Study of hydration kinetics and volume stability in self-compacting cementitious system using granite powders.

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NUST201463420MSCEE15214F

This thesis is submitted in partial fulfilment of
the requirements for the degree of

Master of Science

in

Structural Engineering

National Institute of Civil Engineering (NICE)

School of Civil & Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

2017

This is to certify that

Thesis entitled

Study of hydration kinetics and volume stability in self-compacting cementitious system using admixtures.

Submitted by

NOOR KHAN

Has been accepted towards the partial fulfillment

of

the requirements

for award of degree of

Master of Science in Structural Engineering

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June 2017, Islamabad Pakistan

ACKNOWLEDGEMENTS

In the name of ALLAH, the compassionate. All praises are for ALLAH, who blessed me more than I deserve and made me able to fulfill my research work.

The author pays his profound gratitude to Prof.Dr.Ing. Syed Ali Rizwan,HoD Structure, NUST Institute of Civil Engineering (NICE), for his scholarly guidance, kind support and care throughout the research work. I am grateful to him for his affection, swift checking of the manuscripts and for his frank criticism during the write up.

I am immensely obliged to Dr Syed Muhammad Jamil, Dean at NUST in School of Civil and Environmental Engineering(SCEE), for providing all the facilities and assistance during the research process.

I am grateful to Dr Rao Arsalan khushnod and Dr syed Hassan Farooq for providing the technical assistance and cooperation during the stated research work.

I must not forget the supporting role of my friends and especially Engr. Muhammad Ali Janjua and Engr. Haseeb Taj, student of Ms. Structural engineering at NICE, for providing technical assistance and cooperation during research.

I offer my heartily acknowledgement to my beloved parents and family for providing me financial and moral supports and encourage me to face hurdles with open heart throughout my educational career.

ABSTRACT

Concrete is one of the most extensively used building materials which consume high energy and it causes significant environmental pollution. The present study is targeted to investigate the dilution of cement by granite powders to probe their effects upon reducing the adverse environmental effects of concrete. Huge amount of waste powders is produced during cutting and processing of granite rocks and they pose adverse environmental hazards. Consequently, it's the need of the hour to explore versatile solutions for disposal of these wastes. Present study is an attempt to makes use of such waste in the concrete to make it an environment-friendly material, and the research work lies in the zone of making sustainable concrete by utilizing granite powders in self-consolidating paste systems.

Two types of granite powder were used and their properties, prior to their mixing in concrete, were evaluated by employing XRD, XRF, SEM, EDX and particle size analysis tests. After evaluating properties of powders, they were used as partial replacement of cement. Seven formulations were casted containing granite Black and white powders as 0%, 5%, 10%, 15% replacements. The fresh tests conducted, were water demand, SP contents required for the desired flow, shrinkage, calorimetry, and initial and final setting time, while the hardened properties were investigated by performing compression, flexural, SEM, EDX, and Thermal analysis after casting in prism molds, which were cured till the required date of tests in water at temperature of 20+2 °C. The results indicate that 10% replacement give positive response subjected to granite powder grounded to a sufficient fineness level. Heat of hydration and shrinkage got reduced due to filler effect, angular shape of particles and internal friction.

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Chapter 1: Introduction

1.1 General

In today's era concrete is extensively used materials which is known as manmade rock. In 1900's structural engineers and material technologists tried to optimize the strength of concrete and with the passage of time rise in the strength of concrete was observed due to their efforts and the term "High strength" was under constant revision. Lower water to cement ratio is critical to increase the strength while maintaining workability of mix. In high strength concrete mixes, it is not essential to hydrate every particle of cement, due to lower w/c ratios a portion of cement is left unhydrated so Secondary Raw Materials (SRM) of finer particle size is used as a partial replacement of cement to not lonely densify the mixture but to enhance the strength due to its pozzolanic reactivity. In 1970's compressive strength of concrete surpassed the value of 41MPa (6000 Psi) at 28 days age and was labelled as high strength concrete by American Concrete Institute (ACI). [1] Two milestones that caused great impact in lifting the construction industry were the invention of Super-Plasticizer (SP) and Self-Compacting Concrete (SCC) in 1980s. [2]
To cope with the challenges of modern world, concrete was modified to self-consolidating concrete systems by using chemical and mineral admixtures. Self-consolidating concrete exhibit unique characteristics of self-compaction when placed in form work without the use of external vibrater and maintain an excellent flow [3]. Self-consolidating concrete is a new type of high-performance concrete that can flow, fill the formwork even in the presence of congested steel and gets compacted under self-weight, completely, without the need for any external compaction [4]. SCC has many benefits equated with normal concrete such as the saving of construction time, labor cost, apparatus and noise in construction sites due of the exclusion of vibraters. In addition, SCC makes the construction of heavily steel reinforced structural elements and helping to attain higher quality concrete. [5]. It was developed by the Japanese researchers in University of Tokyo to cater the issues developing in the country due to the lack of skilled labour in 1980s. The work of Okamura [6] was extended under the supervision of Ozawa [7] to produce the first usable version of SCC in 1988. Since then, SCC is being used successfully in Japan [8] and other parts of the world for different construction projects including bridges, high rise buildings etc. SCC generally requires 34%-40% paste [8] which is greater than the conventional concrete, this

