A STUDY OF SELF COMPACTING CEMENTITIOUS SYSTEMS USING METAKAOLIN AND GLASS POWDER

By

Manan Mansoor Qureshi

2010-NUST-MS-PhD-Str Engg-11

A Thesis submitted in partial fulfillment of
the requirement for the award of degree of
Master of Science
in
Structural Engineering

National Institute of Transportation
School of Civil and Environmental Engineering
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This is to certify that the

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Has been accepted towards the partial fulfillment

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(Prof. Dr.-Ing Syed Ali Rizwan, PhD)

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ABSTRACT

Self Compacting Cementitious Systems (SCCS) are a modern technology in the field of high performance concrete which has been used extensively throughout the world. Some major applications of this technology involve massive placements in heavily reinforced sections such as tunnel linings, high rise buildings, rafts and pile foundations, bridge piers, transportation structures, prestressed concrete members and repair of structures like aircraft runways etc. This technology offers a uniform degree of compaction throughout the concrete placement and therefore, a uniform durability of the structure. SCCS contains high powder content with low w/p ratio than conventional concrete, hence, these systems provide a better overall response in terms of volumetric stability, packing density, ease of placement, evolution of heat of hydration, strength development and higher durability. In High Performance Concrete (HPC), all cement particles do not get hydrated. Therefore, in order to economize the system, secondary raw materials (SRM's) are used. These SRM's improve the microstructure and the overall response of concrete in both fresh and hardened state as well as make it more environment friendly.

This research was undertaken to evaluate the feasibility of using Metakaolin (MK), an artificially manufactured pozzolan and Glass Powder, a pozzolan derived from finely crushing and grinding commercially manufactured glass, and to study their benefits in Self Compacting Mortars (SCM's). The parameters studied include the particle characterization of SRM's, flow behavior, strength development, and microstructural characterizations.

The results indicate that Metakaolin and Glass Powder, when used to replace 10% of cement mass in replacement mode, enhance the properties of self compacting mortar formulation like flow, heat of hydration, strength development, microstructure and shrinkage etc. The finer particle size of Metakaolin leads to a higher water/SP demand and faster setting time for formulation with Metakaolin in replacement mode. This is also confirmed by its early and higher calorimetric peak. The formulation with Glass Powder in replacement mode requires more SP content owing to its larger particle size as compared with Metakaolin. This is also confirmed by its setting times and lower calorimetric peak which are delayed as compared with Metakaolin formulations. The Control mix formulation shows a lesser demand for water and SP but shows delayed setting time and slightly lower calorimetric peak as compared with Metakaolin but higher than Glass Powder. The strength development is also an important parameter as strength gain at a specified age varies and depends on the degree of pozzolanic activity which is in turn dependent on the physical and chemical characteristics of the SRM. Metakaolin shows a strength development similar to control mix while Glass Powder shows slightly less strength at comparative ages owing to its larger particle size and slower hydration. This strength evolution is also evident from MIP curves of SCM formulation in terms of pore refinement and at times discontinuous porosity for Metakaolin and Glass Powder. The volumetric stability of the cementitious system is also affected by Metakaolin and Glass Powder as Metakaolin produces more early linear shrinkage than Control mix due to its small size, latent reactivity and early evolution of heat of hydration whereas Glass Powder shows less shrinkage owing to its large particle size and delayed evolution heat of hydration. Thus, we can deduce that both SRM's contribute positively towards enhancing the different characteristics of the cementitious systems and can be incorporated successfully in self compacting cementitious systems.

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LIST OF NOTATIONS

AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society of Testing and Materials
BN	Bentonite
C_2S	Di – Calcium Sulfate
C_3A	Tri – Calcium Aluminate
C_3S	Tri – Calcium Sulfate
C_4AF	Tetra – Calcium Alumino Ferrite
CAH	Calcium Aluminate Hydrate
CH	Calcium Hydroxide
CSH	Calcium Silicate Hydrate
EDAX	Energy Dispersive X – Ray Analysis
GGBFS	Ground Granulated Blast Furnace Slag
GP	Glass Powder
HPC	High Performance Concrete
ITZ	Interfacial Transition Zone
LSP	Lime Stone Powder
MK	Metakaolin
MIP	Mercury Intrusion Porosimetery
OPC	Ordinary Portland Cement
PCE	Polycarboxylate Ether
RILEM	Réunion Internationale des Laboratoires et Experts des Matériaux, systèmes de construction et ouvrages
RHA	Rice Husk Ash
RM	Replacement Mode
SCC	Self Compacting Concrete

SCP	Self Compacting Paste
SCM	Self Compacting Mortar
SF	Silica Fume
SP	Super Plasticizer
SEM	Scanning Electron Microscopy
SRM	Secondary Raw Materials
VMA	Viscosity Modifying Agents
w/c ratio	Water Cement Ratio
w/p ratio	Water powder ratio
XRD	X – Ray Diffraction

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CHAPTER 1 – INTRODUCTION

1.1 General

Self-compacting concrete (SCC) as defined by ACI 237R – 07, is a highly flowable, non-segregating concrete that can spread into place, fill the formwork, and encapsulate the reinforcement without any mechanical consolidation [1]. It is a kind of high performance concrete (HPC) that is highly fluid, able to consolidate under its own weight and is more durable, stronger and easy to place in congested reinforcement. A typical Self Compacting Cementitious System is usually achieved by using conventional concrete materials by using a higher powder content and lower water content and with addition of mineral admixture for improvement in both fresh and hardened states of concrete.

Self Compacting Cementitious Systems (SCCS) are a modern technology in the field of concrete materials which have been used extensively throughout the world. Some major applications of this technology involve massive placements in heavily reinforced sections such as tunnel linings, high rise buildings, rafts and pile foundations, bridge piers, transportation structures, prestressed concrete members and repair of structures like aircraft runways etc. The major benefit of this technology is that it offers a uniform degree of compaction throughout the concrete placement and therefore, a uniform durability of the structure. SCCS contains high powder content with low w/p ratio than conventional concrete, hence, these systems provide a better overall response in terms of volume stability, packing density, ease of placement, heat of hydration, strength development and higher durability. In High Performance Concrete (HPC), all cement particles do not get hydrated. Therefore, in order to economize the system, secondary raw materials (SRM's) are used. These SRM's improve the microstructure and the overall response of concrete in both fresh and hardened state as well as make it environment friendly.

Self Compacting Concrete was first developed in 1988 by Dr Okamura at University of Tokyo. Since then, extensive research has been carried out to improve its properties by incorporating various Secondary Raw Materials (SRM's) along with chemical admixtures in SCCS. However, in Pakistan, despite the abundance of locally available pozzolanic materials like Wheat Straw Ash, Rice Husk Ash (RHA), Ground Granulated Blast Furnace Slag (GGBFS) and Bentonite (BN), there is very little research carried out on the feasibility of using these materials in cementitious systems due to non-availability of response data. Once the results of these SRM's are fully understood, they will hopefully be incorporated in SCCS's in Pakistan.

Self Compacting Concrete was first developed in Japan when the need arose to produce a concrete which would possess enhanced durability, workability and compact under its own self weight without any manual compaction. This was a rising problem in Japanese construction industry due to gradual reduction in number of skilled workers leading to a reduction in quantum of construction. Thus, self compacting concrete was proposed and developed by Okamura [2] in University of Tokyo. Due to its versatile nature and wide range of application, the use of this modern self compacting concrete spread very rapidly throughout the world. However, in Pakistan, the application and use is very limited due to non-availability of chemical and mineral admixtures and cement at cheap prices and also due to lack of comprehension of the basic concepts of self compacting concrete and an over-dependence on outdated construction techniques in our construction industry. This research is carried out to evaluate the use of local secondary raw materials (Metakaolin and Glass Powder) in self compacting cementitious systems.

1.2 Self Compacting Cementitious Systems (SCCS)

Self Compacting Concrete Systems are divided into three basic types depending on how the segregation resistance is achieved. They are powder type, viscosity modifying agent type and combination type. In powder type SCC, a low water-to-powder ratio or high powder content (cement as well as secondary raw material) is used to achieve adequate segregation resistance. Whereas, in viscosity modifying agent type, segregation resistance is mainly achieved by use of high dosages of viscosity enhancing agents. In combination type SCC, segregation resistance is achieved through a combination of both moderate VMA's with low powder contents. This produces a very durable concrete which excellent segregation resistance as it utilizes lower SP contents. Hence, hydration kinetics is not changed to a great extent. The above also implies that the SCC shall have low yield stress as well as adequate viscosity. High deformation is achieved by use of high range super plasticizers and segregation resistance is achieved by any of the above techniques. In this current research, the self compacting mortar (SCM) system, a high powder content (cement and SRM) was used along with polycarboxylic ether (PCE) based powder type super plasticizer Melflux 2651 F. The powders used include cement, Metakaolin and Glass Powder.

1.3 Secondary Raw Materials (SRM's)

Concrete is used throughout the world as a construction material for building infrastructure, dams, tunnels, pavements etc. The process of cement production involves heating calcium carbonate, thus, producing lime and releasing carbon dioxide directly and indirectly through the use of energy whose production involves the emission of CO_2. According to recent survey by USGS [3], global production of cement was 3.3 billion tonnes. This impact of cement production at such a global scale has led to rising energy costs, depletion of natural resources and rise in pollution It is a well established fact that for every one ton of cement produced, 900 kg of CO_2 is released into the atmosphere and cement industry accounts for 5% of global man-made CO_2 emissions [4]. Therefore, an effort has been undertaken to reduce clinker content in cement to reduce cement consumption. This has led to the development of different classes of cements (CEM I, CEM II, CEMIII, CEM IV and CEM V) as per BS EN 197 by adding different materials like slag etc and reducing clinker content [5]. The same can be achieved by reusing industrial wastes and using naturally available environment friendly materials to replace cement. This helps to contribute towards a green future and sustainable development.

These materials are called secondary raw materials (SRM's), supplementary cementitious materials or sometimes as 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 [6]. Secondary Raw Materials (SRM's) can be further classified into two types:

- **Pozzolans**
- **Inert Fillers**

SRM's are usually inert or pozzolanic in nature. Inert fillers usually affect the physical properties of cementitious systems. For example, LSP particles being very fine, improve the packing density of the matrix as well as providing nucleation centers for hydrates, thus enhancing the microstructure of concrete [6]. Pozzolanic SRM's not only provide physical benefits in the matrix but also provide active silica in the matrix which can react with CH (pozzolanic reaction) to produce further cementing compounds (CSH), thus leading to improved durability and increased strength at later stages.

Secondary raw materials are basically used to replace a portion of cement in the concrete matrix in replacement mode. These SRM's acts as filler in voids/pores in the SCC/HPC as not all cement particles are hydrated. Therefore, in order to optimize SCC mix design, a portion of cement is replaced by SRM's so that they can fill the voids in the matrix. The pozzolanic SRM's actively react with calcium hydroxide in the concrete matrix to form further cementitious compounds, thereby refining the pore structure of the system and reducing pore size or making pores discontinuous. This results in increased strength and durability [6]. The replacement of cement content by secondary raw materials also contributes indirectly towards the benefit of the environment by reducing cement demand and thus, reducing the CO_2 emission during the production of cement.

1.4 Pozzolans

A pozzolan is defined in ASTM C 125 [7] as “*a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties*”.

The term "pozzolan" came from a U.S. simplification of "pozzolana" which evolved from the location "Pozzuoli, Italy" where the Romans found a reactive silica-based material of volcanic origin which they called “pulvis puteolanus” [8, 9].

Pozzolans are both naturally occurring in nature and artificially manufactured as by-products of different industrial processes. The processing of natural pozzolans is limited to crushing, grinding and sieving. Artificial pozzolans are usually obtained as by-products of different industrial processes and are tailored for use in concrete applications after careful processing (calcination) at optimum temperature to induce pozzolanic reactivity. Typical examples of pozzolans include Fly Ash, silica Fumes, Metakaolin, Ground Granulated Blast Furnace Slag, Bentonite, Rice Husk Ash, Glass Powder etc.

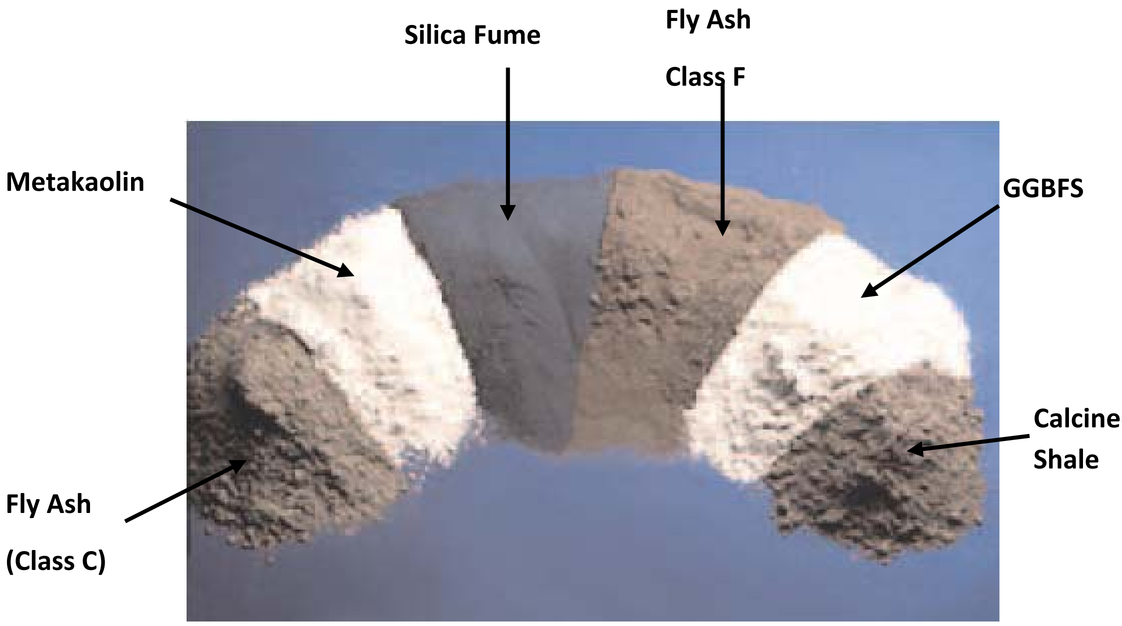


Fig 1.1: Secondary Raw Materials [95]

1.4.1 Natural Pozzolan

Natural pozzolans can occur in two forms: either a consolidated rock-like form underlying a layer of overburden (such as Rhenish trass near Coblenz on the river Rhine or in Bavaria, or in

Romania and the U.S.S.R.), or in fragmentary and unconsolidated forms, which appears to be the more usual type of deposit.

However, the existence of rocks of volcanic origin within a country does not automatically make them suitable for use as pozzolans; pozzolanic materials form from volcanic rock under fairly specific environmental conditions.

The naturally occurring pozzolans include volcanic ashes, opaline shales and cherts, calcined diatomaceous earth and burnt clays [10, 11]. According to ASTM C 618 [12], a variety of naturally occurring materials or their modifications or by-products can be described as pozzolanic materials. However, the pozzolanic materials differ widely in their impact on cement–based systems and this is primarily related to their physical and chemical characteristics. Natural pozzolans conforming to Class N as per ASTM C 618 are further processed which includes drying, grinding and calcining [12].

1.4.2 Artificial Pozzolan

These pozzolans are usually obtained as by-products of different industrial processes. They may or may not require processing before use. According to ASTM C 618 [12], these pozzolans are classified as Class C and Class F type pozzolans depending upon silica (SiO_2) and lime (CaO) content. It must be noted that pozzolans which require calcination to induce pozzolanic activity would also presumably be classified as artificial pozzolans but if calcination was not required, then they would be a natural pozzolan [12]. For example, Fly Ash which is an artificial pozzolan is classified as Type C and Type F depending on the origin of material from which it is derived

- <u>Class C Fly Ash</u>

  Fly ash produced from the burning of younger lignite or subbituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash will harden and gain strength over time. Class C fly ash generally contains more than 20% lime (CaO). Unlike Class F, self-cementing Class C fly ash does not require a cementing agent.

- <u>Class F Fly Ash</u>

  The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash is pozzolanic in nature and contains less than 20% lime (CaO) but does not possess cementing properties and requires a cementing agent like cement to produce cementing compounds (pozzolanic reaction).

1.4.3 Mechanism of Pozzolanic Reaction

When cement particles come into contact with water in the cementitious system, an exothermic reaction takes place leading to release of heat of hydration is released and formation of Calcium Silicate Hydrate (CSH) gel along with Calcium Hydroxide and Ettringite. Calcium Hydroxide ($CaOH_2$) is found in the concrete matrix in shape of hexagonal-shaped crystals having a prominent cleavage. As these cleavage plates have a tendency to split apart under shear, presence of excess Calcium Hydroxide in concrete matrix can lead to weak microstructure and hence, durability problems. Pozzolans reduce weak Calcium Hydroxide (CH) crystals in the matrix by reacting with Calcium Hydroxide. The extent of this reaction depends on the silicate and aluminate phases in pozzolan along with vitreous phase in the matrix. The reaction is generally slower than hydration reaction of the cement, thus resulting in low heat of hydration and strength development. The reaction of hydration of ordinary cement and pozzolanic cement is represented schematically by the simple equation as below:

Portland cement

$$C_3S + H_2O \xrightarrow{\text{fast}} CSH + CH$$

Portland – Pozzolan Cement

$$\text{Pozzolan} + CH + H_2O \xrightarrow{\text{slow}} CSH$$

According to Lea [13], these secondary CSH compounds have lower alkalinity and therefore, offer more resistance to aggressive environments (marine structures).

1.5 Metakaolin

Metakaolin is a manufactured pozzolanic mineral admixture, which significantly enhances many performance characteristics of cement-based mortars, concretes and related products. It is derived from purified kaolin clay, is a white amorphous alumino-silicate, which reacts aggressively with calcium hydroxide, a by-product of cement hydration, to form additional cementing compounds. Metakaolin has a high pozzolanic activity and micro filler properties very similar to those of silica fume. Both Metakaolin (MK) and Silica Fume (SF) increase the water demand of the mixes [14].

The term kaolin is derived from Kao-ling, a village near Jingdezhen, Jiangxi province China. The term loosely translates to “white hill” and has been related to the name of a mountain in China that yielded the first kaolins that were sent to Europe. The meta prefix in the term is used to denote change that is taking place in manufacture of Metakaolin, i.e. the dehydroxylization of kaolinite brought on by the application of heat over a defined period of time. Metakaolin occurs in nature in the form of clay mineral called Kaolinite. Kaolinite is the mineralogical term that is applicable to all kaolin clays. Kaolins are a classification of clay minerals which are phyllosilicates, i.e. a layered silicate material. The study of the stacked arrangement and the individual layers in the stack are the defining factors of classification. Kaolin is a mineral typical of continental weathering where solutions percolate and are purified over time.

The two types of Metakaolin used in this present study are purchased from different international sources. One is MetaStar 501 manufactured by Imerys Performance Minerals North America and the other Metakaolin is imported personally from international suppliers in China.

1.5.1 Deposits of Kaolinite in Pakistan

- **Swat Kaolin**

The Swat Kaolin deposits lie in the low hilly terrain of Shahderai village, 20 km Southwest of Mingora district, Swat valley. The total reserves were estimated 2.8 million tons. The same type of China clay has also been found in Shahdin and Doshagram near Matta [15].

- **Tharparkar Kaolin**

In Sindh, it is found in Nagar Parkar, in Tharparkar District. The investigation of China clay deposits of Nagar Parker area revealed that the clay consists mainly of Kaolinite and quartz along with minor quantity of goethite, etc. The main areas of Nagar Parkar, in Tharparkar District where workable deposits have been proved so far are:

- Paradhoro
- Dedhvero
- Dungri
- Dudwa
- Motijo Vandio

The total reserves proved in these areas are of the order of 3.5 million tons [16].

1.6 Glass Powder

Glass is an amorphous (non-crystalline) solid material. Glasses are typically brittle and optically transparent. The most familiar type of glass, used for centuries in windows and drinking vessels, is soda-lime glass, composed of about 75% silica (SiO_2) plus Na_2O, CaO, and several minor ingredients. Often, the term glass is used in a restricted sense to refer to this specific use. In science, however, the term glass is usually defined in a much wider sense, including every solid that possesses a non-crystalline (i.e. amorphous) structure and that exhibits a glass transition when heated towards the liquid state. In this wider sense, glasses can be made of quite different classes of materials: metallic alloys, ionic melts, aqueous solutions, molecular liquids, and polymers.

Glass in general is a highly transparent material formed by melting a mixture of materials such as silica, soda ash and $CaCO_3$ at high temperatures followed by cooling during which solidification occurs without crystallization [17].

Glass is produced in huge quantities throughout the world due to rapid urbanization and development of infrastructure. The recycling of glass is expensive; therefore, most of the consumed glass is disposed as land-fill at various sites. In United States, approximately 12.8 million tons of waste glass was disposed in 2005 as land-fill while only 2.75 million tons were recycled [18]. New York City alone collects more than 100,000 tons annually and pays material recycling facilities (MRFs) up to $45 per ton for the disposal of the glass which equates to approximately 4,500,000 USD of public money [19]. However, the disposal of waste glass as land-fill is not an environment friendly practice as glass is a non-biodegradeable material. Use of waste glass in construction industry as cement replacement and as aggregate is among the most attractive options because of the large quantity consumptions of the materials, relatively low quality requirements and widespread construction sites.

The main concerns regarding the use of waste glasses as aggregates in cement concrete is the possibility of Alkali Silica Reaction (ASR), a reaction which occurs in concrete, between glass aggregate containing high reactive silica content and alkalis from the cement. This silica reacts with hydroxyl ions in the concrete pore solution and produces a gel which absorbs water and swells. This weakens the ITZ (aggregate-cement bond) and causes cracking [20]. Very limited work has been conducted for the use of ground glass as a cement replacement in concrete [21]. Recently, some attempts have been made to use the waste glasses as raw siliceous materials for the production of Portland cement [22]. It was found that the addition of glass into cement raw mix results in the formation of more liquid phase between 950 and 1250^oC, decreases the C_3S

content in the clinker and results in the formation of NC_8A_3, which results in flash setting due to the high alkali content and the formation of compound $2CaSO_4 \cdot K_2SO_4$ [22]

1.7 Research Objectives

Pakistan is a developing country and we have a vibrant construction industry. However, the overall standard of construction in Pakistan is very low and costly as compared to other developing countries. This is due to the fact that we are using the same out-dated construction techniques from the previous decades and lag behind in our knowledge of modern construction technologies. Even in my personal experience working in a design office, we are more concerned with slump and compressive strength of concrete and disregard other important parameters. It was felt that in order to achieve an efficient design and construction; we have to incorporate modern ideas and techniques in our industry.

Thus, a research program was devised to study locally available Secondary Raw Materials as there is very little research carried out on the feasibility of using these materials in cementitious systems. The focus of this research is to assess the possibility of using Metakaolin and Glass Powder as Secondary Raw Materials in self-compacting cementitious systems. The specific goals were:

- To study the behaviour of fresh concrete including particle characterization,
- Flow characteristics,
- Strength development,
- Microstructural investigation and;
- Volume stability.

The main benefit of this study is to analyze the potential of locally available secondary raw materials (SRM's) and provide physical evidence and information to the local construction industry about the benefits of using these SRM's while utilizing the modern concrete practices. This will prove helpful in improving the quantum of construction in Pakistan and reduce the emission of CO_2. The reduction of cement demand may also help us to save energy for use in more urgent areas. Lastly, it is hoped that once the results of these SRM's are fully understood, they will hopefully be incorporated in SCCS's in Pakistan in modern megastructure construction and repairs.

CHAPTER 2 – LITERATURE REVIEW

2.1 Self Compacting Cementitious Systems

This research encompasses the study of self compacting mortar (SCM) systems which form a part of SCCS. A brief development history of SCCS is presented as follows:

2.1.1 Development History of SCCS

In the mid 1980's, the problem of the durability of concrete structures was a major topic of interest in Japan. To make durable concrete structures, sufficient compaction by skilled workers is required. The Japanese construction industry was faced with a unique problem of growing shortage of skilled labour capable of operating mechanical compactors which led to a similar reduction in the quality of construction work. In such a unique scenario, a need was felt for a concrete that could overcome the problems of defective workmanship [2].

This led to the development of self-compacting concrete, primarily through the work by Okamura [2]. This type of concrete greatly reduced the amount of skilled labour required and was placeable around the clock without any noise [23, 24]. Thus, an ACI committee called "ACI 237R–07 Self Consolidating Concrete" was formed to study all aspects pertaining to the properties of self-compacting concrete, including a fundamental investigation on workability of concrete, which was carried out by Ozawa et al [25, 26] at the University of Tokyo. The first usable version of self-compacting concrete was developed in 1988. Professor Okamura thus defined the properties of the concrete and named it as "High Performance Concrete" [2]. But as the name "High Performance Concrete" was defined as a concrete with high durability due to low water-to-cement ratio by Professor Aitcin et al [27], this term is used to denote High Strength Durable Concrete. So, the name "Self-Compacting High Performance Concrete" was used by Okamura [2].

In the early 1990's, the amount of literature available on this technology was very scarce and the essentials of this technology were mainly kept secret by Japanese corporations to preserve a commercial advantage. However, this technology was rapidly transferred to Europe with the development of third generation polycarboxylate ether based super plasticizers. This technology spread further in the Western direction toward America such that the volume of production of self-compacting concrete in North America reached one million cubic meters in 2002 [28].

As a consequence of this rapid development, many professional societies such as American Concrete Institute (ACI), American Society for Testing and Materials (ASTM), Precast/Prestressed Concrete Institute (PCI) and Réunion Internationale des Laboratoires et Experts des Matériaux, systèmes de construction et ouvrages (RILEM) adopted this technology. Test methods and recommendations on the design and applications were developed. Many seminars and symposiums were held to develop awareness of this excellent technology. ACI, ASTM and Precast/Prestressed Concrete Institute (PCI) have adopted the term Self-Consolidating Concrete as one of the first steps of standardizitation. ASTM has established a subcommittee (C09, 47) in order to standardize nationwide practices for testing properties of SCC [2]. ACI has published a state-of-the art report on Self-Consolidating Concrete in April 2007 prepared by ACI committee 237.

