-S1	0.544	0.54	0.42
CEM II-FA+RHAP-S1	1.208	2.526	2.953
CEM II-FA+SF-S1	0.76	0.64	0.42
CEM I-FA+SF-S1	-	-	0.57
CEM I-FA+RHA-S1	-	-	1.044
CEM I-FA+RHAP-S1	1.87	2.37	2.19
CEM III-FA+RHAP-S1	0.577	0.424	0.084

**Table 8** Reference Intensities of Ca(OH)<sub>2</sub> With Various SRM's using CEM II/A-LL 32.5 R Lafarge

Series	Ref. Intensity at angle 2θ = 34.085 at Age(Days)			
	1	3	7	28
SR1-C2:LSP:S1	369	400	562	441
SR2-C2:FA:S1	272	286	174	234
SR3-C2:FA:RHA:S1	240	222	202	151
SR4-C2:FA:SF:S1	246	106	207	119
SR5-C2:LSP:S2	282	424	471	-
SR6-C2:FA:S2	250	342	299	-
SR7-C2-FA:RHA:S2	196	177	250	-
SR8-C2-FA:SF:S2	199	92	139	-

**Table 9** Reference Intensity of Portlandite at Four Age Intervals

Series	Elements	Angle 2θ, Degrees	Ref. Intensity at Age (Days)			
			1	3	7	28
SR1	Portlandite	34.05	369	400	562	441
SR2	Portlandite	34.05	272	286	174	234
SR3	Portlandite	34.05	240	222	202	151
SR4	Portlandite	34.05	246	106	207	119
SR5	Portlandite	34.05	282	424	471	-
SR6	Portlandite	34.05	250	342	299	-
SR7	Portlandite	34.05	196	177	250	-
SR8	Portlandite	34.05	199	92	139	-



## ANNEXURE C-SCC

Table 1 SCC Mix Ingredients of Formulations

Mix.No\ constituents	1	2	3	4	5	6	7	8	9	10	11
Cement-kg/m <sup>3</sup>	C132.5R, 380	C132.5R- 380	CII-380	CII-380	CII-380	CII-380	CII-380	CII-380	CI-330	CI-330	CII-380
Water- kg/m <sup>3</sup>	168	171	171	171	171	171	171	171	148.5	148.5	171
FA kg/m <sup>3</sup>	147	147	147	147	147	147	147	147	197	197	147
Sand 0-2 mm kg/m <sup>3</sup>	635	635	635	732	732	732	813	898	919	919	893
Aggregate- 2/8 mm kg/m <sup>3</sup>	538	538	538	439	439	439	406	366	376	376	366
Aggregate- 8/16mm kg/m <sup>3</sup>	456	456	455	455	455	455	406	366	376	376	366
SP(%cement mass),kg/m <sup>3</sup>	1.3,4.94	1.8,6.84	1.8,6.8	1.8,6.84	1.9,7.22	1.9,7.22	2,7.6	2.6,9.88	3.4,11.22	4.2,13.86	2.8,10.9
VEA(%cement mass), kg/m <sup>3</sup>	0.64,2.4	0.89,3.4	0.95,3.6	0.95,3.6	1.05,4	1,3.8	1.3,4.94	1.2,4.56	1.3,4.28	1.3,4.28	1.4,5.32
Grading	G1	G1	G1	G2	G2	G2	G4	G6	G6	G6	G6
w/c	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
w/cm	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.28	0.28	0.32

Table 1 -Continued

Mix.No\ constituents	12	13	14	15	16	17	18	19	20	21	22
Cement-kg/m <sup>3</sup>	C1-330	C1-330	CII-340	C1- 300	C1- 330	C1- 300	C11/BM, 340	C11/BM, 350	C1-300	C1-300	C11- 340
Water- kg/m <sup>3</sup>	165	188	153	171	185	171	153	157	171	171	160
FA kg/m <sup>3</sup>	197	197	187	227	197	227	187	177-2	227	227	187
Sand 0-2 mm kg/m <sup>3</sup>	896	793	830	887	789	795	829	819	795	795	815
Aggregate- 2/8 mm kg/m <sup>3</sup>	366	397	415	362	394	398	414	414	397	398	408
Aggregate- 8/16mm kg/m <sup>3</sup>	366	397	415	362	394	398	414	414	397	398	408
SP(%cement mass), kg/m <sup>3</sup>	3.1,10.3	2.65,8.76	1.91,6.46	2.5,7.5	2.5,8.3	2.4,7.2	2.4,8.15	2.4,8.4	2.3,7.2	2.45,7.35	2.2,7.47
VEA(%cement mass), kg/m <sup>3</sup>	1.3,4.3	1.35,4.5	1.5,5.1	1,3	1,3.3	1.2,3.6	0.9,3	0.9,3.15	1.25,3.76	1.12,3.36	1.1,3.75
Grading	G6	G4	G4	G6	G4	G4	G4	G4	G4	G4	G4
w/c	0.5	0.57	0.45	0.57	0.57	0.57	0.45	0.45	0.57	0.57	0.47
w/cm	0.31	0.35	0.29	0.32	0.35	0.32	0.29	0.29	0.32	0.32	0.3

**Table 2** Flow Properties of Mixes Designed for Slump Spread of 65-68 cm

Grading	G4	G6			G4	G6	G4
Mix number	7	8	11	12	13	15	19
T50,s	8.5	7	6	9.3	6.4	8.1	8.5
Spread,cm	65	68	67	68	67	68	68
Funnel, Time, s	12.8	10.3	15.8	14.6	9.2	12.2	15
L-box	11	8.37	13.4	14	7.18	12.3	15.9
T60,s-h2/h1	0.93	0.98	0.92	0.96	0.98	0.96	0.97
J-ring	14.8	12.3	13.3	20	8.91	16.7	13.4
T50, spread. cm	60	63	66.5	62.5	66	63.4	66
Air %	2.7	2.9	2.6	2.8	1.9	2.5	2.2

**Table 3** Flow Properties of Mixes Designed for Slump Spread of 69-72 cm

Grading	G1			G2			G6					
Mix Number	1	2	3	4	5	6	14	17	18	20	21	22
T50,s	6	5.5	5.6	7	8	7	11.5	5.8	9.2	6.7	6.3	9.3
Spread, cm	71	71	69	70	69	71	69	72	71	70.5	71	70
Funnel, Time, s	18	12.4	11.6	9	10.7	10.6	18.8	11.8	18.5	10.1	10.3	15.4
L-box	9	9.6	6.2	7	7	9.2	17.5	12.6	19.6	11.4	9.7	14.1
T60,s- h2/h1	1	1	0.96	1	1	1	0.92	0.96	0.9	0.96	0.93	0.93
J-ring	12	7.7	8.7	10	11.5	11.8	19.6	13.6	17.9	11	12	18.1
T50, spread,cm	63	71	68	69	66.5	68.5	63	63.5	67.5	68.5	67	66.5
Air %	1.0	1.8	1.5	1.7	2.1	1.9	2.5	1.6	2.1	2.1	1.9	2.5

**Table 4** 28 Day Compressive Strength of Some SCC Mixes

Mix Number/Cement Type	Compressive Strength, MPa
9, CI	80
10,C1	75
11,CII	68
12,CI	70
13,CI	66
15,CI	65
16,CI	68
17,CI	70
18,CII/B-M	74
20,CI	68
21,CI	68
22,CII	63