makes SCC a bit uneconomical to be used in large scale construction projects. Also, the higher amount of paste means higher will be the shrinkage and heat of hydration. To account for these issues different Secondary Raw Materials (SRMs) have been discovered and are being used in the world which are cheaply available, they not only increase the strength of the SCC but also helps in obtaining other desired properties of concrete [9, 10]. Most commonly used SRMs include Silica Fume (SF), Limestone Powder and Fly Ash etc. help in enhancing the properties of SCC by their pozzolanic activities and by packing the binder phase of the mix. Since they are by product of industries which would have been wasted otherwise. Their use in concrete makes SCC an environmental friendly concrete.

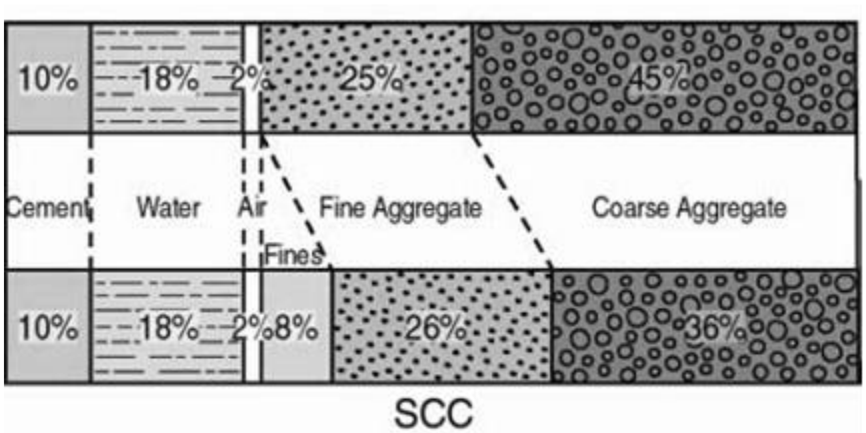


Figure 1.1: concrete mix

Self-Compacting Concrete is currently used in many projects due to its obvious advantages over conventional concrete. High durability, cost effectiveness and eco-friendliness are the driving forces behind the added value of SCC. Other applications of SCC involve placement in heavily reinforced sections, tunnel linings, rafts, bridge piers etc. Use of Secondary Raw Materials (SRM) in SCC have recently gained much popularity in construction industry. Due to the use of concrete at massive scale, it has caused great impact on environment due to discharge of CO2 in atmosphere. A research suggests that with the production of 1 Ton of cement, 0.8-1.3 Ton of CO2 is emitted in air. According to the figures of All Pakistan Cement Manufacturer Association (APCMA) nearly 40 Million Ton of Cement is produced in the country during the last fiscal year [11]. This shows that only Pakistan has added around 52 Million Ton of CO2 through its cement industry.

An admixture is defined as “A material less than water, aggregates and cement used as an ingredient of concrete or mortar, and added to the mix directly before or during its mixing” [12].

SRMs are mostly inorganic materials that show some pozzolanic activity when combined with cement and water. They alter the properties of concrete in hardened and fresh state when partially replaced with cement. ASTM C 125 defines pozzolanic materials as “A siliceous or siliceous and aluminous substantial, which by himself owns slight or no cementitious properties but will, in magnificently powderd form and in the presence of water, react with calcium hydroxide (CH) resulted by hydration of cement at normal temperatures to form mixtures possessing cementitious properties” [13].

1.2 Research objectives

Main objective of this study is to determine the effect and role of two different granite powders on different properties specially hydration kinetics and volume stability of self-consolidating paste system in order to evaluate its practical use in future project.

Secondary objective was to compute the optimum value of replacement to cement, material characterization of two types of granite powders and thermal resistance of SCP containing granite powders.