It is also worth noting that Professor Okamura produced powder-type SCC using locally available materials and used excessive amount of powder content in paste to increase viscosity and improve segregation resistance. Some disadvantages using the above technique were:

- SCC requires higher powder and super plasticizer (SP) contents. Therefore, the material cost is higher [29]. It was reported that in most cases, the cost increase ranged from 20 % to 60 % compared to similar grade conventional concrete [30, 31].
- The increased content of powder and admixture also leads to higher sensitivity (i.e. reduced robustness) of SCC to material variation than that of conventional concrete. Thus, greater care with quality control is required [32].

2.1.2 Definition of SCCS in Literature

Due to its versatile nature and unique characteristics, there are many legitimate definitions of Self Compacting Concrete found in the literature. The European Guidelines for Self Compacting Concrete [33] define SCC as “the concrete that is able to flow and consolidate under its own weight, completely fill the formwork even in the presence of dense reinforcement, whilst maintaining homogeneity and without the need for additional compaction”. Various other authors have put forward their own description of Self Compacting Concrete. Khayat et al [34] states that “Self Compacting Concrete is a special type of concrete that should flow into place and around obstacles under its own weight without segregation and flow blockage and with no significant separation of material constituents thereafter until the setting”.

It must be noted that the various definitions of SCC are derived from its properties in a fresh state. Many authors have put forward their own definition after extensive research. The most common definition is “a concrete that is able to flow under its own weight and completely fill the formwork, and then consolidating without the need for vibrating compaction” [24]. However, due to a lack of standard definition, ACI formed a committee “ACI 237” which was tasked with standardizing SCC and its properties. ACI 237 submitted its report in April 2007 and a standard definition [1] was determined by ballot. Since then, all other definitions of SCC are void and only definition given in ACI 237R – 07 is considered valid.

It is also pertinent to note that the self-compacting cementitious systems are divided into three distinct types based on the number of components the system comprises. These are:

- Single Component System commonly known as self-compacting paste (SCP) system
- Two Components System commonly known as self-compacting mortar (SCM) system
- Three Components System commonly known as self-compacting concrete (SCC) system

However, all of these system have to be studied and developed to achieve our final goal i.e. the successful production of self-compacting concrete, for which we fist have to optimize the SCP system, followed by the SCM system while understanding the various parameters of these systems in great detail.

Miao Liu [35] reports that the self-compacting concrete essentially has three properties in fresh state: filling ability, passing ability and segregation resistance. Filling ability is the characteristic of SCC to flow under its own weight and to completely fill the formwork. Passing ability is the characteristic of SCC to flow through and around obstacles such as reinforcement and narrow spaces without blocking and “Segregation” which is the characteristic of SCC to remain homogeneous during and after transportation and placement. It is the passing ability that distinguishes SCC from other High Performance Concrete [24].

It must be noted that SCC displays a highly thixotropic behaviour as it seems to flocculate rather quickly at rest and it becomes apparently more and more fluid while flowing during typically several tens of seconds [36], other SCC parameters like robustness and consistency retention are also of equal importance. Robustness refers to the ability of SCC to retain its fresh state properties when the quality and quantity of constituent material and the environmental condition change. Consistency retention or open time refers to the time period during which the fresh state properties can be maintained without significant change.

Rheology is the science of deformation and flow of the matter. Rheology of the concrete in fresh state is described by Bingham’s model in which deformation is related to yield stress and segregation resistance is related to viscosity. According to Bingham’s mode, concrete must overcome a limiting stress before it can flow. The model is represented by the equation:

$$\tau = \tau_o + (\mu r^o) \text{ [37]}$$

where τ_o is the yield stress and μ is the plastic viscosity. The shear stress must exceed τ_o for concrete to flow.

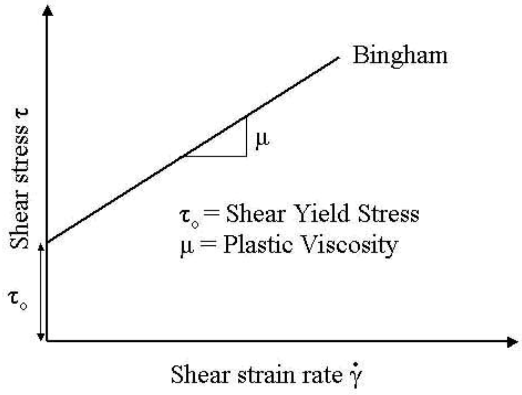


Fig 2.1: Schematic representation of Bingham model [38]

2.1.2.1 Advantages of SCC

Self-compacting cementitious system offers many advantages in various fields of construction.

- Compared to conventional concrete, SCC possesses enhanced qualities, and its use improves productivity and working conditions [29, 39].
- Because compaction is eliminated, the internal segregation between solid particles and the surrounding liquid is avoided which results in less porous transition zones between paste and aggregate and a more even colour of the concrete [40]. Improved strength, durability and finish of SCC can therefore be anticipated. Very good finish effect is shown in achieved. The surface is so smooth and dense that it can reflect light.
- For conventional concrete, the structural performance is improved by increasing reinforcement volumes, limiting cracking by using smaller bar diameters and using complex formwork, resulting in congestion and difficulty of compaction [40, 41]. SCC improves its structural performance by making casting homogeneous concrete, thereby, reducing the volume of reinforcement. It also improves efficiency and effectiveness onsite by reducing the construction time and labour cost.

- SCC also improves the workplace environment by reducing noise pollution and eliminating the health problems of labourers related to the use of vibration equipment such as ‘white fingers’ and deafness [40]. SCC is therefore called ‘the quiet revolution in concrete construction’ [29].

2.1.2.2 Uses of SCC

As a result, the precast concrete products industry has become the biggest user of SCC in Europe [42].

Some further uses of this technology are as light weight reinforced concrete, self-levelling underlayments (SLU’s), slurry infiltrate concrete (grouts) and for rapid repairs and construction at aircraft runways and highways.

2.1.2.3 Further advancements in SCC

Numerous advancements have been made in the field of SCCS as this technology is constantly analysed and optimized. Few significant and important recent studies are summarized as under:-

Rizwan [6] states that “as paste is the vehicles of aggregate phase, good workability can be achieved by reducing the aggregate size and content with an increased paste volume, thus resulting in reduced internal friction.” Further it is suggested that the sand content may be increased to augment the cohesiveness and stability of concrete mix. This may result in higher requirement of super plasticizer content to meet the target flow. This effect is more pronounced in the self-compacting mortar system which is the focus of this study.

Rizwan [6] also suggests that no more than 15 % of coarse aggregate particles shall be elongated and irregular as they tend to increase internal friction, cause internal voids and bleeding and require a higher paste volume. The study also describes the effect of temperature of mixing water on flow and shrinkage which has also been studied in this research. It is also important to note that the addition of even a small quantity of water after addition of admixture can significantly reduce the mix cohesion or lead to slightly inaccurate results which are contradictory to published literature [6].

Rizwan [6] reported that the physical properties of SRM’s like particle size, shape, morphology and porosity etc. play a vital role in determining the water and SP content. Moreover, the chemical properties of SRM’s also affect the water and SP demand e.g. Lime Stone Powder (LSP) with its irregular, abrasive particle shape with high porosity requires a high SP content than

Silica Fume (SF). Thus, we can manipulate this knowledge to our advantage and suitable blends of SRM can be adopted which provide an improved overall response of the cementitious system.

Hence, we can summarize self-compacting concrete as a highly flowable, non-segregating concrete [1], whose characteristics include low w/c ratio, low w/p ratio, use of super plasticizer (SP) and high powder content to produce high flow use of viscosity modifying agents (VMA's) and use of smaller size and less overall content of aggregate. In addition, SCC gives an advantage of ease of placement, superior performance and is known for aesthetic appearance.

2.2 Basic Information on Role of Secondary Raw Materials in SCCS

The primary role of secondary raw materials in SCCS is to modify/improve certain desirable characteristics like early heat of hydration evolution, shrinkage reduction, flow, strength development, durability and microstructure. However, variation in the amount of SRM and their combinations can yield a dramatically different response [33]. Secondary Raw Materials can be both inert and pozzolanic in nature. According to Cordiero et al [43], they influence the physical as well as chemical properties of concrete. Physical effects include the ability of SRM particles to fill in between the voids in the matrix and improve the packing. This ability is a function of their size, shape, texture and internal porosity. They also affect the chemical properties of the matrix by actively reacting with calcium hydroxide, a by-product of cement hydration, to form further cementing compounds.

Studies carried out by Tangpagasit et al [44] suggest that during the first 28 days when most of the hydration occurs, the physical effects of SRM contribute towards strength development while at later stages, the chemical effects (pozzolanic reaction) contribute towards the strength development. Regardless of the reactivity of an SRM, if it is extremely fine, it will generally impart some benefit to mortars and concrete. Small particles, which can fit between cement grains, allow for more efficient paste packing, which in turn reduces bleeding and lowers the mean size of capillary pores. Improved particle packing at the aggregate/paste interface results in a thinner transition zone with a denser, more homogeneous microstructure [45]. In addition, acting together, many small particles have a large total surface area, leading to an increase in reactivity.

Rizwan and Bier [46] reported that when mineral admixtures are added, three effects can be quantified including dilution, heterogeneous nucleation (physical effect) and pozzolanic reaction (chemical effect). These effects depend on the amount and solubility of amorphous silica. The heterogeneous nucleation is a physical process leading to a chemical process involving chemical activation of cement hydrates. It must also be noted that mineral admixture particles act as nucleation centres for hydrates. Rizwan and Bier [46] also reported that the SRM particles also absorb super plasticizer and water through their internal pores. This leads to a higher dosage of super plasticizer and water to achieve the desired flow target.

The work of Cry et al [47] suggests that the amount of cement replacement by SRM has an optimum value above which the beneficial effects are diminished. It also reports that the powder content shall be up to this optimum content to achieve maximum efficiency and result in large gain in compressive strength. This was the reasoning behind the decision to use the SRM's at 10% of the cement mass in replacement mode in this study in line with previous study.

2.2.1 Metakaolin

Metakaolin differs from other secondary raw materials (SRM), like fly ash, silica fume, and slag, in that it is not a by-product of an industrial process; it is manufactured for a specific purpose under carefully controlled conditions [48].

Under normal conditions, kaolin is found to be very stable. However, when it is calcined, the crystalline structure breaks down and the alumina and silica layers become puckered. It acquires an amorphous structure which is in a highly reactive meta-stable state. Mehta [6] has further described that natural pozzolans when calcined can improve their reactivity and improve their performance in cementitious systems. The extent to which this meta-stable is acquired depends upon the calcination temperature. Ambroise et al [49] has studied the effect of calcining on Metakaolin-lime pastes and reports that a temperature of 700^{o}C is optimal. Calcination below this temperature results in more quantity of residual stable, non-reactive kaolinite while at calcining above at about 850^{o}C, recrystallization occurs as kaolin converts into the inert ceramic materials like mullite, spinel and siloca [50].

Metakaolin tends to have a higher reactivity due to its affinity for CH. When cement hydrates, typically 20-30% of the resulting paste mass is CH. This is critical, as CH does not make a significant contribution to concrete strength due to cleavage of CH plates and can be detrimental to durability. Metakaolin reduces this by the formation of CAH which has a high CH demand and eliminates CH by secondary reaction and improves concrete durability [51, 52].

The basic hydration reactions are as follows [51, 52]:

$$2C_3S \quad + \quad 11H \quad \rightarrow \quad \underset{(C\text{-}S\text{-}H)}{C_3S_2H_8} \quad + \quad \underset{(CH)}{3CH}$$

$$2C_2S + 9H \rightarrow C_3S_2H_8 + CH$$

$$C_3A + \underset{\text{(gypsum)}}{3CSH_2} + 26H \rightarrow \underset{\text{(ettringite)}}{C_6AS_3H_{32}}$$

$$2C_3A + C_6AS_3H_{32} + 4H \rightarrow \underset{\text{(monosulfate)}}{3C_4ASH_{12}}$$

$$C_4ASH_{12} + 2CSH_2 + 16H \rightarrow C_6AS_3H_{32}$$

$$\text{MK } [Al_2Si_2O_7] + CH + H \rightarrow \text{C-S-H}, C_4AH_{13}, C_3AH_6, C_2ASH_8$$

Poon et al [53] reported that the degree of pozzolanic reaction was higher at a replacement of 5% of Cement mass by Metakaolin than for 10% and 20% replacement for similar ages. The higher rate of pozzolanic reaction could be attributed to higher amount of cement, thus higher concentration of CH available for reaction with Metakaolin.

Poon et al [54] studied the mechanical and durability properties of Metakaolin and Silica Fume concrete. They reported that Metakaolin concrete has superior strength development and similar chloride resistance to silica fume concrete. The chloride ion penetration was also less for MK and SF based concrete as compared to control concrete.

Schutter et al [55] reported acceleration in hydration indicated by increased rates of heat evolution temperature in SF and MK based mortar systems. Ambroise et al [56] attributed the increased temperature rise of MK mortars relative to that of control mortar mix to the accelerating effect of Metakaolin on hydration. It is significant to note that the maximum observed temperature rise occurs for 10% replacement of cement by Metakaolin.

It is well known that finely divided materials can accelerate OPC hydration. Moreover, if the material shows high pozzolanic activity, the heat produced during hydration is higher in the blended mortar than in an equivalent reference mortar [57]. Because Metakaolin is very small and possesses some latent hydraulic reactivity, it contributes to both heat and strength evolution at very early ages. However, an increase in the hydration heat released can have a negative effect on performance (durability) of the mortars and concretes, mainly due to volume changes (shrinkage) and microcrack formation [55].

Frías et al [57] report that paste mix containing MK actually showed higher total porosities than controls (approximately 16%), likely due to the high water content, although the MK pastes had fewer pores in the 0.01-5.00 µm range and more pores smaller than 0.01 µm, indicating refinement. Additionally, with longer hydration times, there was no significant difference in the capillary porosity of pastes made with 15, 20, or 25% MK.

Khatib and Wild [58] also examined pastes with a w/cm of 0.55 using MIP and reported that MK incorporation led to pore structure refinement, with the proportion of pores having radii smaller than 20 nm increasing significantly as the replacement level increased. At 14 days, pastes with 15% MK had nearly 60% of their total pore volume in sub-20 nm pores, while the control paste had only about 30%. This represents the age at which the percentage of fine pores is the highest and also where strength enhancement by MK reaches a maximum, confirming that the major part of the pore refinement process occurs at a very early age [59]. Poon et al [53] also used MIP to investigate the porosity and pore size distribution of MK pastes. These pastes had lower porosity and smaller average pore diameters than the control and the silica fume pastes at all ages tested (3, 7, 28, and 90 days). This indicates that MK is more effective than silica fume in the refinement of pore structure. These results are different than those reported by both Frías et al [57] and Khatib and Wild [58], who both found MK pastes to have 16 % greater porosity than controls at 28 days. However, these previous studies were conducted at a w/cm of 0.55, while the Poon et al [53] used pastes prepared at a w/cm of 0.30. This also confirms that the w/cm value affects the pore size and distribution and lower value of w/cm with MK incorporation can lead to a better pore refinement and less pore size, thus optimizing the packing of the matrix.

Justice M Joy [60] has reported that the incorporation of Metakaolin reduces free shrinkage in the mortars but increases the chemical and autogenous shrinkage. This is attributed to the lesser amount of water available for evaporation as hydration and pozzolanic reaction of MK consume a significant amount of free water. Caldarone et al [61] reported that 10% replacement of cement by Metakaolin decreases free shrinkage after 156 days of drying at 50% relative humidity. Ding and Li [62] and Brooks et al [63] also reported a decrease in shrinkage relative to controls. This also suggests that due to fine pore structure (pore refinement) and low pore size due to MK, water loss is mostly due to self-desiccation rather than evaporation. This resulting increase in chemical and autogenous shrinkage may not be detrimental as they do not lead to free shrinkage beyond 24 hours.

2.2.2 Glass Powder

Although research on the use of crushed glass as a partial replacement for aggregate dates back many decades [64], work on the use of finely ground glass as a pozzolanic material is relatively recent [65, 66]. The use of waste glass as pozzolan is explored in view of high economic costs of recycling of waste glass as well as the environmental issues related to disposal of waste glass. As the chemical composition of glass does not vary significantly despite their origins, waste glass is potentially a very useful pozzolanic material and appropriate economical applications need to be found for it.

One of the possible channels for the recycling of mixed glass is cement-based materials, but most of existing studies recommend its use only as fine powders [67, 68]. Fine particles of glass powder usually impart pozzolanic activity beneficial to the concrete, while coarse particles are usually deleterious to concrete due to alkali-silica reaction (ASR) and poor ITZ.

The high silica content, high surface area and amorphous structure of GP suggests that it could perform well as a secondary raw material (SRM) and, therefore, could be used to replace a portion of the cement in concrete. Concerns about the use of glass as aggregate in concrete relates to its susceptibility to alkali-silica-reaction (ASR) in concrete as glass, especially if its particle size is small, will itself release enough alkalis to induce ASR [69]. The Na_20 and K_20 in glass could potentially be released, in the form of sodium and potassium ions, into the cement paste and increase the pH of the paste. GP has a higher amount of alkalis than other pozzolans, such as FA and SF, which do not undergo ASR, so glass might prove to be a weaker pozzolan or even induce ASR in reactive aggregates.

This aspect of Glass has been recognized and is the subject of intense research as indicated by the literature cited above or even earlier [70]. However, recent studies have suggested that finely ground glass can produce a pozzolanic reaction, thus inhibiting ASR [71]. Further efforts have also been undertaken to characterize and re-use waste glass as cement or aggregate replacement with some positive results [20, 72].

It is important to recognize that the reactivity of glass depends on its type and composition and physical features such as size, presence of pores and separate solid phases in the glass [20, 73]. For example, binary glasses such as sodium silicate glass behaves differently from soda-lime glass such that the binary glasses cause alkali release and mortar expansion even in combination with low-alkali glass, whereas soda-lime glasses require high alkali contents in the mortar or concrete to enable it to react deleteriously and cause expansion [70, 73].

Generally, the powders of glass containing boron, such as Pyrex glass were found to be more reactive than powder of soda-lime silica glasses [73]. Particle size of glass and alkali content of the mortar or cement are two other important factors influencing the reactivity of glass as aggregate [20, 73, 74].

Shao et aI [75] reports that the pozzolanic activity and strength of concrete made with finely ground WGP, SF and Fly Ash at 30% replacement of cement. The glass sizes used were 150 µm, 75 µm and 38 µm. He reports that the mix with 30% silica fume performed better than the control at 28 days; however, at 90 days age, the concrete with the 38 µm glass powder replacing cement produced concrete that is 8 % higher in strength in comparison to the control. The concrete with finer glass particles achieved higher strength than the concrete with coarser glass particles since finer glass is more reactive.

According to ASTM C 618 [12], a strength activity index of 75% is needed for a pozzolan to be beneficial to concrete. The 75 µm and 38 µm waste glass powder satisfied this requirement and their corresponding mixes achieved results similar to fly ash [66].

Shayan and Xu [76] used GP with particle size smaller than 10 µm to replace 10%, 20% and 30% of the cement in RM. In all cases, the 28 day compressive strength was lower for the mixes with waste glass powder compared to the control. However, the 90 day strength of the concrete was higher or approximately the same as that of the control for all the mixes with waste glass powder. This is attributed to the pozzolanic reaction of the waste glass powder which is slower than the hydration of Portland cement [76].

The work of Schwarz et aI [69] has suggested that it is optimal to replace 10% of cement with WGP when 72% of the particles were smaller than 45 µm. However, the optimum replacement of cement with fly ash was 20%. The concrete paste having 10% replacement of cement with glass had a higher compressive strength than the concrete modified with fly ash at 28 days, however, at 90 days, the fly ash mix had higher strength. This was attributed to the greater pozzolanic activity of fly ash.

Sylvia Nicole Mihaljevic [77] has studied the effect of waste glass powder on the performance of concrete masonry blocks and reports that the replacement upto 10% of cement with waste glass powder has no adverse effects on the performance of concrete blocks and the compressive strength and ASR of waste glass powder and control mix were comparable (a variation of 11%). However, for upto 25% replacement, the waste glass powder mix shows more expansion than the control mix even upto 28 days. Although this expansion was within acceptable limits prescribed in ASTM C 1260 (2007) [78], further testing and investigation is recommended to confirm these findings.

CHAPTER 3 – EXPERIMENTAL PROGRAM

3.1 Materials

In the present study, the effect of Metakaolin and Glass Powder in Self-Compacting Cementitious Systems was evaluated. The basic raw materials involved in this study were Metakaolin, Glass Powder, cement, sand, super plasticizer and water. Metakaolin was from of brand MetaStar 501 from Imerys and from China while Glass Powder was obtained from GLAPOR Glasschaumprodukte, Germany. The experimental program of this study was carried out at Technische Universität Bergakademie Freiberg, Germany.

3.2 Cement

Ordinary Portland Cement (OPC) CEM-I 42.5R obtained from Lafarge Cements, Germany was used in this study. Physical and Chemical Composition of Lafarge CEM-I 42.5R cement as determined by XRF analysis is shown in Table 3.1 below:

Table 3.1: Physical and Chemical Composition of Lafarge CEM-I 42.5R Cement

Physical Properties	**CEM-I 42.5R**
Specific Gravity	3.15
Average Particle Size(µm)	18.42
Normal Consistency (%)	28
Surface Area (m^2/gm)	1.098
Chemical Analysis (%)	
Silicon Dioxide SiO_2	19.17
Aluminum Oxide Al_2O_3	5.21
Ferric Oxide Fe_2O_3	2.39
Magnesium Oxide MgO	2.78
Calcium Oxide CaO	61.12
Sodium Oxide Na_2O	1.25
Potassium Oxide K_2O	1.01
Sulfur Trioxide SO_3	3.30
Loss on Ignition (1000^{o}C)	2.75

3.3 Metakaolin

The Metakaolin used in this study was pre-calcined and finely ground powder type commercially available in 5 kg bags. It was procured from two suppliers: IMERYS MetaStar 501 [79] from IMERYS Performance Minerals, North America and reactive Metakaolin from China as shown in Fig 3.1 below:

Fig 3.1: Imery's MetaStar 501 [79]

The physical and chemical properties of the Metakaolin are shown below in Table 3.2:

Table 3.2: Physical and Chemical Composition of Metakaolins

Physical Properties	**Metakaolin**	
	IMERYS MetaStar 501 [79]	**China Metakaolin**
Specific Gravity	2.5	2.6
Average Particle Size (µm)	4.6	4.5
Moisture Content (%)	1.0	0
Color	Off White	White
pH Value	4-6	-
G.E Brightness	86	80
Chemical Analysis (%)		
Silicon Dioxide SiO_2	52.22	60.53
Aluminum Oxide Al_2O_3	41.41	36.97
Calcium Oxide CaO	0.08	2.50
Magnesium Oxide MgO	0.26	-
Ferric Oxide Fe_2O_3	0.49	-
Sodium Oxide Na_2O	0.01	0.01
Potassium Oxide K_2O	1.73	2.50

3.4 Glass Powder

The Glass Powder (GP) used in this study was obtained from GLAPOR Glasschaumprodukte, Germany [80]. The foam glass products are prepared from high quality recycled waste glass as per DIN 52104-1, Verhafen G [81]. The foam glass was obtained in the form of gravels of approximately 20 mm size as shown in the Fig 3.2 below:

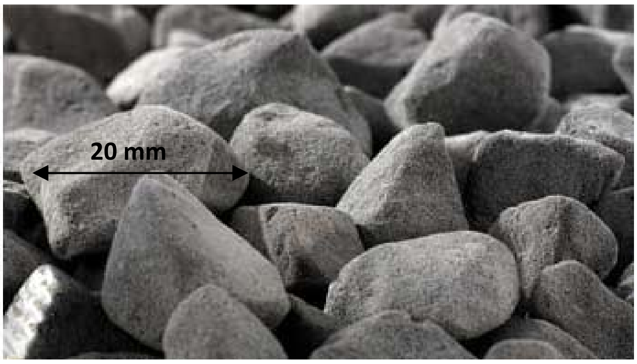


Fig 3.2: Glass Foam Gravels as purchased from GLAPOR [80]

The glass gravels were then milled in the rotating disc type milling machine and the fine powder obtained was sieved through #200 sieves. The physical properties of the Glass Powder (GP) obtained are shown below in Table 3.3 as follows:

Table 3.3: Physical and Chemical Composition of Glass Powder

Physical Properties	Glass Powder
Specific Gravity	2.5
Average Particle Size (µm)	48
Moisture Content (%)	1.0
Color	Gray
Chemical Analysis (%)	
Silicon Dioxide SiO_2	74.66
Aluminum Oxide Al_2O_3	-
Calcium Oxide CaO	11.22
Magnesium Oxide MgO	3.16
Sodium Oxide Na_2O	10.96

3.5 Super Plasticizer

The super plasticizer used in this present study was Melflux 2651F [82] which is manufactured by BASF Corporation. It is a free-flowing, spray dried powder of polycarboxylic ether which is the latest polymer technology. Melflux 2651F super plasticizer typically contains side chains based on polyethylene glycol. It is especially optimized for plasticizing and water reduction of cementitious construction materials. With a relatively low dosage (0.05–1.0% by binder weight), they allow a water reduction up to 40%, due to their chemical structure which enables good particle dispersion. The physical properties of this super plasticizer are shown below in Table 3.4 as follows:

Table 3.4: Physical Composition of Super Plasticizer

Physical Properties	Super Plasticizer
Color	Yellow
Drying Loss (%)	2.0
Bulk Density (kg/m^3)	300 – 600
pH Value (20^{o}C) – 20% solution	6.5 to 8.5
Dosage Recommendation (%)	0.05 – 1.0

3.6 Sand

The sand used in the study was Webber sand. The sand is a slightly coarse form of quartz sand. The Webber sand was sieved carefully and the cumulative passing and retained fraction were weighed to determine the fineness modulus of sand. The particle size of sand was in the range of 0.1 to 1.0 mm. The sieve analysis of the Webber sand was carried out as shown below in Table 3.5:

Table 3.5: Sieve Analysis of Weber Sand

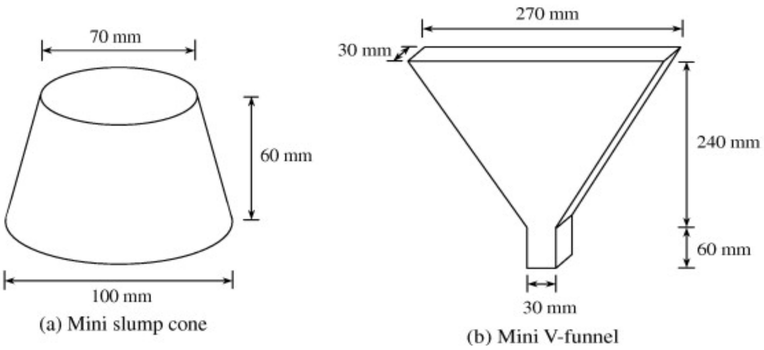
Sieve Size (mm)	Weight of Sand Retained	%age Retained	Cumulative %age Retained	Cumulative %age Passing
2.0	0	0	0	100
1.0	6.5	0.80	0.80	99.2
0.5	329.13	40.75	41.56	58.44
0.25	308.56	38.20	79.76	20.24
0.125	134.57	16.66	96.42	3.58
0.063	25.06	3.10	99.53	0.47
Pan	3.83	0.47	100	0
Sum	**807.55**	**100**	**318.07**	-

Fineness Modulus of Weber Sand = 318.07/100 = 3.18

The fineness modulus of the sand was calculated manually by dividing the cumulative percentage retained by the percentage retained. ACI committee 211R-08 [83] specifies a fineness modulus range of 2.3 to 3.2 for sands with the lower limit indicating fine sand and higher limit denoting coarse sand. Therefore, the Webber sand used in this study is coarse sand.

3.7 Description of Tests

The secondary raw materials (SRM) were first acquired and stored in the laboratory. The Glass gravel was first milled in the rotating disc type milling machine of the Institut für Silikattechnik at Technische Universität Bergakademie Freiberg and sieved through #200 sieve in the Baustoffe labor of Institut für Keramik, Glas- und Baustofftechnik. After preparation of the requisite raw materials for the study, a scientific experimental program was devised. First, the particle characterization of powders was determined using the Beckmann Coulter LS 320 Laser Granulometer. Scanning Electron Microscopy (SEM) using FEI XL 30 Environmental Scanning Electron Microscope with Field Emission Gun (ESEM FEG) was done to determine the particle shape and morphology of the powder particles. The chemical composition of the powder was also determined by X-Ray Fluorescence (XRF) analysis. The specific gravity was calculated manually. The casting of the self-compacting mortar samples was done and the SRM's were used in replacement mode at 10% of cement mass. The water demand and setting time of all formulations was determined using the Automatic Vicatronic machine. The target flow was fixed at 30 ± 1 cm and super plasticizer (SP) demand was determined at water demand for the above target flow by using the Polycarboxylic Ether (PCE) based super plasticizer Melflux 2651F. The flow value and flow times were recorded for each formulation using Hagerman's mini slump cone having dimensions of 6 x 7 x 10 cm^3 and V-funnel as shown below in Fig 3.3.



(a) Mini slump cone

(b) Mini V-funnel

Fig 3.3: Hagerman's Mini Slump Cone and V-funnel

After the flow testing, the prisms of dimensions 4 x 4 x 16 cm^3 were cast for the study of strength development and microstructure evolution of each formulation at different ages. Prisms of size 4 x 6 x 25 cm^3 were also cast into the shrinkage channel of Schwindrinne for measuring volumetric stability of the formulations. The prisms were cured as per DIN 1045 [84] and tested for compressive and tensile strength and the same piece of the prisms broken in strength testing were used for microstructure studies by using SEM and MIP techniques.

3.8 Mixing Regime and Mix Proportions

The mixing was done in the 5L Hobart mixer in the Baustoffe labor of Institut für Keramik, Glas- und Baustofftechnik at TU Bergakademie Freiberg.

The constituents including cement, secondary raw material and super plasticizer were weighed accurately and then fed into bowl of the mixer. Mixing regime consisted of 30 seconds of dry mixing at a slow speed of 145 RPM in the mixer. After dry mixing, the interior walls of the bowl were cleaned and water was added to the mix. After addition of water, the mixture received 2 minutes and 30 seconds of fast mixing at 285 RPM. Thus, the total mixing time was 3 minutes (180 seconds) as per BS EN 197-1 [5].

3.9 Water Demand

As per the European Guidelines for Self-Compacting Concrete [33], the water demand of the cementitious system is often the first step required in the mix design of the self compacting cementitious system. The water demand is the sum of water demand of all binder as well as aggregate phase [85]. The water demand of binder can be calculated by testing the binder in the pre-determined mix proportions in the Vicat apparatus as shown below in Fig 3.4.

Fig 3.4: Electronic Vicat Apparatus "Vicatronic" at TU Freiberg

The water demand for the aggregate phase can be calculated as per the procedures outlined in ASTM C 127 [86] and ASTM C 128 [87] standards. Rizwan [6] reports that the mixing water content for SCCS and HPCS shall not exceed the water demand of the system by a big margin. The water demand of the self compacting mortar system has been calculated in controlled temperature of 20 ± 1 ^{o}C and 60 ± 5 % relative humidity to ensure no undue variations due to change in environmental conditions during testing phase. The results of water demand for all formulations are shown in Fig 4.3 in Chapter 4.

3.10 Setting Times

The setting time of self compacting mortar (SCM) formulation was calculated at the respective water demand of the formulation using the Vicatronic machine as per the provisions of ASTM C 187 [88]. The results are shown in Fig 4.5 in Chapter 4.

3.11 Super Plasticizer Demand

The target flow for all self compacting mortar (SCM) formulations was fixed at 30 ± 1 cm and the amount of super plasticizer content required to achieve the target flow was calculated using Hagerman's mini slump cone [6]. The Hagerman's mini slump cone had as upper diameter of 70 mm and a lower diameter of 100 mm with a height of 60 mm.

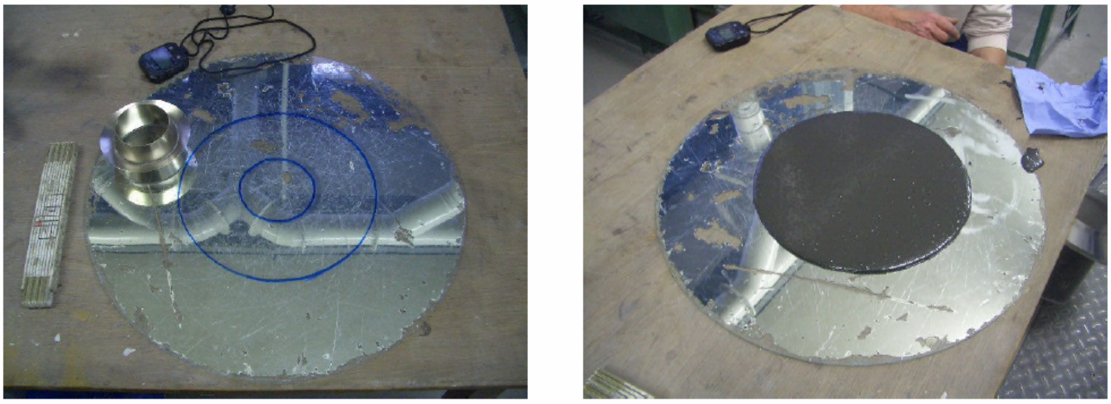


Fig 3.5: Flow spread after removal of cone [6]

The total mass of material required to completely fill the Hagerman's mini slump cone was calculated as 850 grams. The water content of all SCM formulations was kept equal to the water demand of the system during the entire experimental program. The results of SP demand are shown in Fig 4.4 in Chapter 4.

3.12 Strength Testing

The samples were cast into a prism of 40 mm x 40 mm x 160 mm size for the purpose of strength testing. After mixing the materials in the method prescribed above, the material was poured into the prisms.

After casting, the prisms were immediately stored in a water bath at 20 ± 1 ^{o}C temperature and 98 ± 2 % relative humidity. The samples were taken out after 24 hours and the moulds were opened. The prisms were then marked as per specimen designation scheme selected and put in laboratory water at a temperature of 20 ± 1 ^{o}C. The samples were then taken out at the prescribed ages as denoted on the specimen for strength testing in SSD condition.

The samples were tested for flexural and compressive strength using the displacement controlled ToniTechnik Testing machine. In flexure testing, the average of three (3) samples broken in flexure was noted and recorded as the representative flexural strength of that sample as per DIN EN 196 [89] for each prescribed testing age.

From the samples broken in flexure, we chose six (6) samples having cross-sectional area of 40 x 40 mm^2. The compressive strength was recorded as the average of six (6) samples tested as per DIN standards for each prescribed testing age. The results of strength testing in flexure and compression are shown in Fig 4.11 and 4.12 respectively in Chapter 4.

3.13 Calorimetery

The 72 hour calorimeter was done on all SCM formulations at the calculated water and SP demand using an Isothermal Conduction Calorimeter. The samples were prepared from the dry mix of formulations prepared for strength testing and the calorimetery was performed in parallel to these tests. As the calorimetric testing requires a very small sample size 10 grams and an even smaller amount of mixing water as per water demand, special care needs to be exercised while handling the samples. Special care needs to be taken while placing small crucibles along with their lids in the calorimeter to prevent any unnecessary heat conduction to and from the calorimeter. The results of calorimeter were performed on the calorimeter available in the Baustoffe labor of Institut für Keramik, Glas- und Baustofftechnik at TU Bergakademie Freiberg as shown in Fig 3.6. The results of the 72 hour calorimeter are shown in Fig 4.13 of Chapter 4.

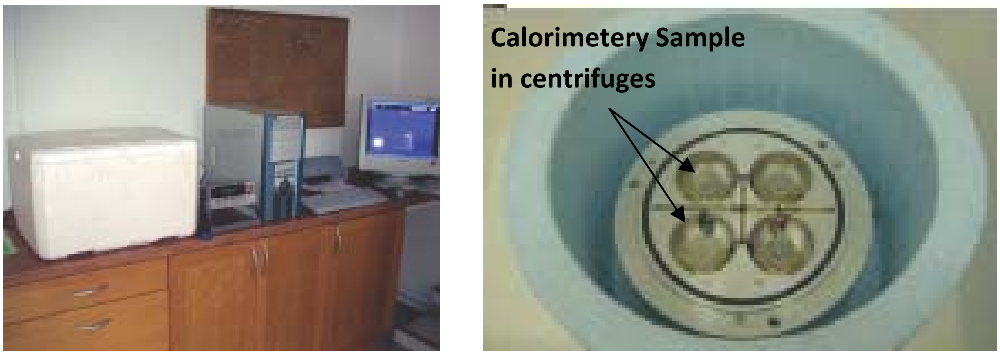


Fig 3.6: Conduction Calorimeter in the Baustoffe labor

3.14 Scanning Electron Microscopy (SEM)

SEM was used to analyze the particle shape, morphology and size (usually to a quantitative extent) of SRM and the samples were put in crucibles which were carbon coated. After putting the powdered samples on the carbon coated crucibles, the samples were gold coated upto 20 ηm and put inside the SEM chamber for analysis as shown in Fig 3.7.

Fig 3.7: SEM machine

For analyzing the hydration progress, microstructure & ITZ of SCM formulation at different prescribed ages, small pieces of about 2-10 mm size were broken using chisel and hammer from samples broken in flexure testing. To study the hydration progress at different ages, it was required to stop the hydration at the prescribed age. To achieve this, the pieces of SCM formulations were dipped in Acetone for about 2 hours [13]. Acetone helps remove all free water in the system available for hydration. The specimen were then submerged into a solution of iso-propanol for about 24 hours [13] to remove the traces of acetone left in the small pieces of samples as shown in Fig 3.8.

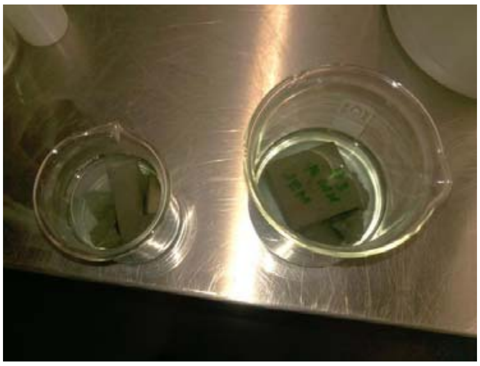


Fig 3.8: Broken pieces of prisms dipped in iso-propanol

The specimen was then put in carbon coated crucibles and gold coated upto 20 ηm for analysis in the SEM chamber. The photographic results of SEM analysis were obtained and the results are shown in Chapter 4 in detail.

Rizwan [6] reports that SEM is a very versatile and helpful tool in analyzing the microstructure of the SCM system, to study in detail the Inter Facial Transition Zone (ITZ) and to identify the progress of hydration process. In Back Scattered Electron mode, it can identify different phases of hydration (CH, Ettringite, CSH gel, alite, belite, etc) and even unhydrated cement particles at low w/p ratios.

3.15 Energy Dispersive X-Ray Analysis (EDAX)

Scanning Electron Microscope was also able to carry out the on-spot chemical analysis i.e. EDAX. Rizwan [6] suggests that EDAX results appear to be just qualitative in nature and not a definitive chemical composition of cementitious system due to large point to point variations across the SCM system. However, in case of metals, it gives a very good idea about the oxide content and composition due to its relative consistency across the system. The EDAX analysis is attached as Annexure B.

3.16 Mercury Intrusion Porosimetery (MIP)

Mercury Intrusion Porosimetery (MIP) was performed using Pascal 440 Mercury Intrusion Porosimeter at Institut für Silikattechnik at Technische Universität Bergakademie Freiberg to study the pore size distribution of SCM formulations. The samples were prepared from prisms broken in flexure. Small pieces of about 5 mm size were broken using chisel and hammer. The hydration was stopped was dipping the pieces in acetone and iso-propanol as described above. After drying the samples, they were subjected to a controlled incremental pressure upto 400 MPa. The measurements of pressure, intruded volume of mercury and pore size and distribution were recorded by Pascal 440 Porosimeter. The cut-off angle between mercury and pore wall was 140^o and the surface tension of mercury was 480 dyne/cm. The results of MIP are shown in Fig 4.20 to 4.28 respectively in Chapter 4.

3.17 Early Shrinkage

For measurement of early 24 hours shrinkage, a modified version of German shrinkage channel called Schwindrinne was used. The channel measured 4 cm x 6 cm x 25 cm and hooked up with a computer to record the variation in length. The linear early shrinkage measurements were made at 20 ± 1 ^oC temperature and 60 ± 5 % relative humidity as shown in Fig 3.9.

Fig 3.9: Modified German Shrinkage Channel “Schwindrinne” on the left, some shrinkage cracks visible on the specimen on the right

The shrinkage measurements were recorded in uncovered condition for SCM formulations so as to approximate field conditions. The temperature of mixing water was varied and hot mixing water temperature of 25 ± 1 ^{o}C and cold mixing water temperature of 15 ± 1 ^{o}C was used respectively. The idea behind using two different mixing water temperatures was to quantify the effect of mixing water temperature on the early shrinkage. The measurements were started after pouring the sample in the channel and zeroing the computer data to record the liner early shrinkage for the first 24 hours. The frontal end of the Schwindrinne was fixed and rear end was flexible and was able to record a displacement of 0.31 microns due to shrinkage or expansion in SCM formulation. The computer was hooked up with Schwindrinne and recorded the shrinkage strains at an interval of 60 seconds upto 24 hours and the data was then imported into Excel sheets. The results of shrinkage for all formulations are shown in Fig 4.29 to 4.32 respectively in Chapter 4. The literature on the measuring device is explained in-depth by Rizwan [6].

3.18 Specimen Designation

A special specimen designation system was designed to identify the type of SCM formulation, its age and the type of SRM. A typical formulation may be written as C1+10MK 1D where C1 denotes the cement; the numeral ‘10’ denotes the mass of secondary raw material (SRM) in terms of percentage of cement mass and MK denotes the SRM used (Metakaolin) and the last letters ‘1D’ denote the age of the sample at the time of testing. The designation does not specify the water and SP content of the system as they were fixed at the water and SP demand of the respective SCM formulation as shown in Annexure A.

CHAPTER 4 – RESULTS

4.1 Tests on Secondary Raw Materials

4.1.1 Particle Characterization by Scanning Electron Microscopy (SEM)

The particle shape, size and morphology are very important parameters in understanding the behavior of Secondary Raw Materials (SRM's) in regards to the flow, strength, shrinkage and microstructure of Self Compacting Mortar (SCM) systems.

a. Metakaolin

The Scanning Electron Microscopy (SEM) photographs of the Metakaolin imported from China (MKCh) used in this study is as shown in Fig 4.1. The average particle size of Metakaolin (MKCh) ranges from 4 to 8 microns as seen in Fig 4.1 which conforms to the particle size given in Table 3.2 of Chapter 3.

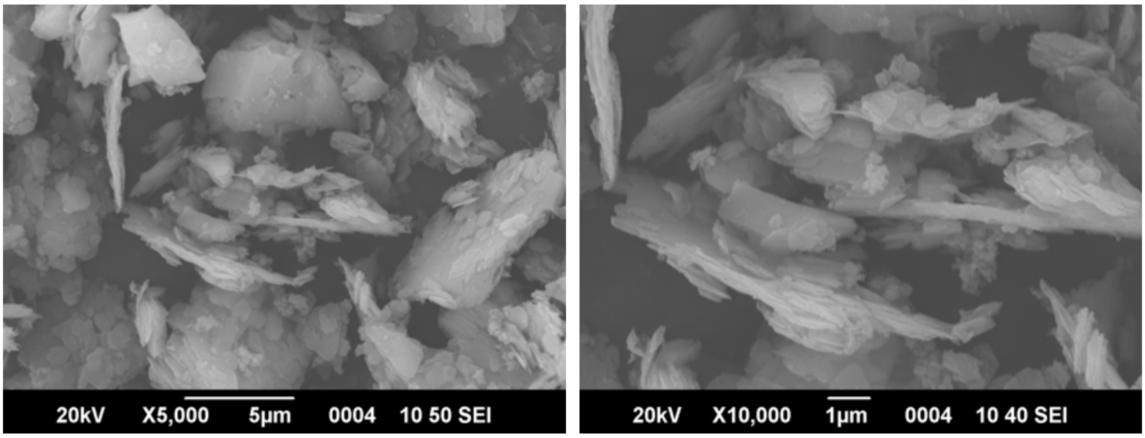


Fig 4.1 (a): SEM Characterization of Metakaolin (MK) at X5000 and X10000 magnification

With respect to Fig 4.1, the SEM photograph demonstrates that the MK particles are irregular in shape with rough, elongated and abrasive texture. This leads to higher internal friction between the particles and requires a higher dosage of super plasticizer for achieving the target flow as shown in Fig 4.4. Small MK particles also act as filler at early age and provide pozzolanic reaction as well.

b. Glass Powder

The Scanning Electron Microscopy (SEM) photographs of the Glass Powder are as shown in Fig 4.2. The variation in particle size is due to milling with some small particles around one comparably large particle.

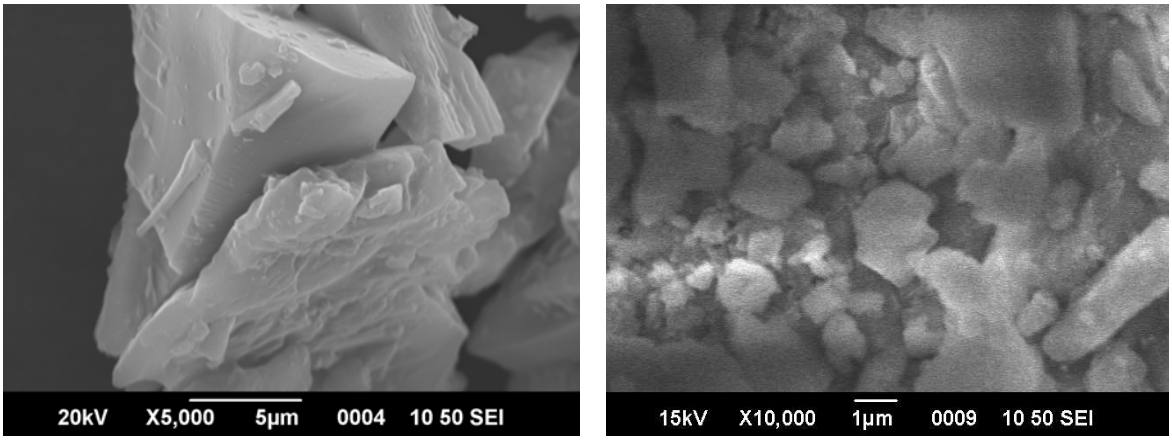


Fig 4.1 (b): SEM Characterization of Glass Powder (GP) at X5000 and X10000 magnification

SEM photograph in Fig 4.2 clearly demonstrates that the Glass Powder particles are irregular in shape with relatively smooth and glassy texture. This leads to lower internal friction between the particles and thus, GP has a relatively lower water demand but a slightly higher SP demand due to large and irregular size of particles. The results of water and SP demand are shown in Fig 4.3 and 4.4 respectively.

4.1.2 Particle Characterization by Granulometery

The particle size of CEM1, Metakaolin and Glass Powder was determined by Laser Granulometery using the Beckmann Coulter LS 320 Laser Granulometer. The particle size of the materials is shown below in Fig 4.2;

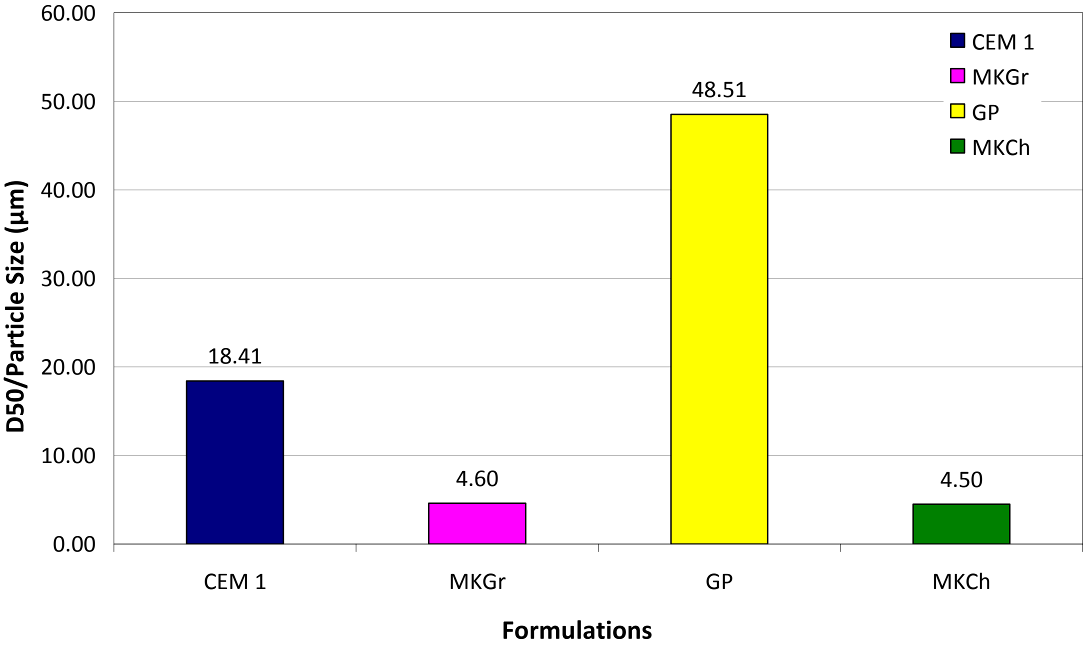


Fig 4.2: Average Particle Size of Raw Materials

The average particle size of Metakaolin was about 4.6 and 4.5 microns respectively. CEM 1 was also very fine having a size of 18.41 microns. Glass Powder was about 48.51 microns which is large as compared to Metakaolin and CEM 1 which can be attributed to the milling process.

4.2 Tests on Self Compacting Mortar (SCM) System

4.2.1 Water Demand

Fig 4.3 shows the water demand of the different formulations used in this study. It was observed that the water demand increases when SRM's were used in replacement mode at 10% of cement mass in the formulation with the exception of GP whose behavior is explained in the above SEM analysis. The tabulated results of water demand are given in Table 3 of Annexure A.

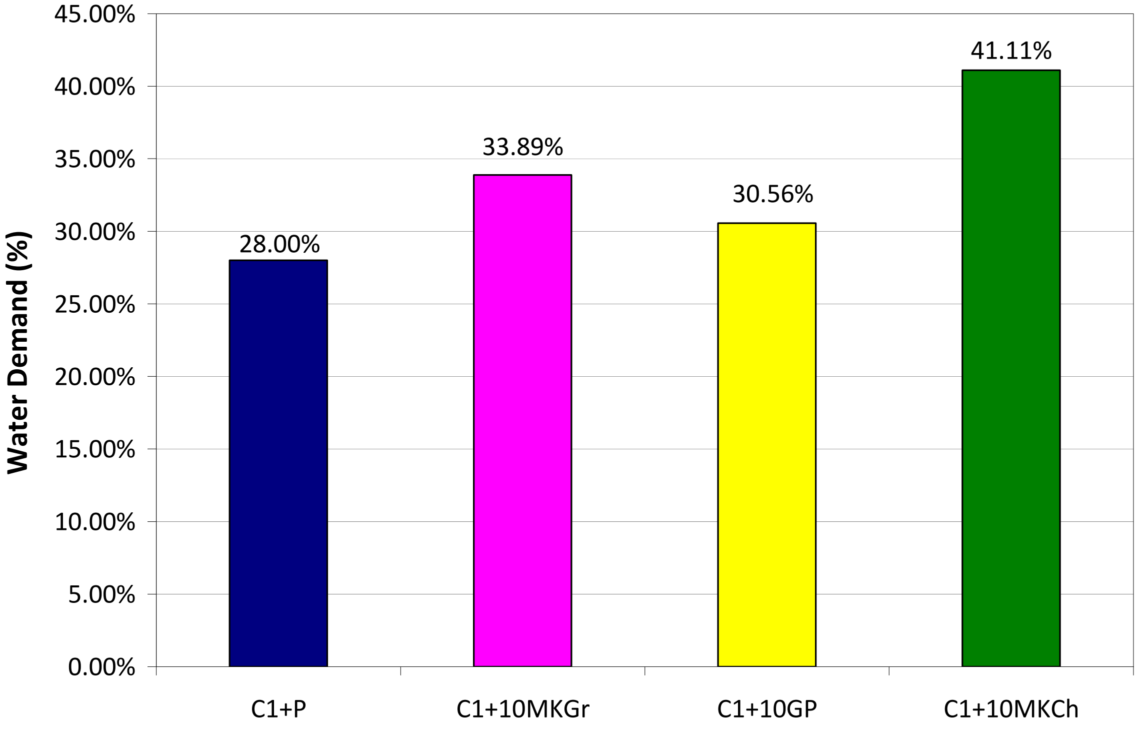


Fig 4.3: Water Demand for SCM Formulations

4.2.2 Super Plasticizer (SP) Demand

Fig 4.4 shows the super plasticizer (SP) demand of the different formulations at a target flow of 30 ± 1 cm. It was observed that when SRM's were used in replacement mode at 10% of cement mass in formulations, the SP demand of the system was increased. The tabulated results of SP demand are given in Table 4 of Annexure A.