1.3 Research significance

Granite industries produce high amount of wastes during cutting and polishing causing serious environmental hazards. If these wastes are utilized in concrete industries in a properly engineered way would be a value able resource and environmental friendly. The scope of this research is limited to the use of those wastes powders in SCP system as partial replacement of cement.

Chapter 2: literature review

2.1 Self-compacting concrete

The two important aspects of Self-Compacting Concrete are deformability and segregation resistance. Deformability is mainly attained by using High Range Water Reducing Agents (HRWRA) generally recognized as Super Plasticizer (SP) and restricting amount of coarse aggregate (50% of solid volume liable on its size). Segregation resistance can be achieved by using Viscosity Enhancing Agent (VEA) and controlling w/p ratio. SCC possess low w/c ratio, higher amount of powders (having particle size < 125 micron) along with mineral admixtures like SF, FA etc that advances properties of SCC in hardened and fresh state through their dilution effect and pozzolanic activities [14]. To make sure that SCC would flow under its own weight through heavily congested reinforcements without disturbing stability of the mix require proper mix design, to make sure that every aggregate particle is engulfed by the paste system to avoid segregation. Okamura and Ozawa [15] sketched a simple procedure of attaining self-compatibility as shown.

a. Increasing powder content
b. Reducing coarse aggregate (size and quantity)
c. Reducing w/c ratio
d. Using SP and VMA for making the recipe flowable and stable.

ACI 237-07 guidelines for proportioning the trial mix of SCC and laboratory tests to be conducted to ensure the required properties, rapid of these guidelines are as under.

Greater the water cement ratio the greater will be segregation, bleeding and the lower will be strength and durability. By increasing the paste content with lower w/c ratio ensure less internal friction and admirable flowability. High powder contents are required along with VEA to improve viscosity and avoid segregation.

Absolute volume of coarse aggregate*	28 to 32% (>1/2 in. [12mm] nominal maximum size)
Paste fraction (calculated on volume)	34 to 40% (total mixture volume)
Mortar fraction (calculated on volume)	68 to 72% (total mixture volume)
Typical *w/cm*	0.32 to 0.45
Typical cement (powder content)	650 to 800 lb/yd^3 (386 to 475 kg/m^3) (lower with a VMA)

Table 2.1: Proportioning Guidelines of ACI for SCC

By avoiding mechanical vibration and using high powder content increases the homogeneity of concrete and enhances strength and durability. The demand of high amount of powders (mainly cement) render concrete uneconomical and less feasible for practical use at large scale. Due to high powder requirement SRM, s like SF, FA, Granite powders etc. are used for dilution of cement. SRM, s plays the role of filler to reduce porosity, enhance or modify other properties of concrete like shrinkage, calorimetry and strengths. To cater the powder requirement researcher are focusing on using various blends of SRM, s. Rizwan et al, found that "using FA and LSP individually may have few disadvantages like LSP due its porous and rough surface offers great resistance against the flow and increases SP demand while FA retards the hydration reaction. However, by using them as a blend will enhance the properties of concrete. [16]. Various blends of FA and LSP have already been used by various researchers to find the optimum percentage of replacement that gives desired results. Rizwan et al, reported that using FA at 20% and LSP at 80% performed better than other formulation in Paste system. Wahab [17] et al, reported that LSP and FA used gives better results at (50%) among the others by enhancing strength and flow with reduced shrinkage.

2.2 Secondary raw materials (SRM, s)

Concrete as equated to other construction materials is one of the most justifiable materials when evaluating following the concept of embodie energy [18]. However, as upto 15 billion tons of concrete is being presently produced per annum around the globe which makes it the largest material flow on planet earth. Concrete production in construction industry has the biggest influence on the environment of this planet in terms of greenhouse gas discharge. It is supposed, that in near future concrete construction could be responsible for about 10% of the total greenhouse gas release on earth. Concrete has a problem. Previously started through its use in countless architectural millstones, ranging from the largest tower blocks to the enormous car parks, concrete's environmental credentials are also now coming under scrutiny. The use of this material is so widely spread that the cement production of the world now contributes more than 5% of annual anthropogenic global CO2 production, where China with its booming construction industry produces around about 3% of global CO2 emission alone. This problem will only get worse with passage of time with the growth of construction industry, already productions have reached over 2 billion tone amounts per year, and by the end of 2052, concrete use is forecasted to reach four times the amounts used in 1990. This enormous production of concrete at such a global scale has led to increased cement production, rising energy costs, depletion of natural resources and created a constant damage for the human environment. It is a well-established fact that for each ton of cement production contributes to round about 900 kg of CO2 into the atmosphere and cement production alone accounts for 5% of global man-made CO2 emissions [19]. According to data from the IEA (International Energy Agency) report cement production will hit 4 billion tons around 2050 the major part of it due to construction in Asian countries as depicted [20]