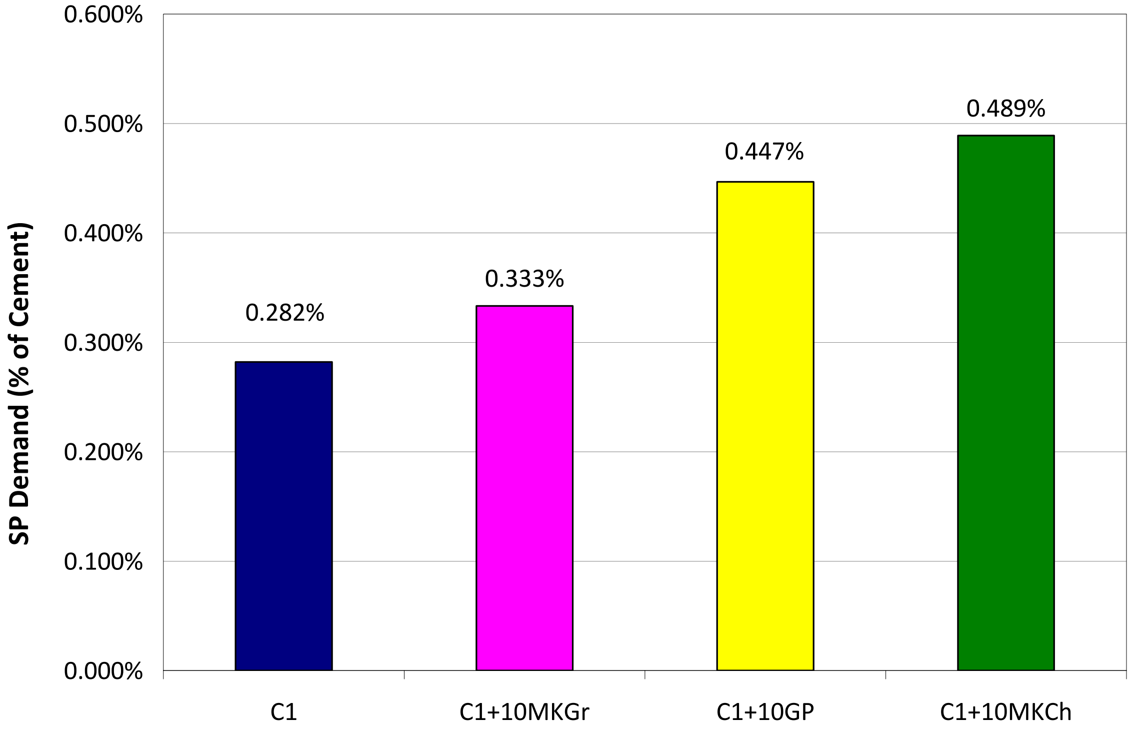


Fig 4.4: SP Demand for SCM Formulations

4.2.3 Setting Times

Fig 4.5 shows the variation of setting times of all formulations. The tabulated results are shown in Table 3 of Annexure A.

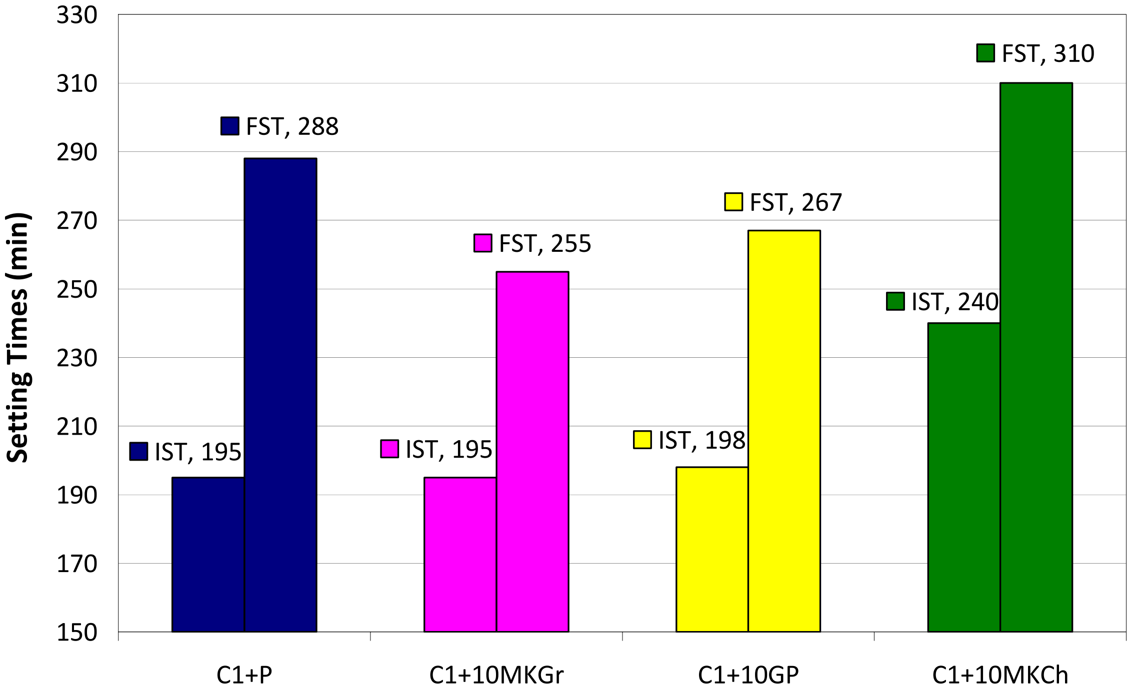


Fig 4.5: Setting Times of SCM Formulations

4.2.4 Flow of SCM formulations

Fig 4.6 shows the flow times for a spread of 25 cm for all formulations using the Hagerman's mini slump cone and Fig 4.7 shows the total spread time for SCM formulations. The particle characterization of SRM affects the flow behavior of the formulations.

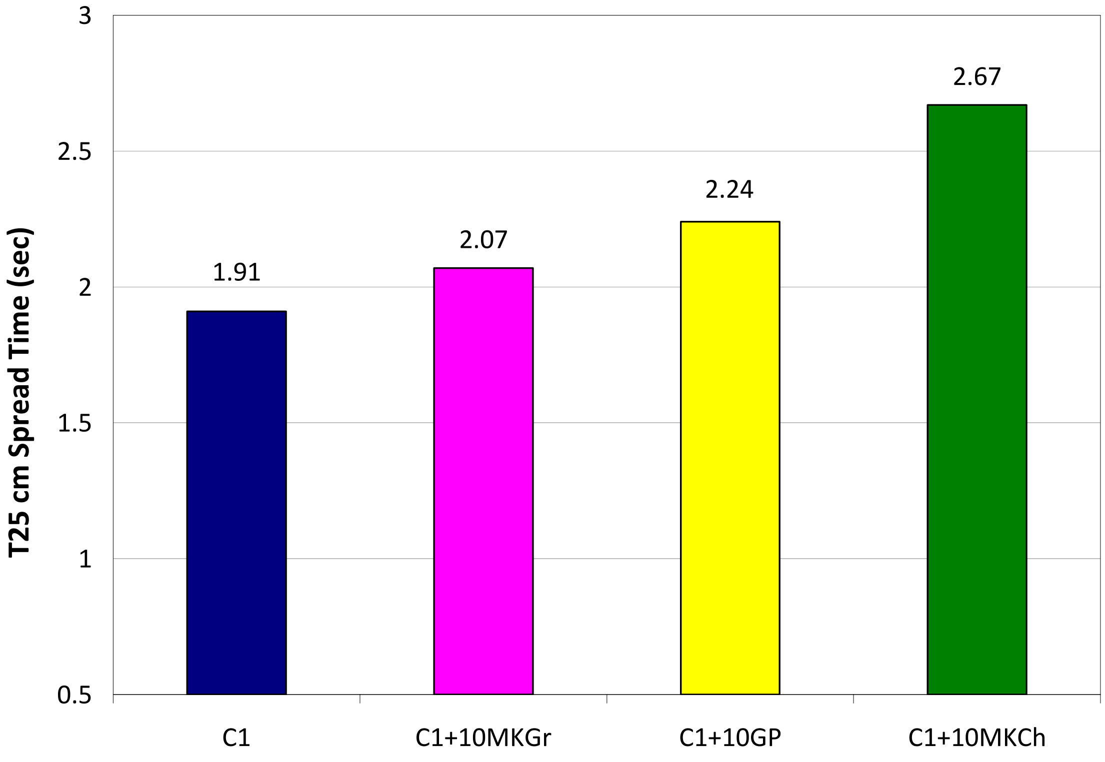


Fig 4.6: Variation of T_{25} time of SCM formulations

Rizwan [6] has proposed that T25 cm time seems to be a better flow index for the comparative flow response of SRM's in HP SCM systems. This enables us to measure accurate flow times for SCM formulations as even viscous mortars keep on creeping for sometime after pouring. Rizwan [6] has based T25 cm spread time on an 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; therefore, the spread time was selected for 25 cm flow again at a diameter ratio of 2.5. Rizwan [6] also states that T25 cm time and V-funnel time seem to be a direct function of the viscosity of the formulation.

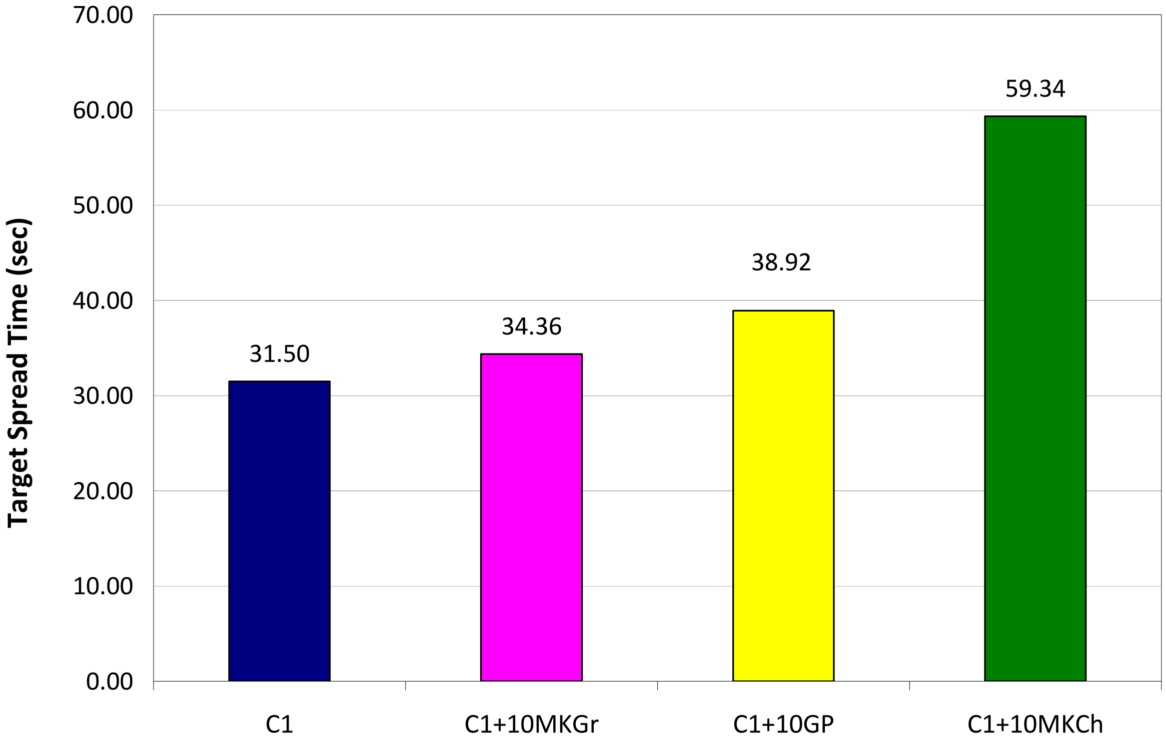


Fig 4.7: Variation of Target Spread time of SCM formulations

From the above result, we can clearly see that CEM 1 has the least target spread time. Metakaolin Metastar 501 (found in Germany) has a small particle size and its particles are rough, abrasive and somewhat elongated. Therefore, it has a large surface area and requires more water and SP content to overcome its internal friction and achieve self flow. Therefore, it produces slightly increased flow timings as shown in Fig 4.6 and 4.7 respectively. Glass Powder also requires higher SP content to achieve self flow. This can be attributed to its irregular shape leading to higher internal friction and internal porosity as shown in SEM photograph in Fig 4.19, which in turn produces retarded flow timings as shown in Fig 4.6 and 4.7 respectively. Metakaolin imported from China also shows a further increase in SP content and has a small particle size, thereby increasing its surface area. However, the Metakaolin is hydroxylated (removal of water) and thus its particles have an affinity for each other as they absorb water, thereby causing retarded flow timings.

Fig 4.8 shows the relationship between T_{25} time and the target spread time for the formulations.

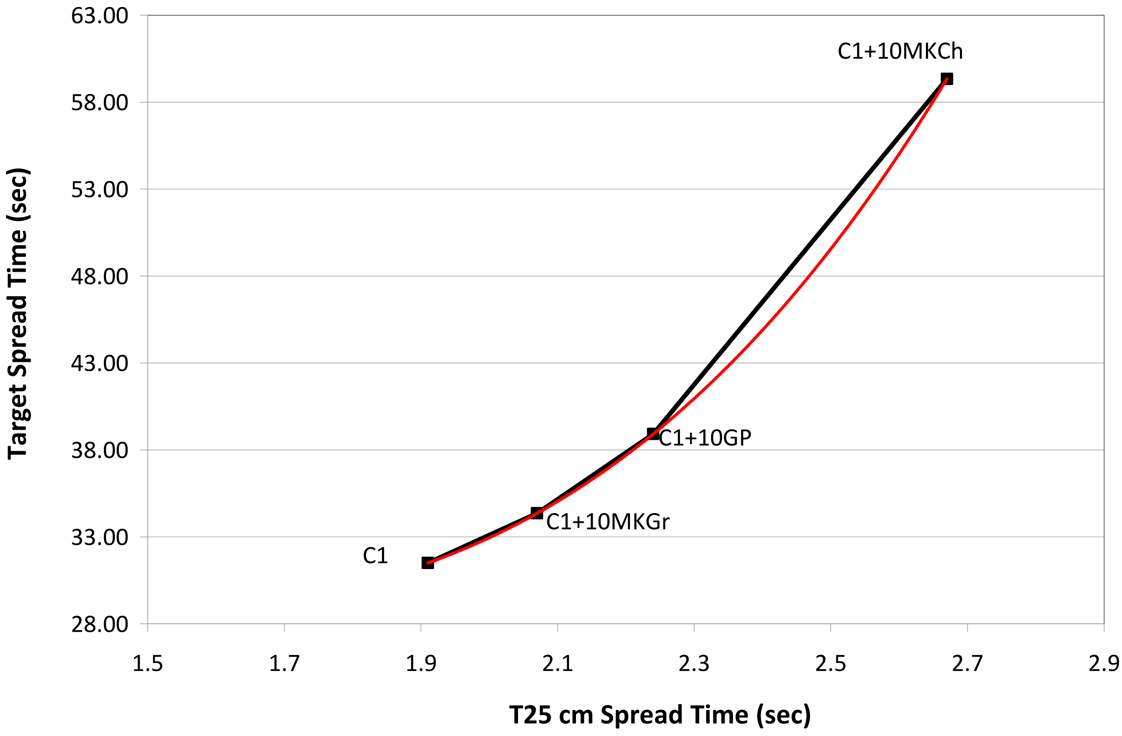


Fig 4.8: Relationship between T_{25} time and Target Spread time of SCM formulations

The V-funnel times of SCM formulations are shown in Fig 4.9 to get an idea of the viscosity of the formulations.

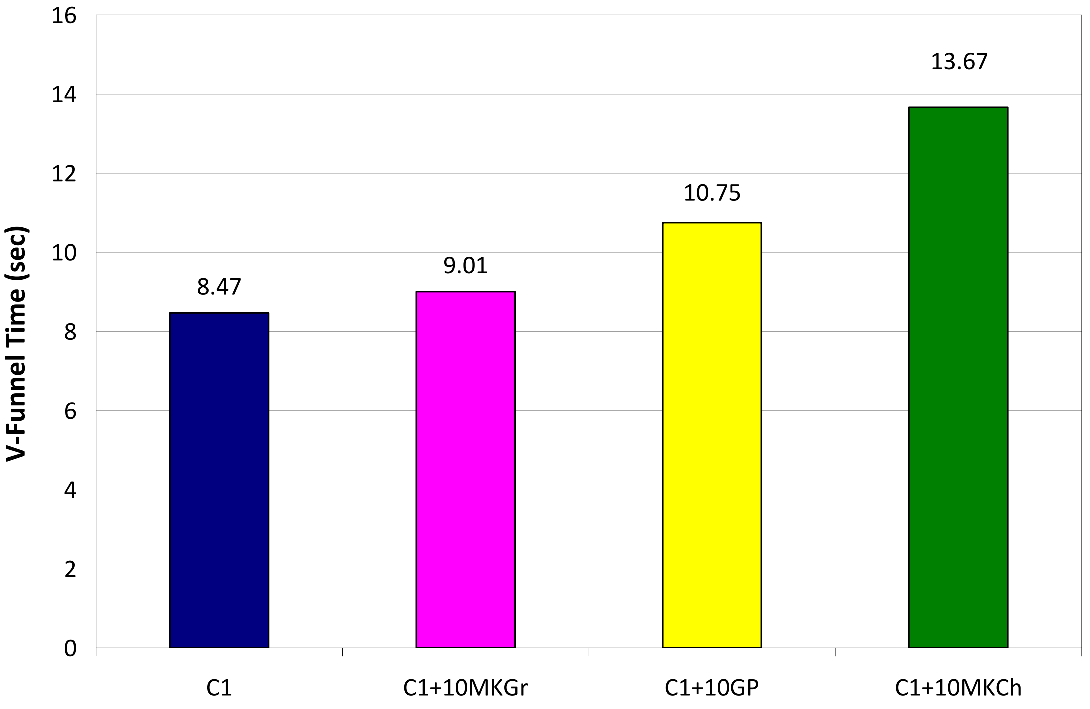


Fig 4.9: Variation of V-Funnel time of SCM formulations

The V-funnel time of a formulation can be interpreted in terms of viscosity. From above Fig 4.9, we can clearly see that Metakaolin exhibits less V-funnel time due to its small particle size as it shows less resistance to flow. Glass Powder has a larger particle size and thus, produces higher V-funnel time.

The above value of flow timings and V- funnel times show a similar trend as they tend to increase with increase in SP and water demand. This indicates that the formulations with increased flow timings have more viscosity and internal resistance to flow as compared to formulations with reduced flow times. The relationship between the T_{25} time and V-funnel time is plotted as shown in Fig 4.10.

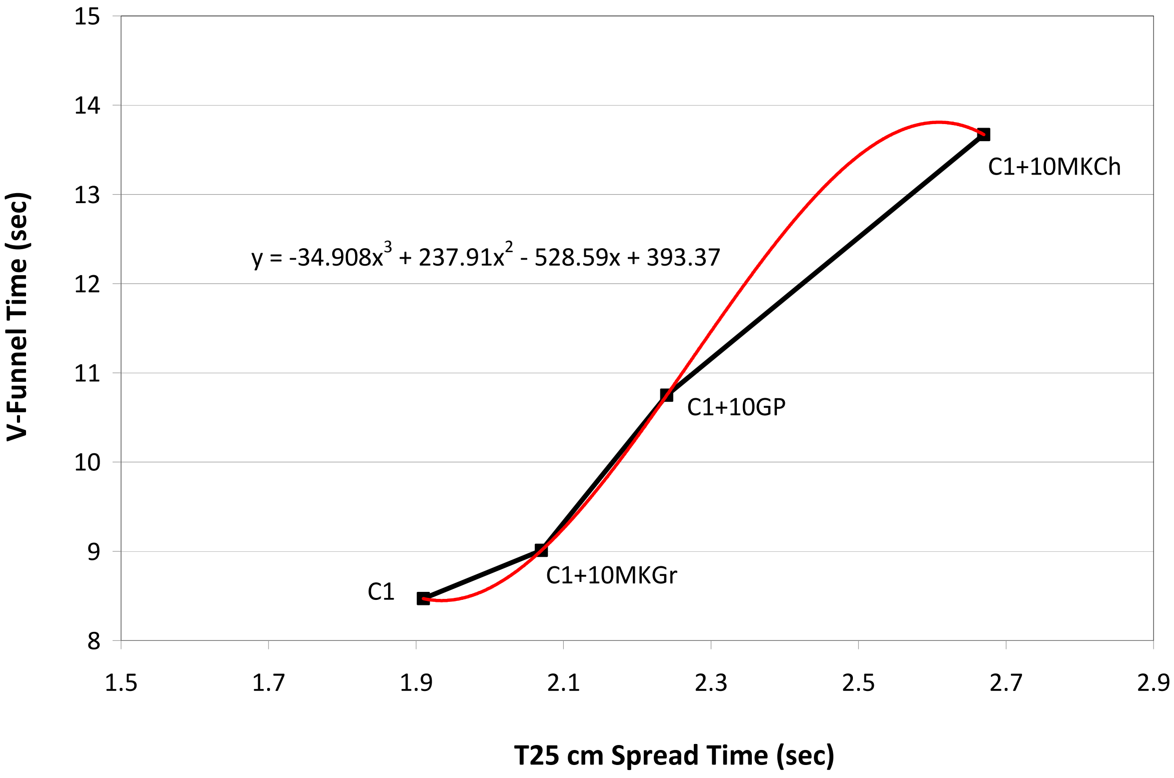


Fig 4.10: Relationship between T_{25} time and V-Funnel time of SCM formulations

4.2.5 Strength of SCM formulations

The results of flexural and compressive strength of the SCM formulations are given in Fig 4.11 and 4.12 below. The specimen was tested at 4 different ages i.e. 1 day, 3 days, 7 days and 28 days.

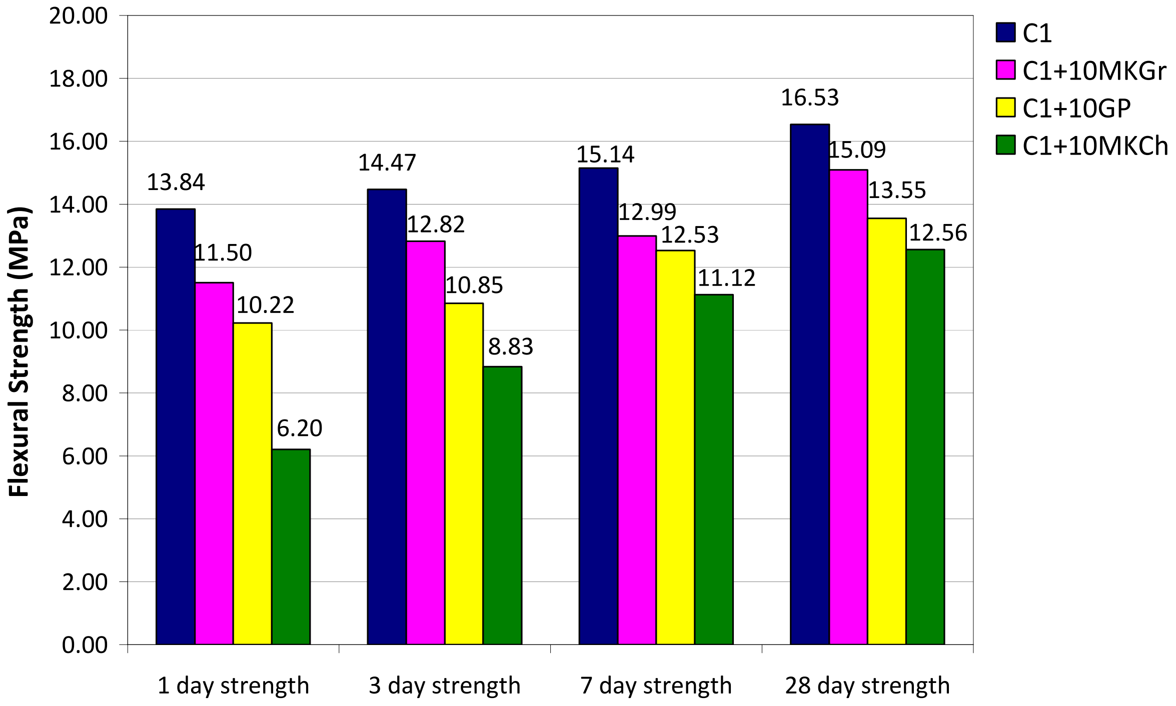


Fig 4.11: Flexural Strength of SCM formulations

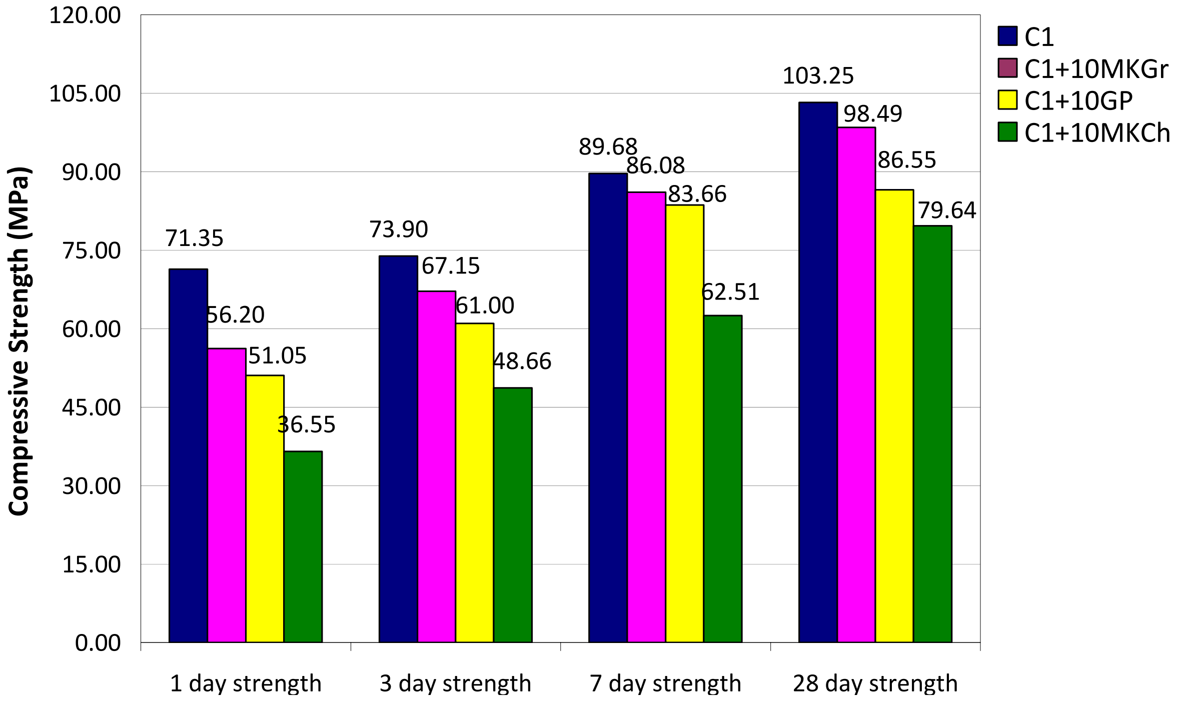


Fig 4.12: Compressive Strength of SCM formulations

The results of flexural and compressive strength both follow a similar trend and clearly show that at early ages, the strength of control mix is about 21% more as compared to MK formulation but at 28 days, the strength is almost equal. GP develops strength more slowly as compared to MKGr as it has a large particle size, thus causing a delayed strength response and evolution of heat of hydration. MKCh also shows a very slow strength response as compared to GP but at 28 days, it has comparable strength suggesting a pozzolanic reaction.

4.2.6 Calorimetery

The purpose of performing 72 hours calorimetery was to observe the effects of results of addition of SRM on the heat of hydration released and the changes in the hydration kinetics of the formulations. The evolution of heat of hydration of Metakaolin, Glass Powder and Control mix show a similar trend to the strength development. Fig 4.13 shows the graphic representation of heat flow of various formulations for duration of 72 hours. All formulations show an immediate peak which represents the hydration of C_3A phase which cannot be measured completely due to its rapid peak. The main calorimetric peak which commences after a dormant period up to 6 hours following C_3A hydration is due to C_3S hydration which is the most important phase in strength development. A separate cutout of the first 6 hours is also inserted to show the dormant period.

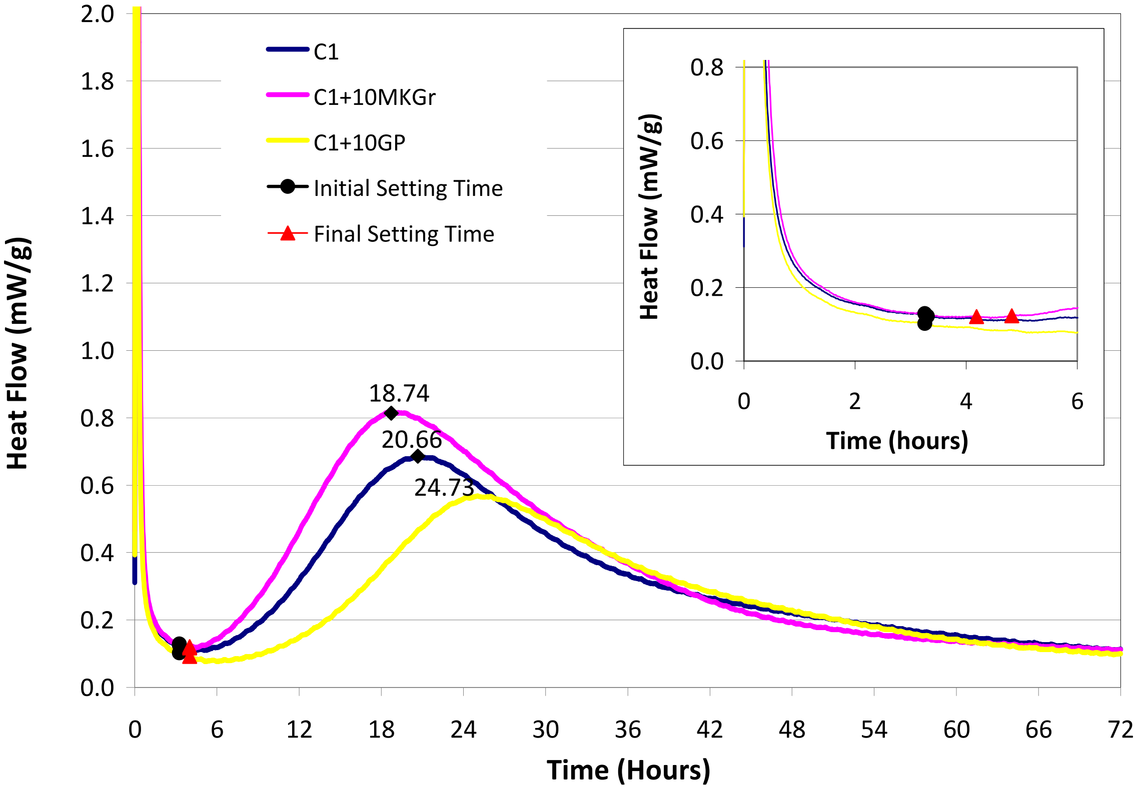


Fig 4.13: Heat Flow of SCM formulations by Calorimetery

4.2.7 Study of Microstructure by Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy and EDAX of various formulations were done on SCM samples at the age of 1 day and 3 days. All formulation showed varying degree of growth of needle-like crystals called Ettringite along with the hexagonal shaped crystals of Calcium Hydroxide $Ca(OH)_2$ and Calcium Silicate Hydrate (CSH) gel is also visible alongside the ITZ at various places. The detailed graphs of EDAX at various places of interest are shown in Annexure B.

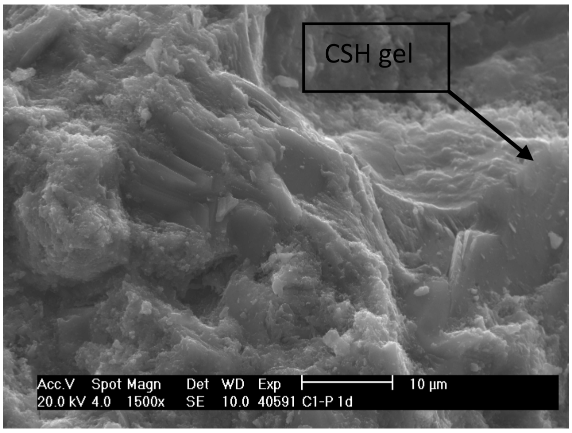


Fig 4.14: SEM photograph of SCM sample of CEM 1 at the age of 1 day

Fig 4.14 below shows the formation of large amount of CSH gel at 24 hours (1 day) indicating that the hydration of C_3S phase is commenced. This can also be confirmed by calorimetric peak of CEM 1 which lies between 20 to 21 hours.

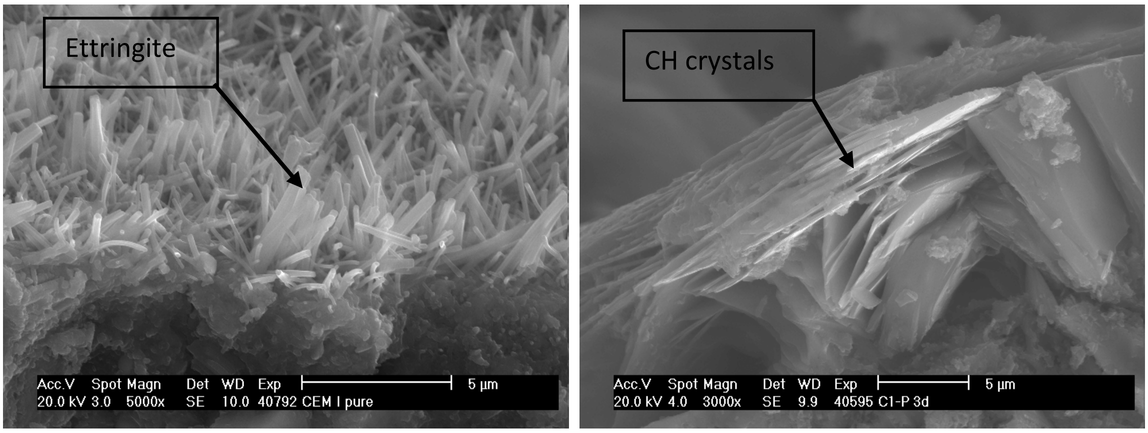


Fig 4.15: SEM photograph of SCM sample of CEM 1 at the age of 3 days

Fig 4.15 shows the formation of needle-like ettringite crystals in the formulation as well as calcium hydroxide crystals. The ettringite crystals are expansive in nature and start forming in the matrix as the heat of hydration evolves and there is space in the matrix for crystals to grow. Also the presence of weak CH crystals ensures a poor microstructure and there is space for products of hydration to grow.

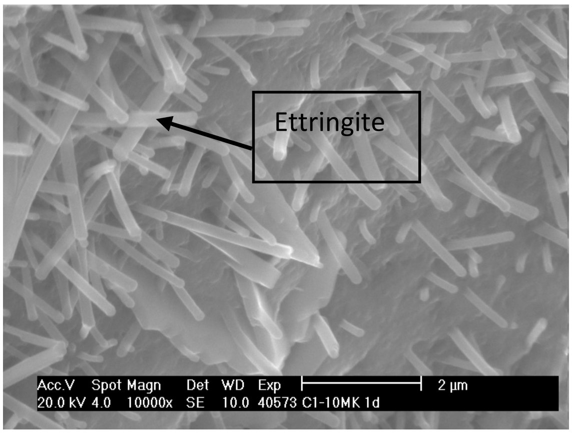


Table 4.1: EDAX

Element	Wt %	Mol %
Na_2O	00.09	00.09
MgO	01.30	01.87
Al_2O_3	01.85	01.05
SiO_2	29.48	28.38
SO_3	00.49	00.35
K_2O	00.50	00.31
CaO	65.61	67.67
TiO_2	00.11	00.08

Fig 4.16: SEM photograph of SCM sample containing 10% MK in Replacement Mode at the age of 1 day

Fig 4.16 also shows formation of ettringite in the MK formulation after 24 hours (1 day) as compared to CEM 1 which showed ettringite after 3 days. This can be attributed to the early calorimetric peak of MK. The EDAX of this photograph shows a high percentage of CaO and SiO_2 indicating the formation of hydration products (ettringite, CSH gel and CH crystals). EDAX graph of Table 4.1 is shown in Fig 1 of Annexure B.

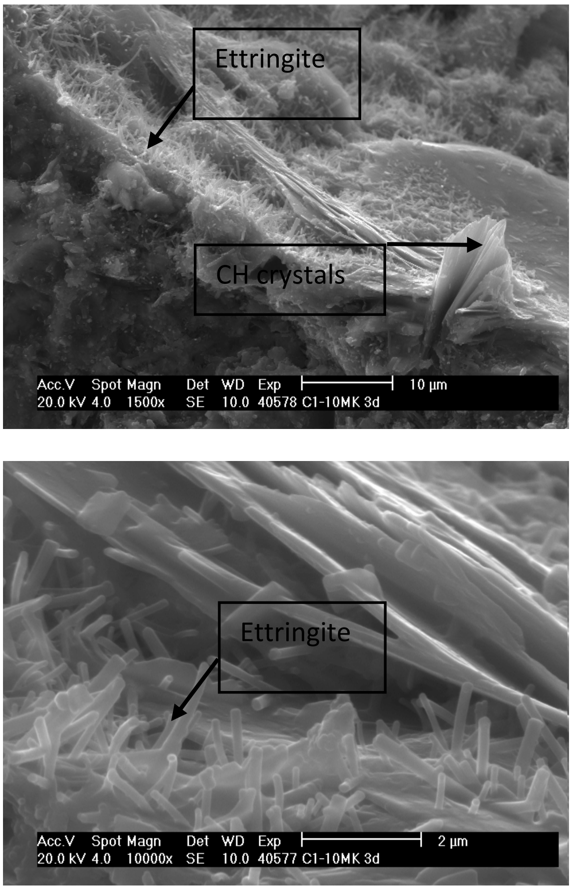


Table 4.2: EDAX

Element	Wt %	Mol %
Na_2O	00.09	00.09
MgO	02.54	03.99
Al_2O_3	11.05	06.87
SiO_2	30.81	32.51
SO_3	10.27	08.13
K_2O	03.17	02.13
CaO	40.36	45.64
Fe_2O_3	01.81	00.72

Fig 4.17: SEM photograph of SCM sample containing 10% MK in Replacement Mode at the age of 3 days

Fig 4.17 also shows the presence of ettringite in the formulation as well as CSH gel. There is also a lack of CH crystals, thus indicating that the Metakaolin is successful in reacting with CH to produce further cementitious compounds. The EDAX shows a reduced CaO content and increased SiO_2 content at 3 day age as compared to 1 day age showing the reduction of Calcium Hydroxide due to pozzolanic reaction. The EDAX graph of Table 4.2 is shown in Fig 2 of Annexure B.

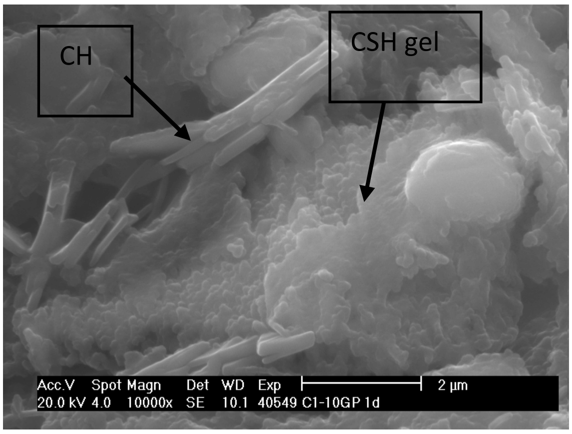


Table 4.3: EDAX

Element	Wt %	Mol %
Na_2O	00.94	00.95
MgO	03.28	05.06
Al_2O_3	07.80	04.77
SiO_2	24.51	25.42
P_2O_5	00.21	00.09
SO_3	06.63	05.16
K_2O	01.32	00.87
CaO	49.85	55.39
TiO_2	00.40	00.31
Fe_2O_3	05.06	01.97

Fig 4.18: SEM photograph of SCM sample containing 10% GP in Replacement Mode at the age of 1 day

Fig 4.18 also shows formation of CH crystals in the formulation as well as CSH gel. This shows that the hydration of GP based formulation has commenced but its pozzolanic reaction is not started as GP acts as filler only. This can also be confirmed by its delayed calorimetric peak and retarded strength development. EDAX graph of Table 4.3 is shown in Fig 3 of Annexure B.

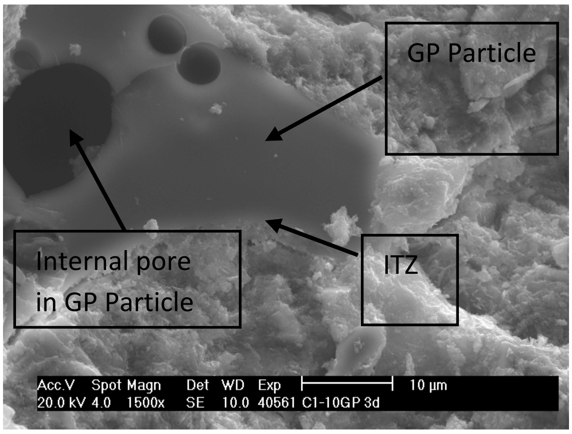


Table 4.4: EDAX

Element	Wt %	Mol %
Na_2O	10.48	10.19
MgO	02.15	03.21
Al_2O_3	02.22	01.31
SiO_2	75.31	75.50
SO_3	00.34	00.26
K_2O	01.26	00.81
CaO	07.88	08.47
TiO_2	00.35	00.26

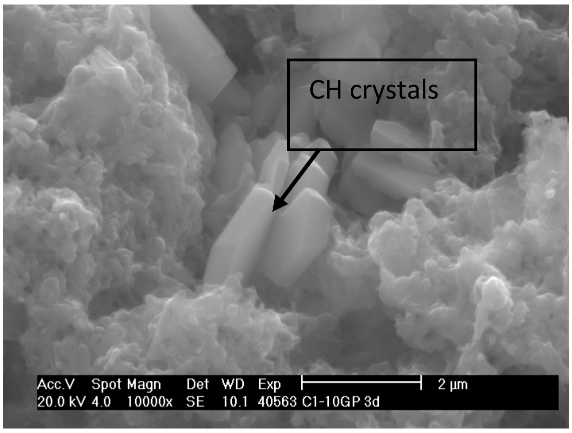


Fig 4.19: SEM photograph of SCM sample containing 10% GP in Replacement Mode at the age of 3 days

Fig 4.19 also shows the presence of CH crystals in the formulation as well as CSH gel and the ITZ of the formulation. The GP has a large size and therefore, its has a thick ITZ leading to a poor microstructure. The presence of CH crystals also indicates the poor pozzolanic capability of GP owing to its large particle size. EDAX graph of Table 4.4 is shown in Fig 4 of Annexure B.

4.2.8 Mercury Intrusion Porosimetery (MIP)

Mercury Intrusion Porosimetery (MIP) was done on the samples to get an idea of the pore size distribution and extent of pore refinement by the SRM's. MIP was done on samples upto the age of 3 days as there is little refinement in pore structure after 3 days [6]. The values of pore size, total porosity and bulk density of the samples are measured automatically by the Pascal 440 Mercury Intrusion Porosimeter and imported into Excel sheets. Fig 4.20, 4.21 and 4.22 show the results of pore radius, total porosity and bulk density of the formulations at the ages of 1 day and 3 days respectively.

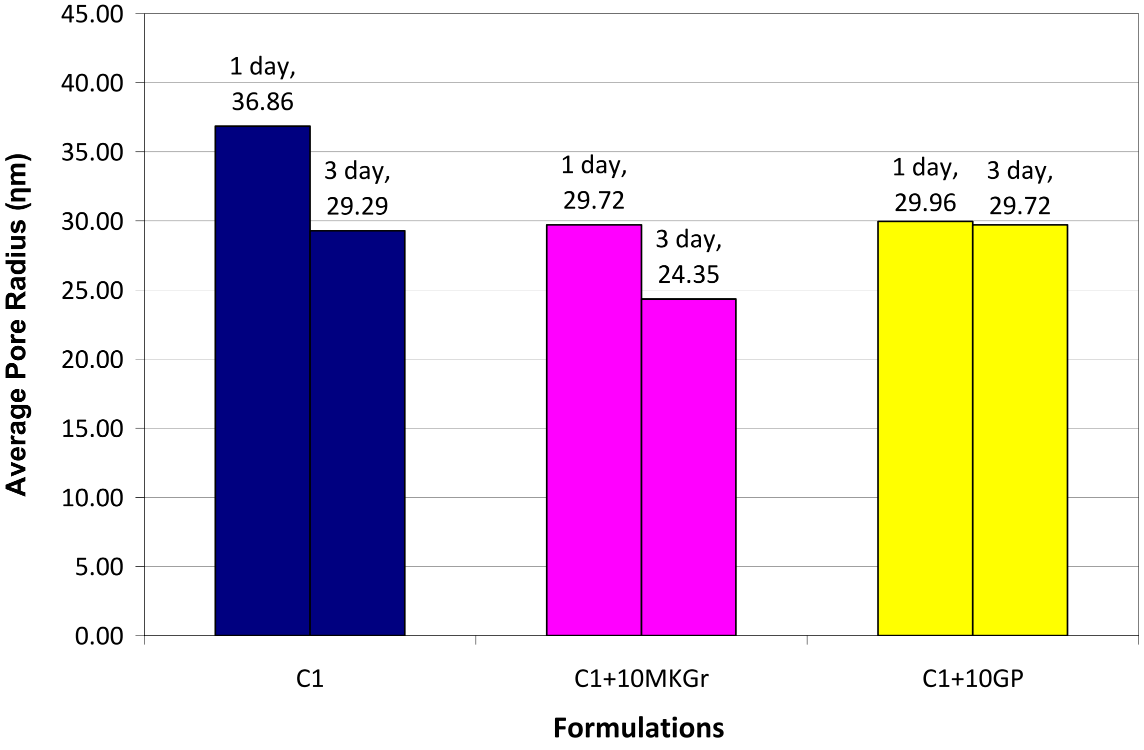


Fig 4.20: Average Pore Radius of SCM formulations at 1 and 3 days

Fig 4.20 shows the evolution of average pore radius of SCM formulations with age. As hydration commences, the average pore radius decreases. The Control mix has higher average pore radius as compared to MK based formulation because of small size of Metakaolin. Also, Glass Powder does not shows significant decrease in average pore radius from 1 day to 3 days as its rate of hydration is slowest as shown by its calorimetric curve.

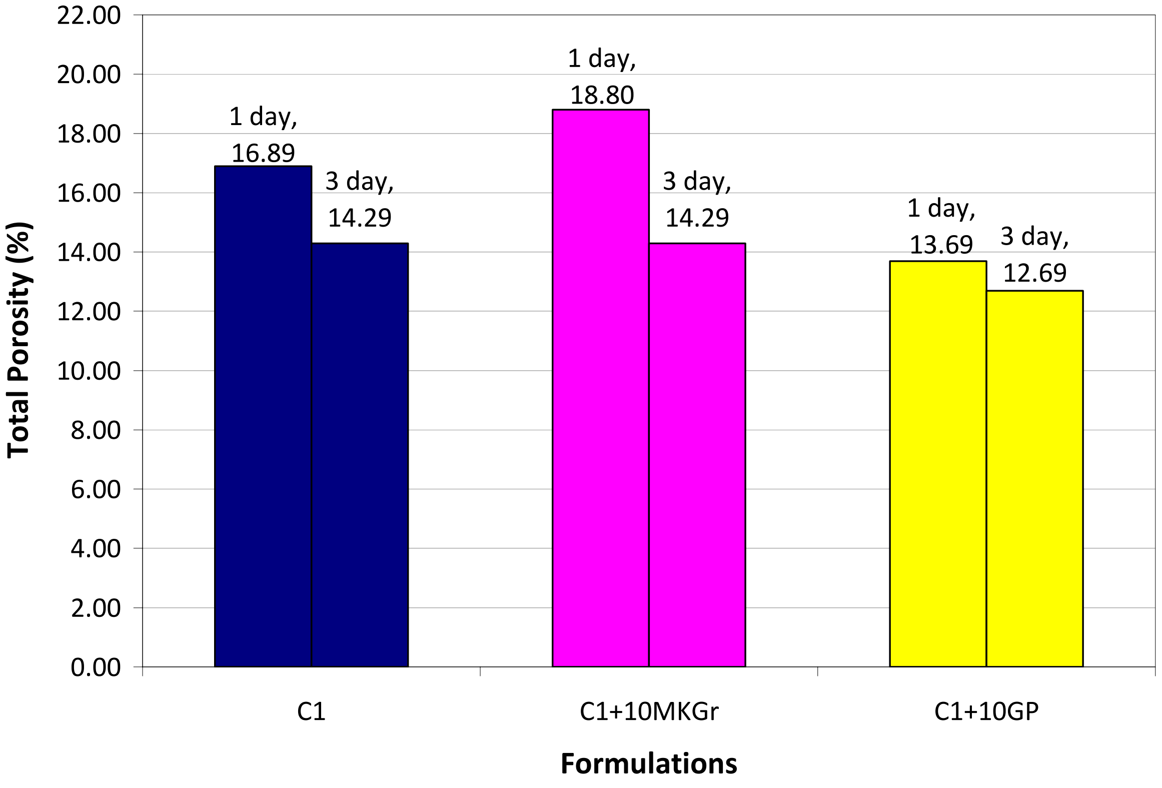


Fig 4.21: Total Porosity of SCM formulations at 1 and 3 days

Fig 4.21 shows the evolution of total porosity of SCM formulations with age. All formulations show decrease in porosity with age as the products of hydration (CSH gel, ettringite and Calcium Hydroxide crystal) grow in empty spaces inside the matrix. The trend of total porosity evolution is similar to average pore radius as decrease in pore radius also results in reduction in porosity with age.

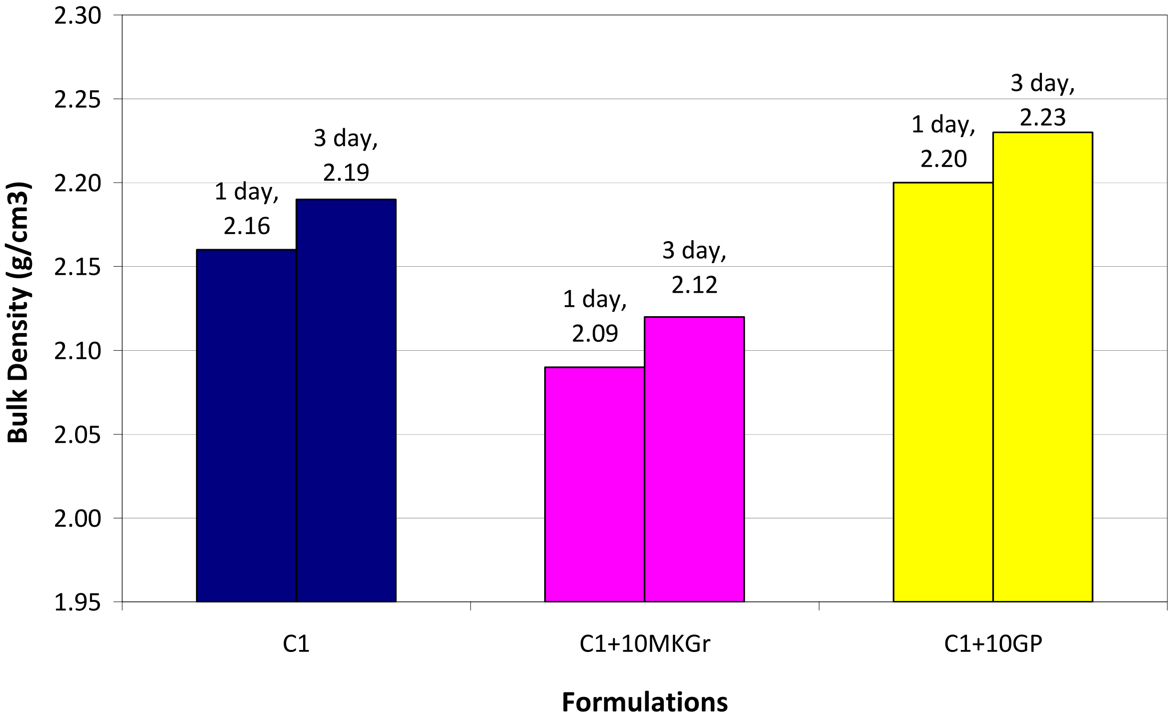


Fig 4.22: Bulk Density of SCM formulations at 1 and 3 days

Fig 4.22 above shows the bulk density of the SCM formulations. They also show a similar trend to Fig 4.21 as Bulk Density is a direct function of total porosity. Hence, the bulk density of formulation increases with age as the total porosity decreases. The relationship between the pore size and the volume of mercury intruded was also plotted by importing the data into Excel sheets. Fig 4.23, 4.24 and 4.25 respectively show the relationship on a logarithmic scale.