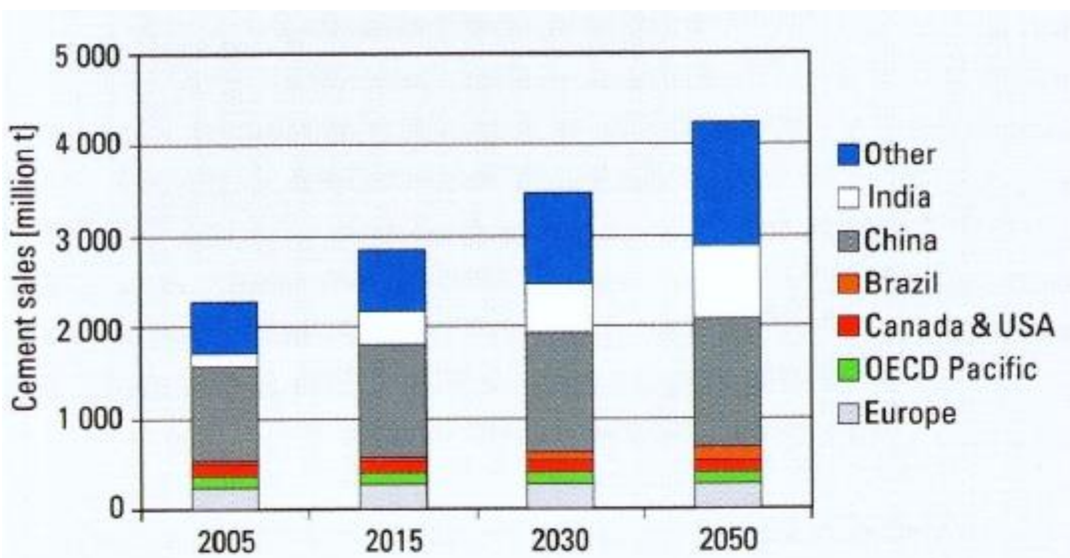


Figure 2.1: Cement sales predicted from IEA report [17].

In order to reduce CO2 emissions, commonly practiced approach in Europe according to EN 197 is the replacement of clinker by latent hydraulic, pozzolanic or even inert, finely ground additives. As an effort to reduce clinker content in cement to reduce CO2 emission, which lead to the development of different classes of cements (CEM I, CEM II, CEMIII, CEM IV and CEM V) as per EN 197 by adding different materials like slag etc. and reducing clinker content [21]. The same can be achieved by reusing industrial wastes and using naturally available environment friendly materials to replace cement. These materials are called secondary raw materials (SRMs) or supplementary cementitious materials (SCMs). "SRMs are mostly inorganic materials that may also have pozzolanic and/or latent hydraulic properties. They are usually very fine-grained materials, which are added to the concrete mix to improve the fresh & hardened properties of concrete (mineral admixtures), [22], or as a partial replacement for Portland cement as in case of blended cements. As per ASTM C 125, a Pozzolanic material may be defined as "A siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide (CH) produced by cement hydration at ordinary temperatures to form compounds possessing cementitious properties" [23]. The mechanism of a pozzolanic reaction has a beneficial effect on the various properties of concrete and is irrespective of the fact that whether the pozzolanic material is added to concrete in the form of a mineral admixture or as a component of blended Portland cement. The basic function of SRMs addition is to modify / improve the properties of cement based systems which may include the control of early heat evolution, reduction in shrinkage, better packing, optimization of flow, enhancement of strength, improvement of microstructure economy and the durability of cement based systems." The most commonly used SRMs are Fly Ash, Silica Fume, and Ground Granulated Blast Furnace Slag, properties and effect imparted by these SRM on fresh and harden stage properties of SCC are well studied and certain perimeters are already defined to achieve optimum results. Whereas other SRMs as lime stone powder, marble powder, bagasse ash. Quarry dust, glass powder, metakaolin, and some more materials are still under study to fully understand their properties and effects in both short and long term. Pakistan is rich in various natural resources a variety of secondary raw materials are widely available all across Pakistan, which are studied so that they can be incorporated in production of cost effective SCC without compromising on the standards of construction industry.