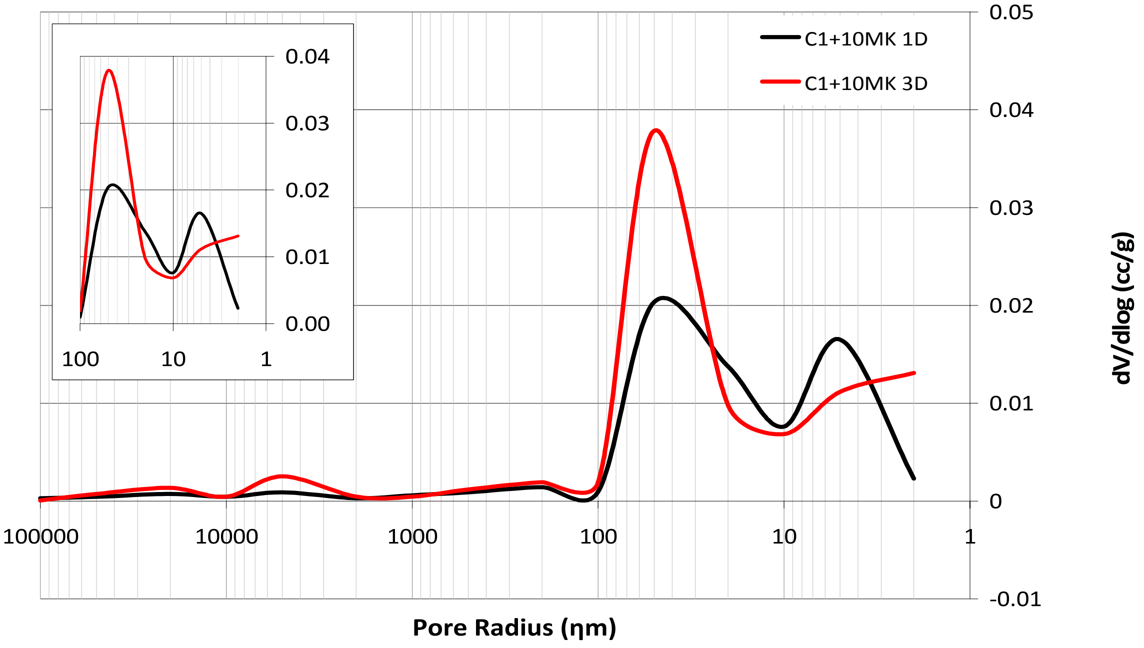


Fig 4.23: MIP Results of C1 formulations at 1 and 3 days

Fig 4.23 shows the development of pore size of CEM 1 formulation. The intruded volume is higher in CEM 1 formulation as compared to Metakaolin and Glass Powder showing that the SRM have an effect on pore refinement.

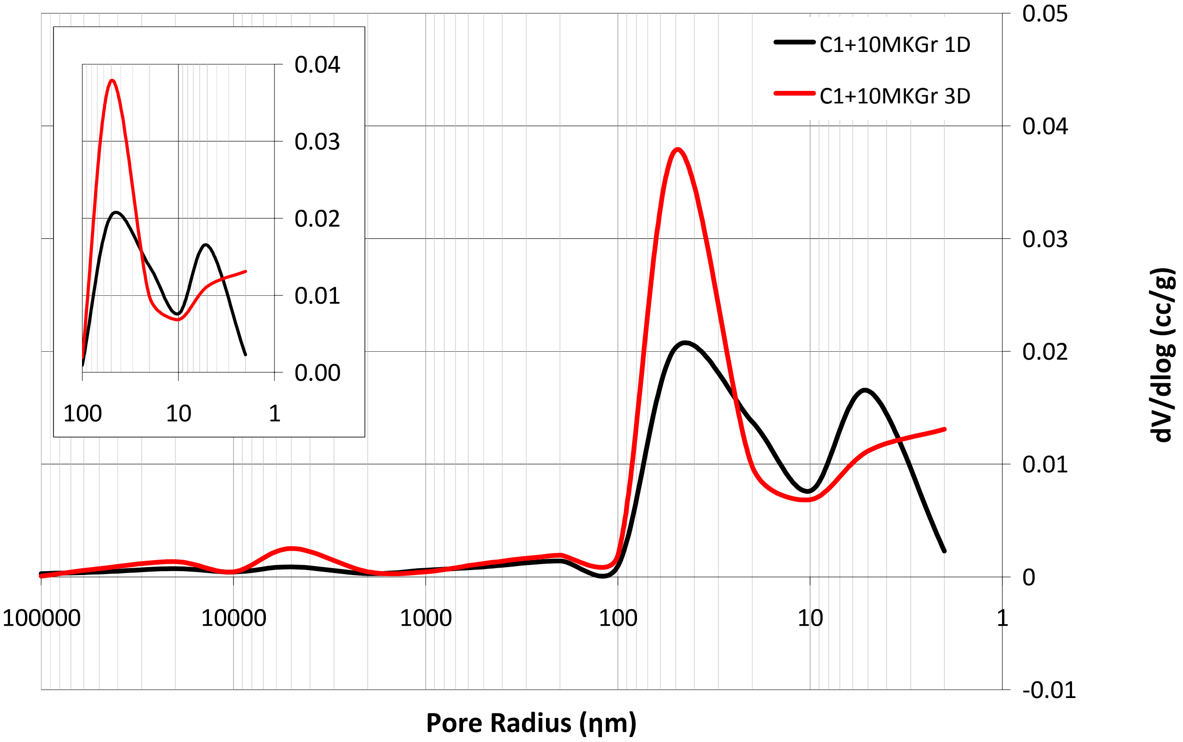


Fig 4.24: MIP Results of C1+10MKGr formulations at 1 and 3 days

Fig 4.24 shows a bi-modal MIP curve for C1+10MKGr formulation. This type of curve can be interpreted as having two groups of different pore sizes [6]. However, after 1 day, there is pore refinement due to pozzolanic reaction of Metakaolin but beyond that; there is no further improvement in pore structure.

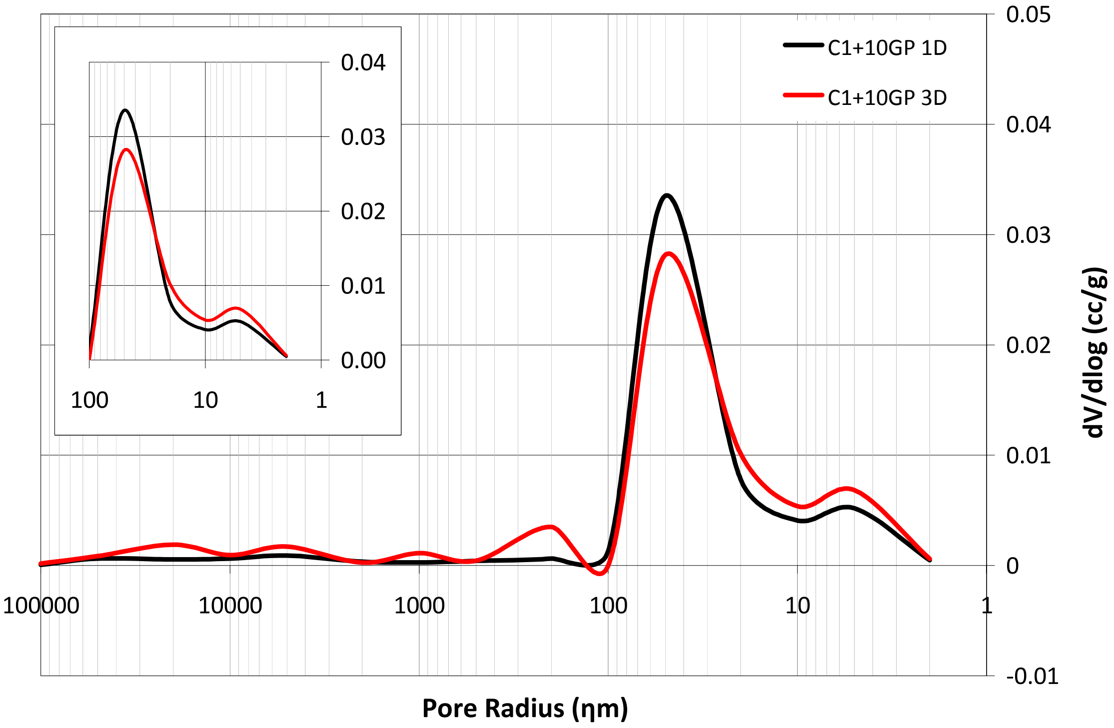


Fig 4.25: MIP Results of C1+10GP formulations at 1 and 3 days

Fig 4.25 shows the MIP curve for C1+10GP formulation. There is no huge difference between pore size between the age of 1 and 3 day, however, intruded volume is greater at 1 day. This suggests that some pores may have discontinuity at 3 days suggesting pore refinement. The relative intruded volume in MK and GP formulation is shown in Fig 4.26 and 4.27 below;

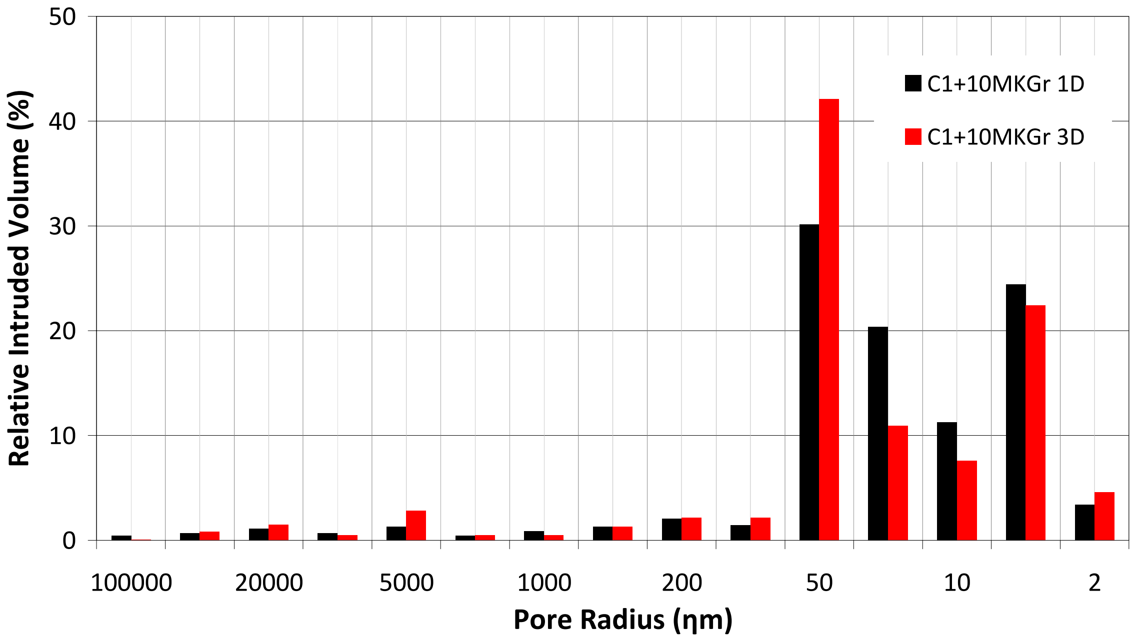


Fig 4.26: Pore Size Ranges of C1+10MKGr formulation at 1 and 3 days

Fig 4.26 shows the bi-modal nature of MIP curve of Metakaolin as it shows an increase in smaller sized interconnected pores at 1 day. Due to interconnected pores, the intruded volume at pore size of 50 m is less for 1 day as compared to 3 day. However, the volume of these small interconnected pores decreases significantly and they are discontinued at 3 day age.

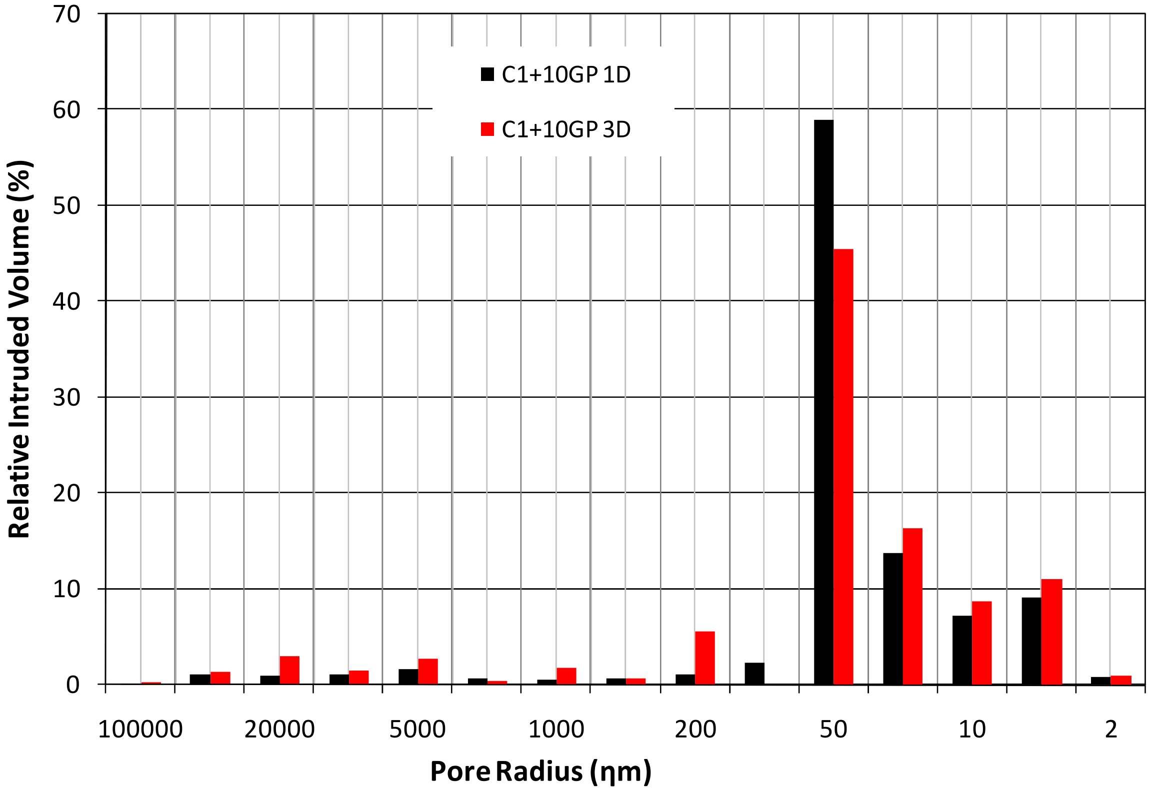


Fig 4.27: Pore Size Ranges of C1+10GP formulation at 1 and 3 days

Glass Powder formulation shows a slightly different pattern as shown in Fig 4.27 above. It has more number of larger pores at 1 day age which is due to the delayed pozzolanic reaction of Glass Powder owing to its larger size but at 3 days, the number of larger pores has decreased and smaller sized pores has increased suggesting pore refinement. The threshold pore radius of the SCM formulations is also plotted at the ages of 1 and 3 days. Fig 4.28 shows the variation in threshold pore radius of formulation with age. All formulation show a decrease in threshold pore radius from the age of 1 day to 3 days suggesting pore refinement. Furthermore, the partial MIP curves of Pore Radius against Intruded Volume for all three formulations are plotted as shown in Fig 1 to Fig 3 in Annexure C.

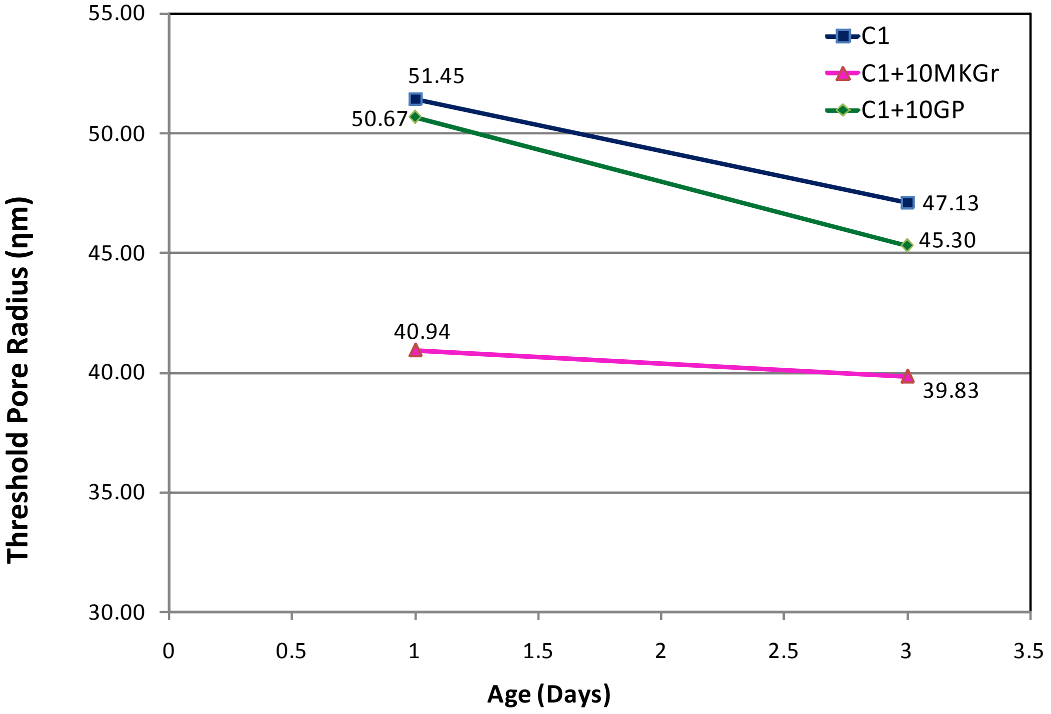


Fig 4.28: Threshold Pore Radius of SCM formulations at 1 and 3 days

4.2.9 Effect of Mixing Water Temperature on Early Shrinkage

The early shrinkage measurement for SCM formulations were recorded upto 24 hours to get an idea about the effect of mixing water temperature on the early shrinkage of the formulations. The linear early shrinkage was recorded at hot and cold mixing water temperatures of 25 ± 1 ^{o}C and 15 ± 1 ^{o}C. The shrinkage strains were recorded on a modified version of German shrinkage channel called “Schwindrinne” and the results are imported into Excel sheets. Figs 4.29 to Fig 4.32 show these results. Metakaolin produces more shrinkage than Control mix due to its small size, latent reactivity and early evolution of heat of hydration whereas Glass Powder shows less shrinkage owing to its large particle size and delayed evolution heat of hydration.

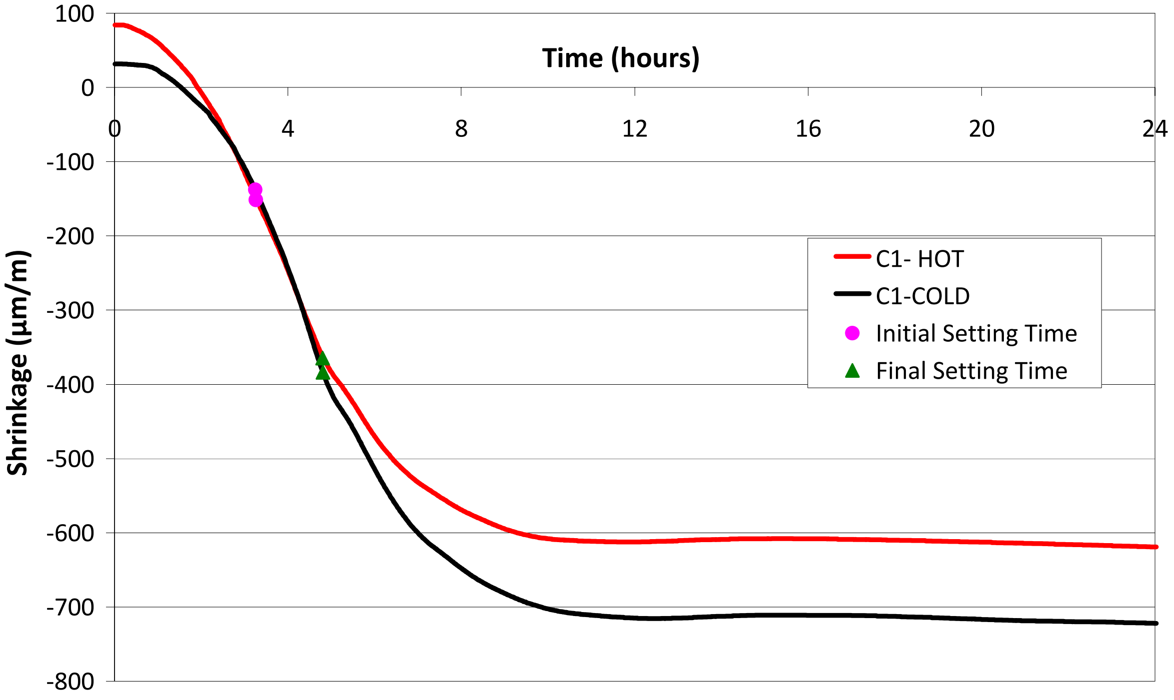


Fig 4.29: Shrinkage of C1 formulation during first 24 hours

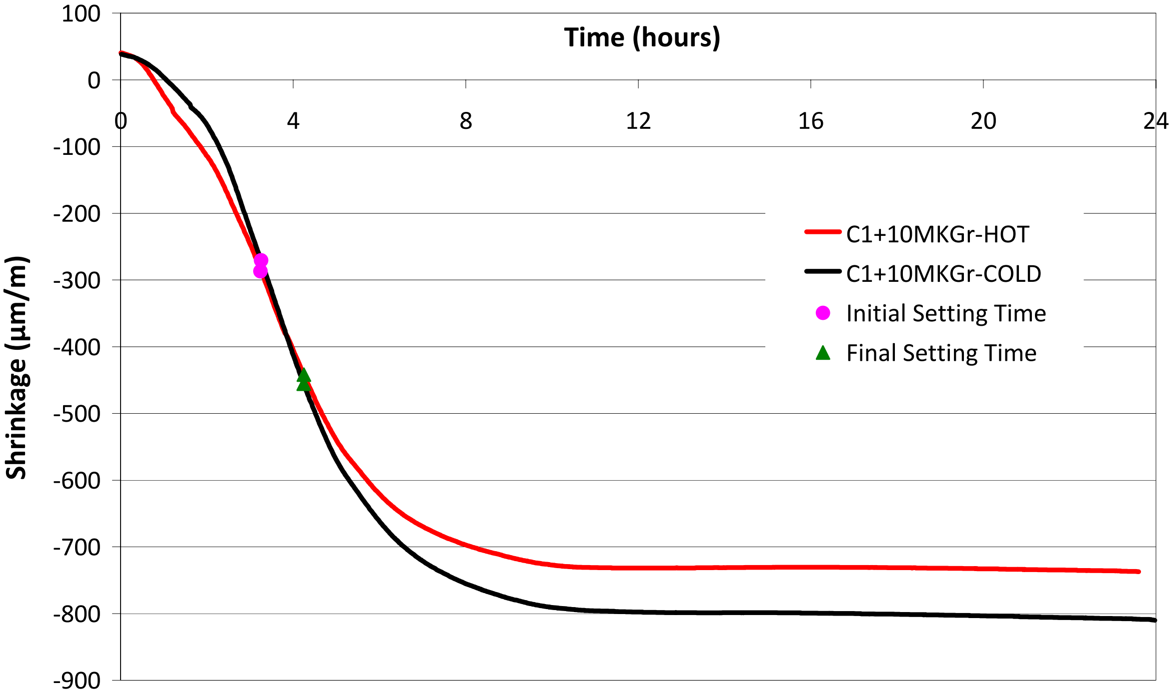


Fig 4.30: Shrinkage of C1+10MKGr formulation during first 24 hours

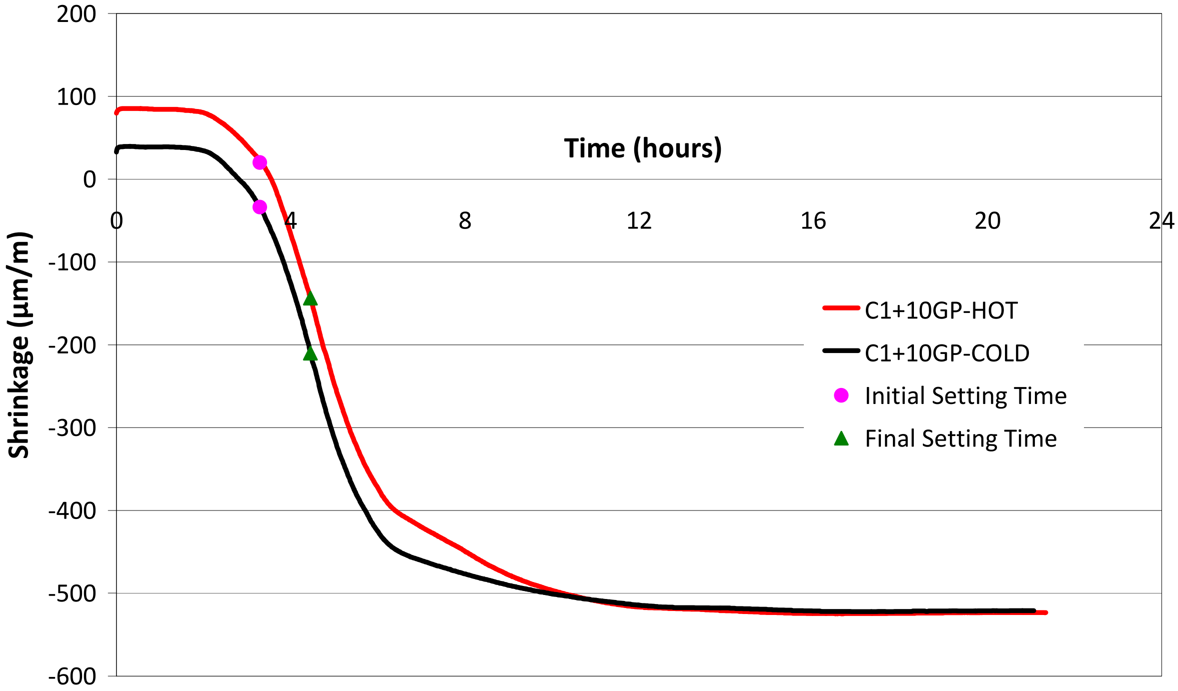


Fig 4.31: Shrinkage of C1+10GP formulation during first 24 hours

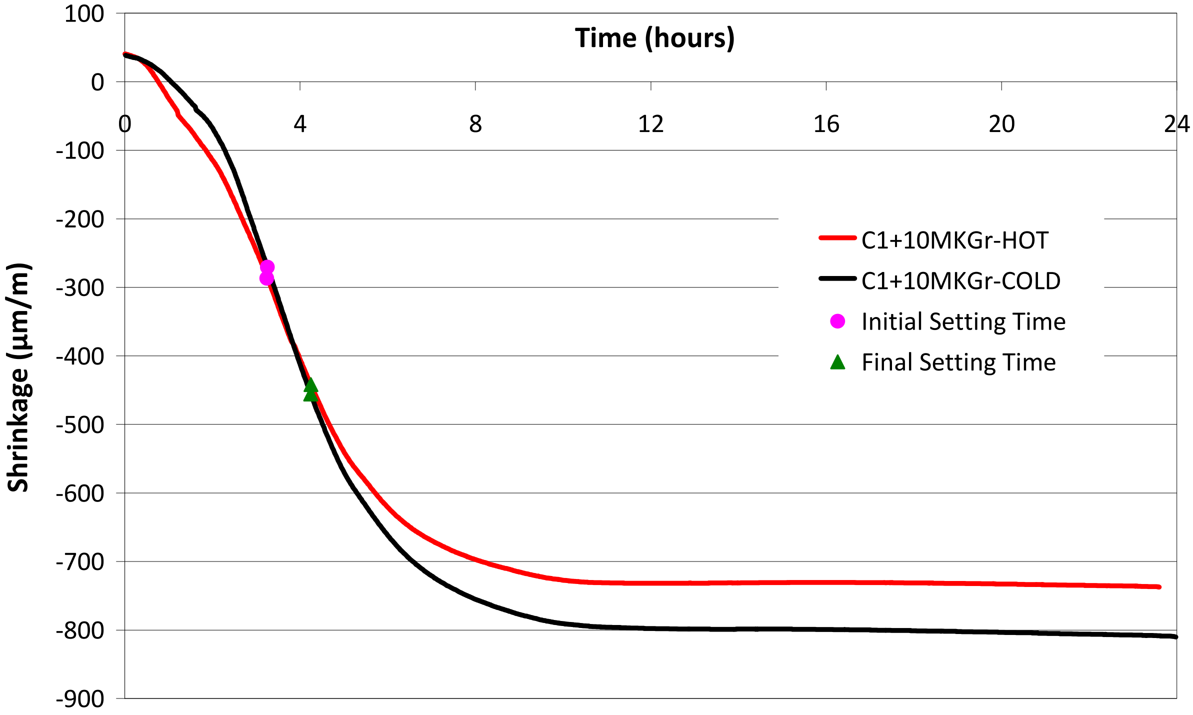


Fig 4.32: Shrinkage of C1+10MKCh formulation during first 24 hours

Fig 4.29 to 4.32 shows the shrinkage of SCM formulations for the first 24 hours. They follow a similar trend showing some initial expansion for hot water and generally show reduced shrinkage for hot water as compared to cold water. The difference between hot and cold water shrinkage for Control mix more (about 100 µm/m) as compared to C1+10MKGr (about 75 µm/m) suggesting that the response of MKGr and Control mix is similar. However, the slightly higher total shrinkage value of MKGr as compared to Control mix can be attributed to its higher heat of hydration evolution as shown in its calorimetric curve in Fig 4.13. MKCh formulation shows the highest amount of early linear shrinkage of about 3500 µm/m while the difference between hot and cold mixing water shrinkage is 200 µm/m. Glass Powder formulation has the least amount of early linear shrinkage for both cold and hot water (520 µm/m) and shows no difference in the shrinkage values for hot and cold water. This can be attributed to slow reaction and heat of hydration evolution of GP as compared to MK and Control mix.

CHAPTER 5 – DISCUSSIONS

5.1 Particle Characterization, Water and Super Plasticizer Demand and Setting Times

Particle shape, size and morphology of secondary raw material (SRM) are very important parameters for understanding their behavior in terms of water demand, SP demand, flow, strength, shrinkage and microstructure of SCM formulations.

SRM particles play a very prominent role in the packing of the mix due to their small particle size. If they are almost twice as small as cement particles, they enhance the packing and reduce porosity in hardened state. It is found that SRM which are three times smaller than cement particles can pack the mix completely in the voids between cement grains. This packing behavior of the mix tends to increase the water demand of SRM based mixed formulations as the introduction of small particles increases the surface area and hence, more water is required to lubricate the mix effectively.

Metakaolin had a much smaller particle size and thus, a greater specific surface area as compared to the CEM-I 42.5R cement as mentioned in Table 3.1. Hence, the water demand of MK formulation tends to be higher than the control mix water demand as shown in Fig 4.3. This may result in the presence of small internal pores and the Fig 4.28 clearly shows that MK tends to reduce the internal pore size.

The particle size of Glass Powder was slightly greater than the particle size of cement as it was milled from large 20 mm size gravels. Due to this effect, the water demand is slightly more for GP formulation as shown in Fig 4.3 and also leads to a slightly larger pore size in GP formulations.

The SP demand of SCM formulations for MK and GP are also higher than control mix as SP is also absorbed by the SRM which depends on the surface area available [90]. The SRM photographs shown in Fig 4.1 (a) and 4.1 (b) also indicate an irregular shape and abrasive texture of SRM particles which increase the internal friction and increase SP demand. The SRM’s (GP) also has some internal porosity which requires a high water and SP demand.

The setting times of formulations with MK and GP in 10% replacement mode also tend to show a delayed setting. This is due to the higher SP demand as SP acts as a retarder as well as the reduced cement content in the matrix tends to delay the onset of hydration.

5.2 Flow of Self Compacting Mortar (SCM) systems

After the initial observations regarding the water demand, SP demand and setting times, the flowability of the SCM formulations was investigated. V-funnel and Hagerman's mini slump cone are usually adopted to investigate these parameters.

The slump test using Hagerman's mini slump cone aims to investigate the yield stress, deformability and filling ability of the SCM formulation. This is determined by two basic parameters: the total spread time and the time for a spread of 25 cm called T_{25} time. The total spread indicates the deformability or yield stress while the T_{25} time indicates the viscosity of flow as well as rate of deformation. The smaller value of T_{25} time indicates a low yield stress, high deformability and low viscosity due to low internal resistance between powder particles.

The V-funnel time represents the time required by a defined volume of SCM to flow through a narrowing section. This indicates the viscosity as well as passing ability of the SCM formulation to overcome the internal and external friction encountered during the flow [32, 91]. Higher w/p ratio leads to lesser V-funnel times and vice versa. The V-funnel time also depends on the particle size, shape, morphology and surface texture of the SRM particles and in case of mortars, it also depends on the total fine aggregate content and its fineness.

The SCM formulation of MK and GP had higher yield stress and high viscosity as indicated by the increase in T_{25} time and V-funnel time as shown in Fig 4.6 and 4.9 respectively. The abrasiveness and irregular shape of the GP and MK particles offer internal friction during flow. The MK also tends to have an affinity to water as it is in calcined, dehydroxylated form while GP particles have internal porosity leading to absorption of free water. These effects tend to reduce the amount of free water available for lubrication of powder particles and increase viscosity.

5.3 Strength of Self Compacting Mortar (SCM) systems

Rizwan [6] reports that in SRM based cementitious systems, the strength is dependent upon the particle size, degree of pozzolanic activity and degree of packing. A larger particle size, low pozzolanic activity and loose packing in the matrix results in the reduction of strength.

The strength of the SCM formulation with MK and GP in 10% replacement mode gave lower value of flexural and compressive strength than the control mix. At the age of 28 days, the strength of MK formulation was almost equal to that of control mix and it is expected to increase beyond the compressive strength of control mix due to the pozzolanic reaction at later ages.

The particle size of SRM's tends to have a dominant role in strength development due to their role in efficient packing of the mix as well as their pozzolanic action. Smaller size SRM pack the mix more efficiently, leading to reduced porosity. As porosity is a direct function of degree of packing, it controls the strength of the mix. Thus, smaller size SRM particles pack efficiently in the voids between cement grains resulting in better packing, lower porosity and consequently improved strength. Metakaolin having a very small particle size, produced better packing and as a result, gave better performance as compared to Glass Powder in terms of strength. This aspect can also be confirmed by the Mercury Intrusion Porosimetery results of SCM formulation as shown in Fig 4.20 to 4.22 respectively.

The strength development also depends on the pozzolanic reactivity of the SRM particles. Pozzolanic activity depends on the amount of amorphous Silica SiO_2 and Alumina Al_2O_3 available in the pozzolan. Metakaolin is noticeably more reactive than Glass Powder as it has purely amorphous phases having undergone calcinations during its manufacture and thus, gives more strength than GP.

It was also observed that the rate of strength gain increased with age in SCM formulation containing MK and GP in replacement mode as shown in Fig 4.11 and 4.12 respectively. This is due to the delayed start of pozzolanic reaction as the pozzolanic reaction converts free lime (calcium hydroxide) into cementitious compounds and at the start, there is no free lime available in the mix. The increase in production of free lime (calcium hydroxide) as a consequence of cement hydration results in a noticeable increase in strength gain due to increase in pozzolanic reaction. With the passage of time, ultimately all free lime is converted into cementitious compounds and greater strength and durability of mix is achieved as calcium hydroxide is a weak crystal and its absence improves the microstructure and consequently, strength of the mix.

5.4 Microstructure of Self Compacting Mortar (SCM) systems

Rizwan [6] reports that the decrease in maximum pore radius is not very significant between the ages of 3 to 7 days and this further diminishes between 7 and 28 days. Hence, we examined the SCM formulation at the ages of 1 day and 3 days with SEM photographs as shown in Fig 4.14 to 4.19 to study the products of hydration. All SCM formulations exhibited the growth of needle-like crystals of Ettringite, hexagonal crystals of calcium hydroxide $Ca(OH)_2$ and formation of CSH gel to various extent.

EDAX microanalysis report of the formulations also showed the presence of CSH gel, Ettringite and $Ca(OH)_2$ as denoted by the high percentage of CaO, SiO_2 and Al_2O_3. The EDAX spectrum reveals higher peaks of Ca, Si and Al as shown in Figure 1 to 4 in Annexure B. One particular point of interest is the EDAX report for C1+10GP at 3 days which shows high silica content. This is due to the EDAX analysis taken in the vicinity of a Glass Powder (GP) particle.

The MIP was done to evaluate the pore size and distribution of SCM formulations. The pore size of MK formulation was found to be less than other formulations due to pore refinement of SCM formulation by Metakaolin. The MIP curve for all SCM formulations shows that the majority of pores are in the range of 10 to 100 ηm. Metakaolin also have a more pronounced secondary curve between pore radius of 1 to 10 ηm showing that it has a greater number of smaller size pores than C1 and Glass Powder based formulations. This pore refinement can be attributed to the effect of hydration and the pozzolanic capability of the SRM. Cook et al [92] reports that the threshold pore width may provide a better idea of material durability and influences the permeability characteristics of the cementitious system. Based on the above argument, the smaller threshold pore radius of Metakaolin may exhibit improved durability at later stages. The increased total porosity of control mix may be attributed to a better interconnectivity of pores inside the matrix at the age of 1 and 3 days.

The increased intruded volume of mercury in Metakaolin shows that MK has internal porosity. However, at 3 days, it has a lower amount of intruded volume which confirms pore refinement due to pozzolanic ability of Metakaolin.

5.5 Calorimetery of Self Compacting Mortar (SCM) systems

The hydration of cement and evolution of heat of hydration is a complex phenomenon and depends upon various factors. It can influence setting times, strength gain and pore refinement and therefore, affects both the early age behavior and long term performance of concrete. The knowledge and measurement of heat flow is necessary to get an estimate of the formation of hydrates [92] and development of a suitable of curing regime [6].

Calorimetery is one of the techniques used to determine the heat flow with respect to time. The calorimetric curves of various SCM formulations show the evolution of heat flow over a period of 72 hours. To understand the heat flow during hydration and the effect of SRM on heat evolution, it is necessary to understand the pattern of the curves. The initial phase or the 1st peak occurs immediately at the start of addition of water and so cannot be measured correctly by the calorimeter. This represents the reaction of the aluminate phase (C_3A) which starts as soon as cement rains come into contact with water. This is followed by a dormant phase in which the hydration slows down rapidly and allows the concrete to be poured before the onset of hardening which is the main reaction leading to setting and strength gain. The actual reasons for the presence of this dormant period are still unknown but two theories have been put forward to explain the process. According to the first theory, a protective layer forms around the cement grains after the initial heat release preventing further reaction till the onset of acceleration period. However, this theory lack circumstantial and scientific evidence to support itself and is therefore, not reliable. The second theory implies that no protective layer forms; rather the induction period occurs due to the slow development of hydrates by nucleation. This theory fails to explain the dramatic slowdown of the rate of reaction after the initial heat release nor is there an explanation of the slow reaction of highly soluble Alite phase [93, 94].

The dormant period ends after a few hours due to the growth of two main hydration products, calcium hydroxide and calcium silicate hydrate (CSH) gel. At this point, an acceleration period starts and there is a gradual rise in the calorimetric curve. This can be attributed to the C_3S hydration which continues for 15 to 20 hours. The start of the acceleration period can also be correlated to the initial setting time of the mix. The hydration of the next phase (C_2S) usually starts after 15 hours, hence there is a deceleration after reaching the second peak but the hydration of C_2S continues steadily and then decreases gradually before ceasing.

Calorimetric peak of SCM formulation with MK in replacement mode gives us the highest second peak due to its pozzolanic activity and micro-filler effect. The reduction in heat liberated by GP formulation is due to dilution effect caused by the reduction of cement content in the mix. However, the hydration kinetics increases with the addition of MK and GP as they act as nucleation sites for the deposition of hydrates.

5.6 Shrinkage of Self Compacting Mortar (SCM) systems

The early 24 hours shrinkage measured in this study is the sum of various parallel, overlapping and simultaneous mechanisms including plastic shrinkage, chemical shrinkage, autogenous shrinkage and drying shrinkage. Shrinkage is caused by the consumption of water either internally during hydration or suction by SRM as well as externally due to loss to outside environment as a result of continued hydration. The cementitious system may also experience expansion due to the growth of expansive crystals in the matrix and re-absorption of bleed water in the system. The linear, volumetric early shrinkage was recorded using the modified German shrinkage channel Schwindrinne.

The temperature of the mixing water had a prominent role in the shrinkage/expansion of the SCM formulations. There was a noticeable increase in expansion in all SCM formulations initially due to increase in temperature of mixing water and the amount of shrinkage increased with the addition of SRM in replacement mode due to their increased water and SP demand which leads to an increase in the drying and chemical shrinkage and thus, increases the early 24 hours shrinkage values for SCM formulation. The shrinkage recovery due to the difference of mixing water temperature can be attributed to the expansion due to absorption by GP and MK, thus leaving less room for growth of expansive calcium hydroxide crystals.

CHAPTER 6 – CONCLUSIONS AND RECOMMENDATIONS

6.1 General

This research work provides useful information and data about the use of Metakaolin and Glass Powder as SRM in Self Compacting Cementitious Systems. The particle size, shape and morphology have an important influence on the water demand, SP demand, flow behavior, volumetric stability, microstructure, strength development and durability of self compacting mortar systems.

6.2 Conclusions

The important conclusions drawn from this work are summarized as follows:

- Metakaolin and Glass Powder formulations require a higher dosage of Super Plasticizer to achieve target flow as compared to control formulation. This increase in SP demand is more pronounced in case of Metakaolin due to its smaller particle size and consequently larger surface area, thus requiring more water to lubricate its particles resulting in more water and SP demand. Glass Powder requires a higher SP demand because of its internal porosity.

- The results of 72 hours isothermal conduction calorimetery indicate the acceleration effect Metakaolin has on cement hydration. The rate of heat evolution is more pronounced in Metakaolin formulation as compared to control mix while Glass Powder formulation exhibits delayed hydration which can be seen from the calorimetric peaks of the three formulations. The evolution of heat of hydration also affects the shrinkage of the formulation and it was observed that MK formulations show increased shrinkage as compared to control mix whereas the GP formulation exhibited the least amount of shrinkage which is concurrent with their respective calorimetric peaks.

- SCM formulations containing MK in replacement mode give compressive strength almost equal to that of the control mix at 28 days age. However, the rate of strength gain with age is appreciably more in MK formulation. Hence, it is predicted that the strength of MK formulation is likely to surpass that of Control mix at later ages due to its pozzolanic reaction. However, due to the larger particle size and weak pozzolanic reaction of GP, the GP formulation produces slightly less compressive strength at the same ages.

- The results of MIP curves show that the threshold pore radius of GP and MK formulations is less than Control mix which indicates that the SRM have improved the packing of the SCM formulation and thus, the durability of the mix is enhanced by MK and GP.

- The incorporation of MK and GP improves the microstructure of the SCM formulation and thus, leads to a strong and durable concrete.

- The SCM formulation exhibit large flow timings with higher yield stress and adequate viscosity due to their irregular shape and abrasive texture.

- The incorporation of MK and GP can lead to a green concrete by replacing the cement content, thus reducing the cement consumption and reducing CO_2 emissions into the environment. This leads to a concrete which is environment friendly and desirable for its strength and durability.

6.3 Recommendations

The study recommends the following based on this work:

- Research must be extended to Self Compacting Concrete (SCC) systems using the same secondary raw materials investigated in this research.

- Resistance of the SCM formulation against acid attack and exposure to sulphate attack may also be investigated to get an idea regarding their performance under adverse environmental conditions.

- It is recommended that the blends of Metakaolin and Glass Powder along with inert fillers like LSP in Self Compacting Cementitious Systems (SCCS) may be investigated.

REFERENCES

[1] ACI 237R – 07; "Self Consolidating Concrete", Report by ACI Committee 237, Published April 2007.

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

[3] http://minerals.usgs.gov/minerals/pubs/commodity/cement/mcs-2011-cemen.pdf, accessed on June 12, 2012.

[4] Mahasenan, N.; Smith, S. and Humphreys, K.; "The Cement Industry and Global Climate Change: Current and Potential Future Cement Industry CO_2 Emissions", Greenhouse Gas Control Technologies - 6th International Conference 2003, pp 995–1000

[5] BS EN 197–1 (2000); "Cement - Part 1: Composition, specifications and conformity criteria for common cements", British Standards.

[6] Rizwan, S. A.; "High-Performance Mortars and Concrete using Secondary Raw Materials", PhD Thesis, Technische Universität Bergakademie Freiberg, Germany, October 2006, ISBN 978-3-639-17878-4, pp. 1-132.

[7] ASTM C 125 "Standard terminology relating to concrete and concrete aggregates"; 2007.

[8] Spence, R.J.S. and Cook, D.J., "Building Materials in Developing Countries", Wiley, London, 1983, pp 125-157

[9] Davis, R.E., "A review of pozzolanic materials and their use in concretes", Symp. On Pozzolanic Materials in Mortars and Concretes, ASTM STP-99, 1950, 3-15

[10] Daniel, D. G. and Lobo, C. L.; "User's Guide To ASTM Specification C94 On Ready-mixed Concrete",

[11] Stanton, T. E and Blanks, R. F.; "Symposium on Use of Pozzolanic Materials in Mortars and Concretes", ASTM committee C07 on Lime, October 10 – 14, 1949.

[12] ASTM C 618 – 12; "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete", Developed by subcommittee C09.24, 2012.

[13] Hewlett, P. C; "Lea's Chemistry of Cement and Concrete", 4th Edition, Butterworth Hienemann, ISBN-340-56589-6, pp. 154-161, 493-496.

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

[15] http://www.swatian.com/history/mineral.html, accessed on 02 June 2012

[16] http://www.psf.gov.pk/abstract.php?id=170, accessed on 07 June 2012

[17] http://en.wikipedia.org/wiki/Glass, accessed on 08 June 2012

[18] Environmental Protection Agency (EPA); "Municipal solid waste generation, recycling, and disposal in the United States: facts and Figures for 2005", EPA-530-F06-039. October 2006.

[19] Chesner, W. H." Waste glass and sludge for use in asphalt pavement, in: H. Inyang, K. Bergeson (Eds.), Utilization of Waste Materials in Civil Engineering Construction, American Society of Civil Engineering, New York, 1992.

[20] Jin, W.; Meyer, C. and Baxter, S.; "Glasscrete — concrete with glass aggregate", *ACI Materials Journal 97,* (March–April 2000) 208–213.

[21] Y. Shao, T. Lefort, S. Moras, D. Rodriguez, "Studies on concrete containing ground waste glass, Cement and Concrete Research, 40 (1) (2000) 91–100.

[22] Shi, C. and Zheng, K.; "A review on the use of waste glasses in the production of cement and concrete", Resources, Conservation and Recycling, Volume 52, Issue 2, December 2007, Pages 234–247.

[23] Wallevik, O. and Nielsson, I.; "Self-compacting concrete- a rheological approach", Proc. International Workshop on Self-Compacting Concrete, Kochi University of Technology, Japan, pp. 1998.

[24] Domone P. L. J. (2006b.) "Self-compacting concrete: An analysis of 11 years of case studies". *Cement and Concrete Composite* 28(2); 197-208.

[25] Okamura H. and Ozawa K.; "Self-compactable high performance concrete", International workshop on high performance concrete, Detroit, American Concrete Institute; 1994. p. 31–44.

[26] Okamura H. and Ozawa K.; "Mix design for self-compacting concrete", *Concrete Library*, JSCE, No. 25, 1995, pp. 107–20.

[27] Gagne, R.; Pigeon, M. and Aitcin, P. C.; "Deicer Salt Scaling Resistance of High-Performance Concrete made with different cements", Volume 126, Pages 185-200, August, 1991.

[28] 3rd International RILEM Symposium on Self-Compacting Concrete, Edited by Wallevik, O. H. and Nielsson, I., Pages: 1056, 2003.

[29] The Concrete Society, BRE. 2005; "Technical report No. 62: Self-compacting concrete: a review", Day RTU, Holton IX, editors, Camberley, UK, Concrete Society, Surrey GU17 9AB, UK.

[30] Nehdi, M. L.; Pardhan, M. and Koshowski, S. (2004); "Durability of self-consolidating concrete incorporating high-volume replacement composite cements", *Cement and Concrete Research* 34(11):2103-2112.

[31] Ozawa, K. (2001); "Utilization of new concrete technology in construction project - Future prospects of self-compacting concrete", The 2nd International RILEM Symposium on Self-Compacting Concrete, Ozawa, K. and Ouchi, M.; editors, 57-62.

[32] Walraven, J. C. (1998); "The development of self-compacting concrete in the Netherlands", International Workshop on Self-compacting Concrete, 87-96.

[33] European Guidelines for Self Compacting Concrete, May 2005, EFNARC, http://www.efnarc.org/publications.html, accessed on 14 April 2012.

[34] Khayat, K. H; Ghezal, A. and Hadriche, M. S.; "Utility of Statistical Models in Proportioning Self Consolidating Concrete", 1st International RILEM Symposium on Self Compacting Concrete , 13-15 Septembet 1999, Stockholm, Sweden, pp. 345-358.

[35] Miao Liu; "Wider Applications of additions in self-compacting concrete", PhD Thesis, University College, London, England.

[36] Roussel, N.; "A thixotropy model for fresh fluid concretes: Theory, validation and applications", Laboratoire Central des Ponts et Chaussées, France, 31 May 2006.

[37] Barnes, H. A.; Hutton, J. F., Walters, K.; "An Introduction to Rheology", Elsiever, copyrighted 1989.

[38] http://www.theconcreteportal.com/rheology.html, accessed on 1st August, 2012.

[39] De Schutter, G.; Bartos, P. J. M.; Domone, P. L. J. and Gibbs, J.C. (2008); "Self-compacting concrete", Whittles Publishing.

[40] RILEM TC 174 SCC (2000); “Self compacting concrete: State-of-the-art report of RILEM technical committe 174-SCC”, Skarendahl A, Petersson O, editors, RILEM Publications S.A.R.L., France.

[41] Okamura H. and Ouchi M. (2003a); “Applications of self-compacting concrete in Japan”, The 3rd International RILEM Symposium on Self-Compacting Concrete, Wallevik, O. H. and Nielsson, I., editors, RILEM Publications S.A.R.L., Bagneux, France. 3-5.

[42] Skarendahl, A. (2003); “The present - The future”, The 3rd International RILEM Symposium on Self-Compacting Concrete, Wallevik O. H. and Nielsson I., editors, RILEM Publications S.A.R.L., Bagneux, France, 6-14.

[43] Cordeiro, G. C.; Toledo Filho, R. D. and Fairbairn, E. M. R.; “Effect of calcination temperature on the pozzolanic activity of sugar cane bagasse ash”, *Construction and Building Materials*, Volume 23, Issue 10, October 2009, Pages 3301–3303

[44] Tangpagasit, J.; Cheerarot, R.; Jaturapitakkul, C. and Kiattikomol, K.; “Packing effect and pozzolanic reaction of fly ash in mortar”, *Cement and Concrete Research* 35 (2005),pp. 1145– 1151.

[45] Wild, S.; Khatib, J. M. and Jones, A. (1996); “Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete”, *Cement and Concrete Research*, 26(10), pp. 1537-1544.

[46] Rizwan, S. A. and Bier, T. A.; “Self-Compacting Mortars using Various Secondary Raw Materials”, *ACI Materials Journal,* USA, Vol. 106, No. 1, January-February 2009, pp 25-32.

[47] Cyr, M.; Lawrence, P. and Ringot, E.; “Efficiency of Mineral Admixtures in Mortars: Qualification of the physical and chemical effects of fine admixtures in relation with compressive strength”, Cement and Concrete Research, 36 (2006), pp. 264-277.

[48] Ramlochan, T.; Thomas, M. and Karen A Gruber, K. A.: “The effect of metakaolin on alkali–silica reaction in concrete”, *Cement and Concrete Research,* Volume 30, Issue 3, March 2000, pp. 339–344.