2.3 Granite powder

Granite industries produce high amount of wastes during cutting and polishing causing serious environmental hazards. If these wastes are utilized in concrete industries in a properly engineered way would be a value able resource and environmental friendly. It mainly composed of silica, iron, alumina, magnesium, calcium with small amount of potassium, magnesium and titanium. The chemical composition is controlled by the parental rock. In recent past various researches have been done by using granite powder as a substitute of cement, fine and course aggregates.

"The granite sludge wastes mainly composed of components like SiO2, Al2O3, CaO and Fe2O3 based composites, with their minor particle size guaranty its use in mortar industry. A stimulating development in compressive strength was obtained by gradually replacing CaCO3 filler with Granite Sludge, enhancing the compressive strength. On the other hand, 10% cement replacement can be used with Granite Sludge without compromising of 28-day compressive strength. Both results support the use of Granite sludge wastes in mortar due to their suitable particle size distribution and latent pozzolanic activity". [24]

Recommended that improvement in compressive strength, corrosion cracking time were observed. Insignificant changes in hydration products, micro structure and degree of hydration occur. [25]

Established that finely grounded granite quarry sludge waste can produce denser matrix can improve resistance to ASR, chloride attacks without compromising workability and strength [26].

Determined that use of granite at 20% replacement can improve workability, possess higher long-term strengths, improve resistance to chloride penetration, frost and drying shrinkage [27].

Concluded that granite and marble waste powders could be successfully used as mineral additives. However, a mixture of these powders will result in better results [28].

2.4 Effect of particle size distribution

The important factor that effect the overall performance of self-compacting cementitious systems (SCCS) is the porosity which directly depends upon particle size distribution (PSD) of individual elements and hydration of cement particles in any of the sub-systems of SCCS. Degree of packing is a function of particle size distribution in a mix. The particle-size distribution (PSD) of a powder, granular materials or particles dispersed in fluid, is a list of values or a mathematical function that defines the relative amount, typically by mass, of particles present according to size [29]. Higher packing density results in lowering the porosity and higher degree of hydration of cement results in lower porosity also but influence of PSD upon packing density and hydration kinetics is different. Packing density is higher if wider range or distribution of PSD is adopted but degree of hydration reduces when a narrow range of PSD is used packing density is lower but degree of hydration is higher [30]. Rizwan, S. A. et al during his research establishes a positive relationship between rheological properties and packing density of aggregate phase within the concrete mix [31]. Better particle packing leads to a better performance of mixing water in terms of its contribution towards better fluidity and workability of a system.

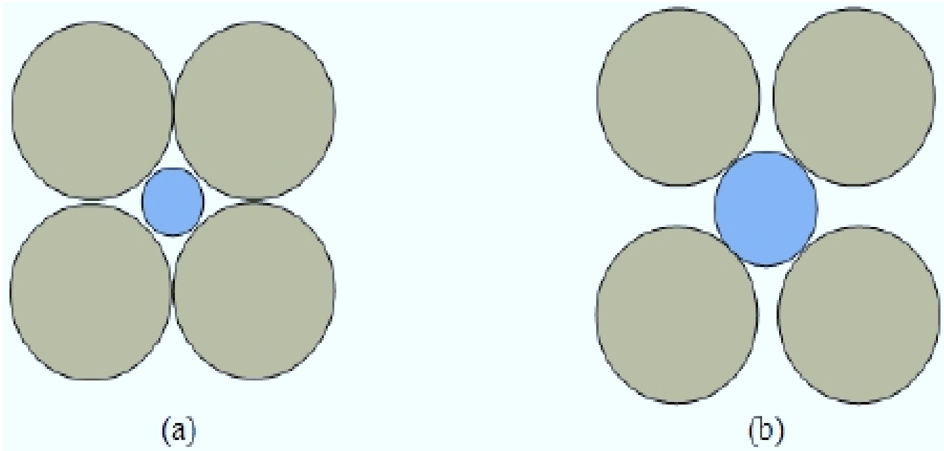


Figure 2.2: Effect of Relative particle size on packing (Sajjad 2011)

It is believed that in a self-compacting concrete system the most efficient component regarding self-compaction is fine aggregate whose improved PSD can highly increase the workability, stability and ultimately durability of the SCC in the longer terms. It is not only the self-compacting mortar system (SCMS) which controls the bleeding and segregation due to optimization of PSD for the fine sand of the concrete mix, but suitable blends of different secondary raw materials also enhance the response of any self-compacting system. The best utilization of the packing density concept in self-compacting mortar (SCM) systems and self-compacting concrete (SCC) systems is to have sufficient amount of paste available in the mix mainly for the two purposes-filling the voids of the aggregate phases and serving as transporter of the aggregate phase.