[49] Ambroise, J.; Murat, M., and Pera, J. (1985); “Hydration reaction and hardening of calcined clays and related minerals: V. Extension of the research and general conclusions”, *Cement and Concrete Research*, 15: 261-268.

[50] Bensted, J. and Barnes, P. (2002); “Structure and Performance of Cements”, 2nd Edition, New York: Spon Press.

[51] Mindess, S.; Young, F. and Darwin, D. (2003); Concrete, 2nd Edition, Prentice Hall, Upper Saddle River, NJ.

[52] Poon, C.S.; Kou, S.C. and Lam, L. (2002); “Pore size distribution of high performance metakaolin concrete”, *Journal of Wuhan University Of Technology-Materials Science Edition*, 17(1): 42-46.

[53] Poon, C.S.; Lam, L.; Kou, S.C.; Wong, Y.L. and Wong, R (2001); “Rate of pozzolanic reaction of metakaolin in high-performance cement pastes”, *Cement and Concrete Research*, 31(9): 1301-1306.

[54] Poon, C. ; Kou, S.C. and Lam, L.; “ Compressive strength, chloride diffusivity and pore structure of high performance metakaolin and silica fume concrete”, *Construction and Building Materials,* Volume 20, Issue 10, December 2006, Pages 858–865.

[55] El-Hadj Kadri, Kenai, S.; Ezziane, K.; Siddique, R. and De Schutter, G.; “Influence of metakaolin and silica fume on the heat of hydration and compressive strength development of mortar”, Applied Clay Science 53 (2011) 704–708.

[56] Ambroise, J.; Maximilien, S. and Pera, J.; “Properties of Metakaolin blended cements”, Advanced Cement Based Materials, Volume 1, Issue 4, May 1994, Pages 161–168.

[57] Frías, M.; de Rojas, M. I. S. and Cabrera, J. (2000); “The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin-cement mortars”, *Cement and Concrete Research*, Volume 30, Issue 2, February 2000, Pages 209–216.

[58] Khatib, J.M. and Wild, S. (1996); “Pore size distribution of metakaolin paste”, *Cement and Concrete Research*, Volume 26, Issue 10, October 1996, Pages 1545–1553.

[59] Khatib, J.M. and Wild, S. (1998); “Sulphate resistance of metakaolin mortar”, *Cement and* Concrete Research, Volume 28, Issue 1, January 1998, Pages 83–92.

[60] Justice, J. M.; “Evaluation of Metakaolins for use as Supplementary Cementitious Materials, MS Thesis, Georgia Institute of Technology, April 2005.

[61] Caldarone, M. A.; Gruber, K. A. and Burg, R. G (1994); “High reactivity metakaolin (HRM): a new generation mineral admixture for high performance concrete”, *Concrete International*, Volume 16, Issue 11, Pages 37-41.

[62] Ding, J. T. and Li, Z. J. (2002); “Effects of metakaolin and silica fume on properties of concrete”, ACI Materials Journal, Volume 99, Issue 4, Pages 393-398.

[63] Brooks, J. J.; Johari, M. A. M. and Mazloom, M. (2000); “Effect of admixtures on the setting times of high-strength concrete”, *Cement and Concrete Composites*, Volume 22, Issue 1, Pages 293-301.

[64] Johnston, C. D.; “Waste glass as coarse aggregate for concrete”, Journal of Testing and Evaluation 2 (5) (1974) 344–350.

[65] Shayan, A. and Xu, A.; “Performance of glass powder as a pozzolanic material in concrete: A field trial on concrete slabs”, *Cement and Concrete Research*, 36 (2006) 457–468.

[66] Pattengil, M. and Shutt, T. C.; “Use of ground glass as a pozzolan”, Albuquergue Symposium on Utilization of Waste Glass in Secondary Products. Albuquerque, New Mexico, U.S.A., 1973, pp. 137–153, Jan. 24–25.

[67] Girbes, I.; Suesta, C.; Lopez-Tendero, M. and Belena, I. (2004); “Recycled glass cullet as partial Portland cement replacement, Sustainable Waste Management and Recycling: Glass Waste”, Proceedings of the International Conference Organised by the Concrete and Masonry Research Group, Kingston University, London (England) 14-15 September 2004, M.C. Limbachiya and J.J. Roberts (eds), pages 141-148.

[68] Shi, C.; Wu, Y.; Riefler, C. and Hugh Wang, H. 2005; “Characteristics and pozzolanic reactivity of glass powders”, *Cement Concrete Research*, Volume 5, No. 35, pp. 987-993.

[69] Schwarz, N; Cam, H and Neithalath, N.; “Influence of a fine glass powder on the durability characteristics of concrete and its comparison to fly ash, *Cement and Concrete Composites*, Volume 30, Issue 6, July 2008, Pages 486–496.

[70] Pike, R. G.; Hubbard, D. and Newman, E. S.; “Binary silicate glasses in the study of alkali-aggregate reaction', Highway Research Board Bulletin 275 (1960) 39–44.

[71] Terro, M. J. (2006); “Properties of concrete made with recycled crushed glass at elevated temperatures”, *Building and Environment*, Volume 41, Issue 5, May 2006, Pages 633–639

[72] Taha, B. and Nounu, G. (2008); "Properties of concrete contains mixed colour waste recycled glass as sand and cement replacement. Construction and Building Materials, Volume 22, Issue 5, May 2008, Pages 713-720.

[73] Figg, J. W.; "Reaction between cement and artificial glass in concrete", Proceedings 5th International Conference on AAR in concrete, Cape Town, South Africa, 1981, paper S252/7.

[74] Meyer, C. and Baxter, S.; "Use of recycled glass for concrete masonry blocks." NYSERDA, Report 97-15, November 1997.

[75] Y. Shao, T. Lefort, S. Moras, D. Rodriguez, Studies on concrete containing ground waste glasses, Cem Concr. Res. 30 (2000) 91– 100.

[76] Shayan, A. & Xu, A. 2004; "Value-added utilization of waste glass in concrete", *Cement and Concrete Research*, Volume 1, No. 34, Pages 81-89.

[77] Sylvia Nicole Mihaljevic; "Effects of Waste Glass and Polymer Addition on the Performance of Concrete Masonry Blocks", MS Thesis, McMaster University, Hamilton, Ontario, Canada, October 2009.

[78] ASTM C1260 – 07; "Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)"

[79] http://www.imerys-perfmins.com/pdf/MetaStar_501_for_Concrete.pdf, accessed on 07 June 2012.

[80] http://www.glapor.com/files/glapor_techn_data_gravel_engl_120104.pdf, accessed on 07 June 2012.

[81] DIN 52104-1:1982-11; " Prüfung von Naturstein; Frost-Tau-Wechsel-Versuch; Verfahren A bis Q"

[82] http://www.construction-polymers.basf.com/portal/streamer?fid=348371, accessed on 07 June 2012.

[83] ACI 211R – 08; "Guide for Selecting Proportions for High-Strength Concrete Using Portland Cement and Other Cementitious Materials", Reported by ACI Committee 211, December 2008.

[84] DIN 1045; "Concrete, reinforced and prestressed concrete structures"

[85] Rizwan, S. A.; Bier, T. A. and Ahmad, H.; “Self-Compacting Concrete – A useful technology”, Pakistan Engineering Congress, 70th Annual Session Proceedings, Vol. 70, pp 293-318, December 2-4, 2006, Lahore.

[86] ASTM C127 – 12; “Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate”.

[87] ASTM C128 – 12; “Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate”.

[88] ASTM C187 – 11e1; “Standard Test Method for Amount of Water Required for Normal Consistency of Hydraulic Cement Paste”.

[89] DIN EN 196 “Methods of testing cement”.

[90] Barger, G. S.; Lukkarila, M. R.; Martin, D. L.; Lane, S. B.; Hansen, E. R.; Ross, M. W. and Thompson, J. L.; “Evaluation of a Blended Cement and a Mineral Admixture Containing Calcined Clay Natural Pozzolan for High-Performance Concrete”, Proceedings of the Sixth International Purdue Conference on Concrete Pavement Design and Materials for High Performance, Purdue University, West Lafayette, Indiana, November 1997, 21 pages.

[91] Rizwan, S. A. and Bier, T. A.; “Role of Mineral Admixtures in High Performance Cementitious Systems”, Proc. 2nd All Russian International Conference on “Concrete and reinforced Concrete-Development trends”, Vol. 3,”Concrete Technology”, 5-9 September 2005, Moscow, Russia. pp 727-732. ISBN 5-98580-013-x.

[92] Cook, R. A and Hover, K. C; “Mercury porosimetry of hardened cement pastes”, Cement and *Concrete Research*, Volume 29, Issue 6, June 1999, Pages 933–943.

[93] H. Kada-Benameur, H.; Wirquin, E. and Duthoit, B.; “Determination of apparent activation energy of concrete by isothermal calorimetery”, *Cement and Concrete Research*, Volume 30, Issue 2, February 2000, Pages 301–305.

[94] Scrivener, K. L.; “Advances in Understanding Cement Hydration”, Proceeding of International Conference Ibausil 17, Weimar, Germany, September 2009.

[95] Adnan, A.; “Study of Quarry Dust, Glass Powder and Ground Granulated Blast Furnace Slag as SRM’s in Self Compacting Cementitious Systems”, MSc Thesis, NIT (NUST), Islamabad.

ANNEXURE A – BOGUE'S LIMIT CALCULATIONS, MIX PROPORTIONS, WATER DEMAND, SUPER PLASTICIZER DEMAND AND SETTING TIMES OF SCM FORMULATIONS

Table 1 – Bogue's Limit Calculation of CEM I 42.5R [13]

Clinker Phase	Formula (Oxides* in Percentage)	Calculated Value of CEM I 42.5R (%)
Tetra – Calcium Aluminoferrite (C_4AF)	3.043 (Fe_2O_3)	7.27
Tri – Calcium Aluminate (C_3A)	2.65 (Al_2O_3) – 1.692 (Fe_2O_3)	9.76
Tri – Calcium Silicate (C_3S)	4.071 (CaO) – 7.6 (SiO_2) – 6.718 (Al_2O_3) – 1.43 (Fe_2O_3) – 2.85 (SO_3)	55.30
Di – Calcium Silicate (C_2S)	2.867 (SiO_2) – 0.7544 (C_3S)	13.24

* Value of Oxides in Percentage taken from Table 3.1

Table 2 – Mix Proportions of all formulations

S/No	Type	Cement (grams)	SRM (grams)	Water (grams)
1	**CEM 1**	500	-	140.0
2	**C1+10MKFr**	450	50	152.5
3	**C1+10GP**	450	50	185.0
4	**C1+10MKCh**	450	50	137.5
5	**C1+10GP [95]**	450	50	136.0

Table 3 – Water Demand and Setting times of all formulations

S/No	Type	SRM Content (%)	WD (%)	IST (min)	FST (min)
1	**CEM 1**	-	28.00	195	288
2	**C1+10MKFr**	10	33.89	195	255
3	**C1+10GP**	10	30.56	198	267
4	**C1+10MKCh**	10	41.11	240	310
5	**C1+10GP [95]**	10	30.25	298	333

Table 4 –SP (Melflux 2651F) demand for Target Flow of 30±1 cm for all formulations

S/No	Type	Mixing Water (%)	SRM Content (%)	SP Content (%)
1	**CEM 1**	28.00	-	0.282
2	**C1+10MKFr**	33.89	10	0.333
3	**C1+10GP**	30.56	10	0.447
4	**C1+10MKCh**	41.11	10	0.489
5	**C1+10GP [95]**	30.25	10	0.160

Table 5 – Flow Times for all formulations

S/No	Type	SRM Content (%)	T_{25} cm Time for 30±1 cm (sec)	T total time for 30±1 cm (sec)
1	**CEM 1**	-	1.91	31.50
2	**C1+10MKFr**	10	2.07	34.36
3	**C1+10GP**	10	2.24	38.92
4	**C1+10MKCh**	10	2.67	59.34
5	**C1+10GP [95]**	10	1.09	25.00

Table 6 – V-Funnel Times for all formulations

S/No	Type	SRM Content (%)	V-Funnel Time (sec)
1	**CEM 1**	-	8.47
2	**C1+10MKFr**	10	9.01
3	**C1+10GP**	10	10.75
4	**C1+10MKCh**	10	13.67
5	**C1+10GP [95]**	10	4.84

ANNEXURE B – ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDAX)

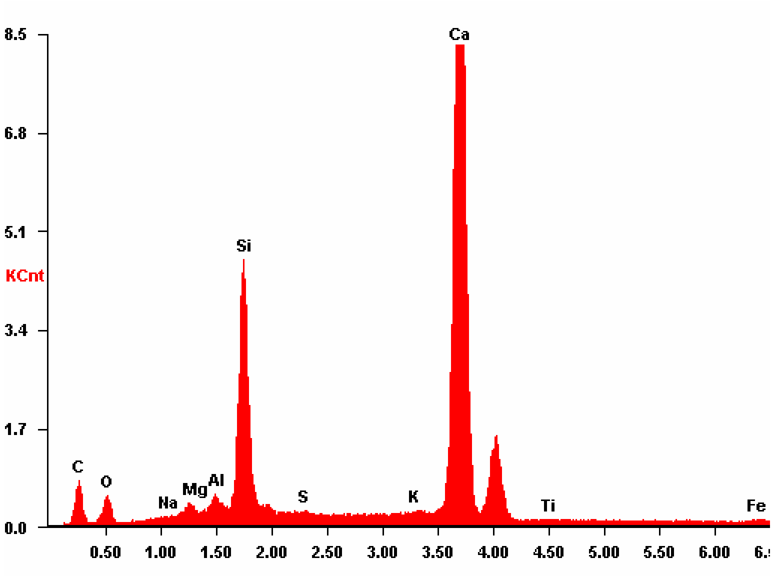


Figure 1: EDAX of SCM sample containing 10% MK in Replacement Mode at the age of 1 days

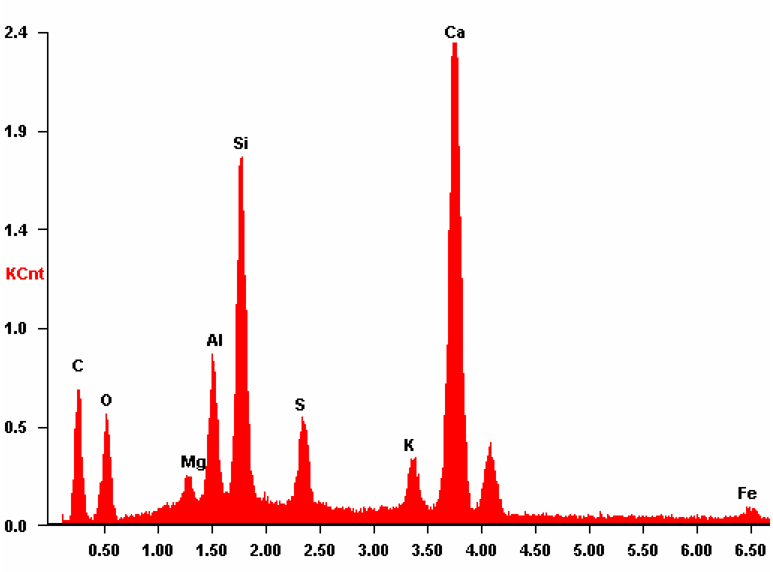


Figure 2: EDAX of SCM sample containing 10% MK in Replacement Mode at the age of 3 days

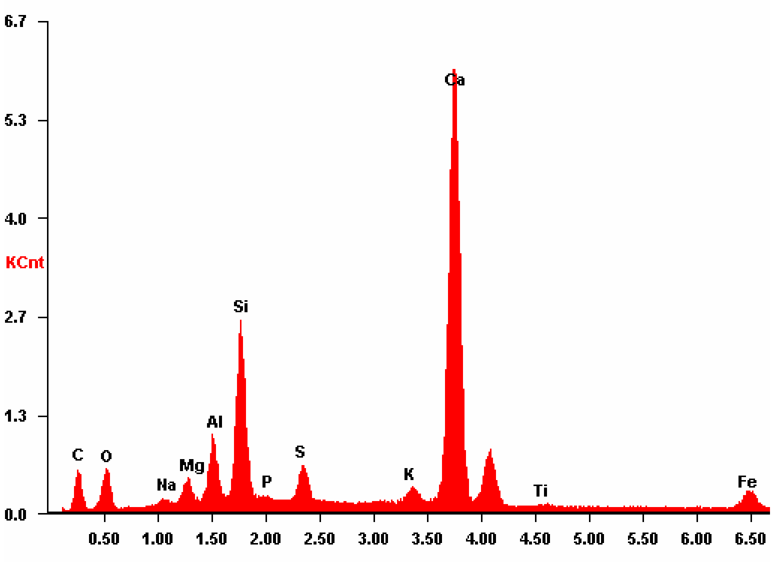


Figure 3: EDAX of SCM sample containing 10% GP in Replacement Mode at the age of 1 day

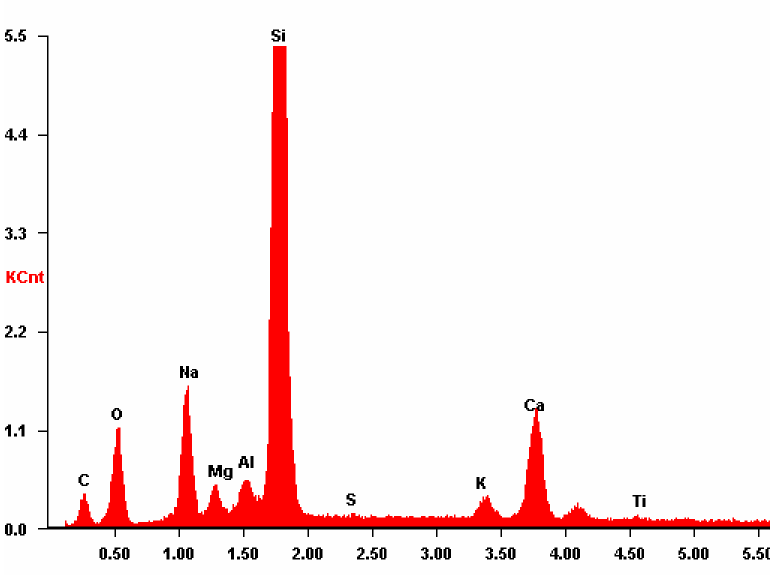


Figure 4: EDAX of SCM sample containing 10% GP in Replacement Mode at the age of 3 days

ANNEXURE C – MERCURY INTRUSION POROSIMETERY (MIP)

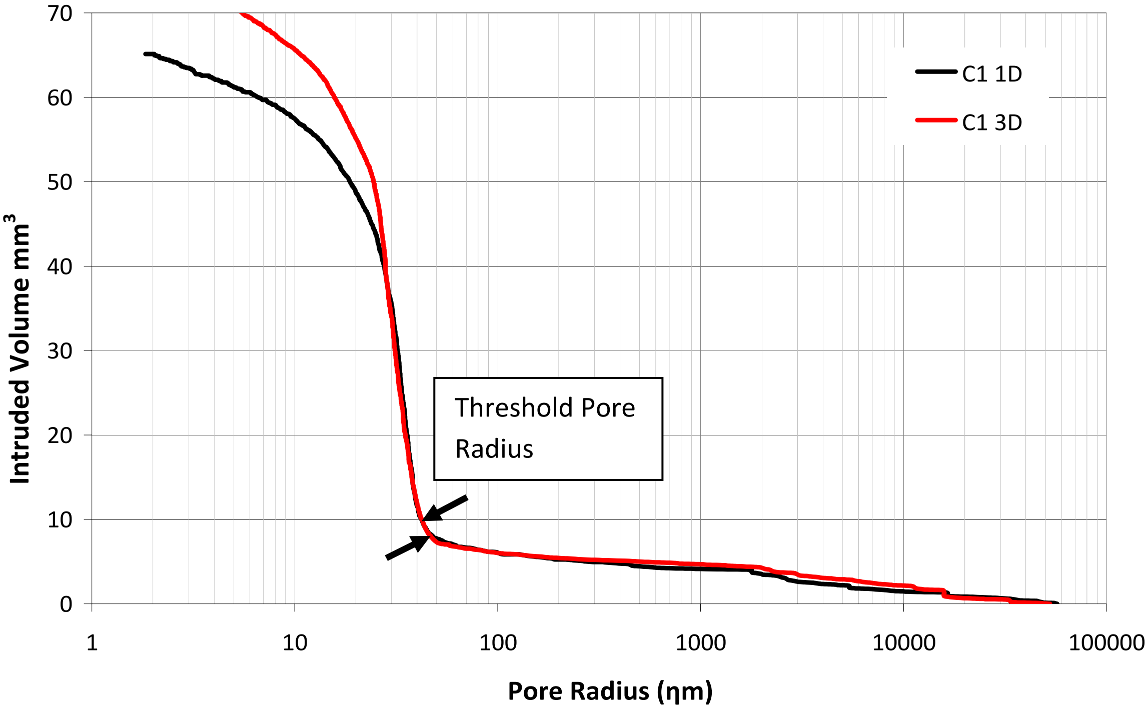


Figure 1: Relationship of Pore Radius and Intruded Volume of C1 formulation at 1 and 3 days

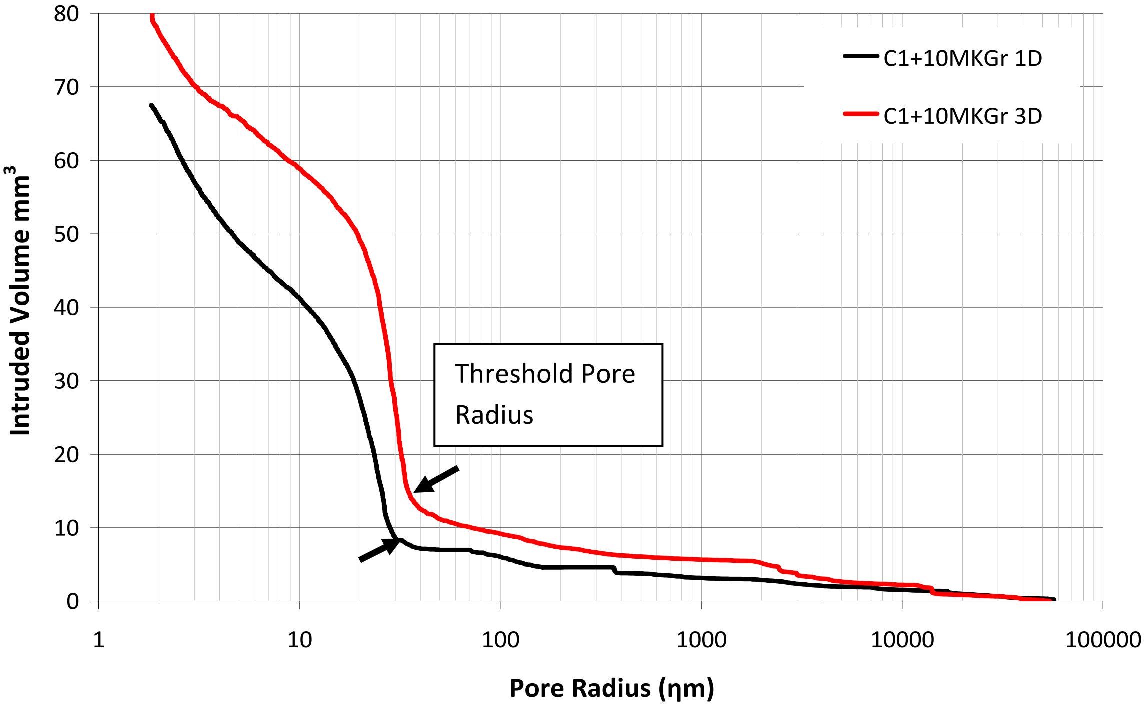


Figure 2: Relationship of Pore Radius and Intruded Volume of C1+10MKGr formulation at 1 and 3 days

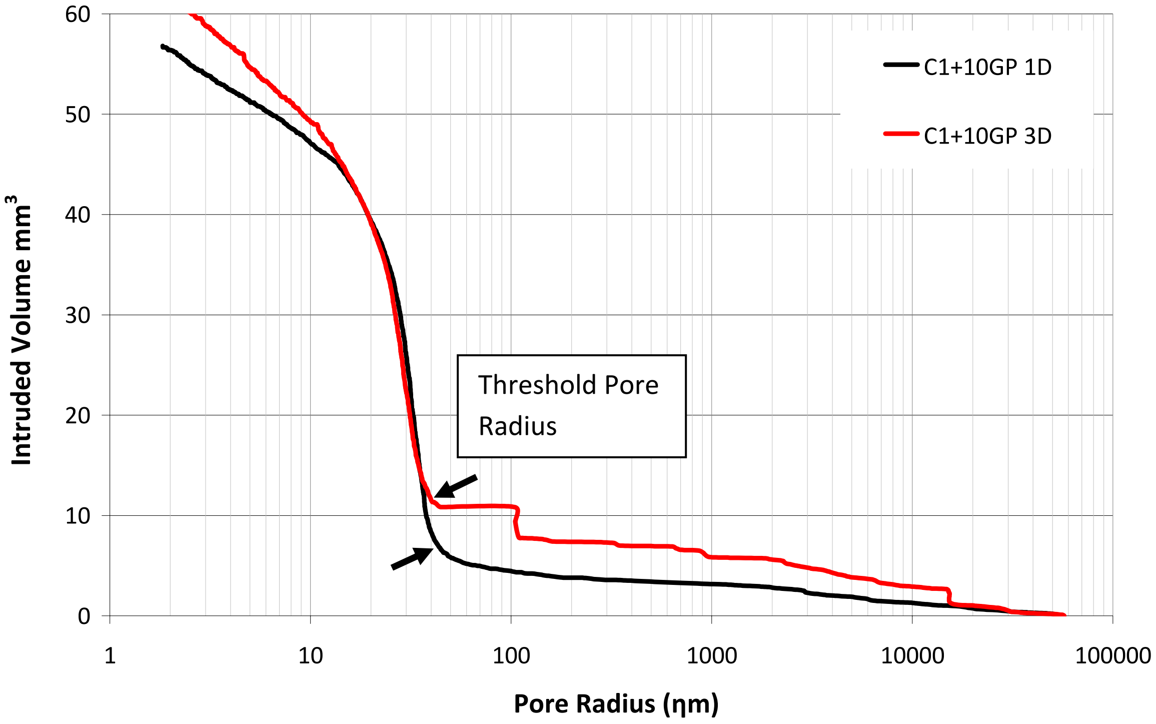


Figure 3: Relationship of Pore Radius and Intruded Volume of C1+10GP formulation at 1 and 3 days