2.5 Calorimetry

Calorimetry is the process of measuring the heat of chemical reactions, performed with a calorimeter. Scottish physician and scientist Joseph Black, who was the first to recognize the distinction between heat and temperature, is said to be the founder of the science of calorimetry [32]. The heat of hydration of concrete influences the workability, setting behavior, strength gain rates and pore structure development, thus affecting early age behavior as well as long term performance of concrete. Mainly hydration kinetics of cement involves two types of phases which are Silicate Phases (C2S & C3S) and Aluminate Phases (C3A & C4AF). Silicate phases are negatively zeta potentials and aluminate phases are positive zeta potentials. In impure state, these cement phases are known as Alite (C3S), Belite (C2S), Portlandite (C3A), Ferite (C4AF). General pattern of hydration of cement is shown in Fig. 2.3. Stages involved in cement hydration are of heat release, dormant period, and acceleration and deceleration stage during which various phases of cement hydration products are formed. A typical pattern of cement hydration is shown below.

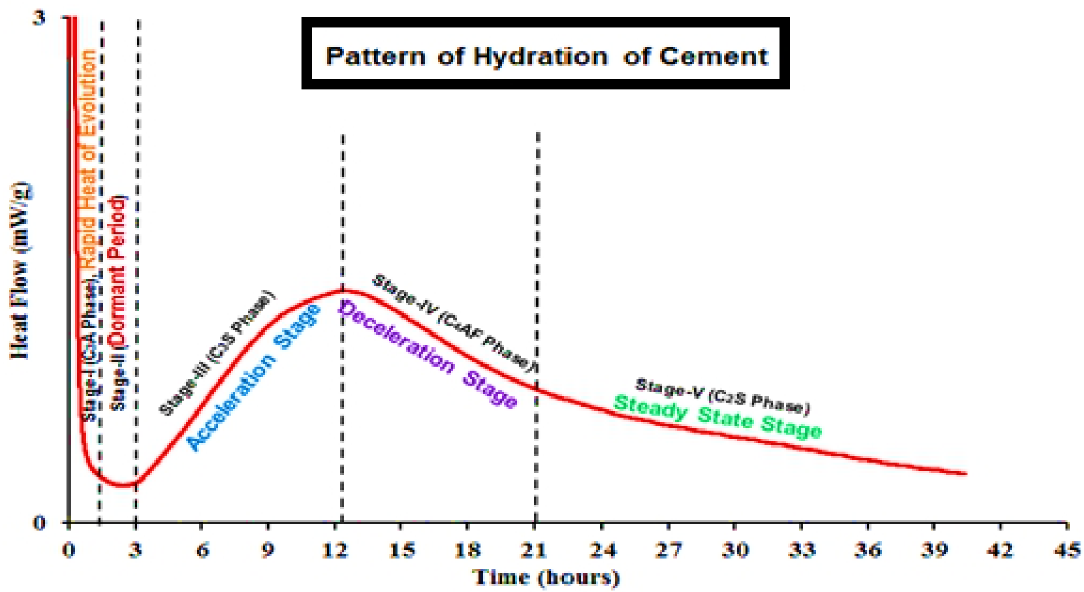


Figure 2.3 : Hydration of cement

Stage-I. Rapid heat of evolution by C3A formation. This normally lasts for few minutes.

Stage-II. Period of relative inactivity or induction, (Dormant Period).

Stage-III. This is the acceleration stage which involves maximum rate of heat evolution. This is the beginning of C3S phase at the end of the induction or dormant period.

Stage-IV. This is deceleration stage attributed to C4AF phase. This stage is diffusion control stage.

Stage-V. This is a steady state stage under the influence of C2S phase.

The hydration of cement during its early stage plays a decisive role in workability & strength development of concrete. Concrete undergoes a phase change from plastic state to elastic state due to chemical reactions taking place during the first few days after mixing. During the plastic state properties of concrete are described by its rheology (yield stress and viscosity). Change from plastic to elastic state is due to development of micro structure because of the chemical reactions taking place on the surface of cement particles. The C-S-H growing from the cement grains are responsible for setting of the cement and strength development [33]."

2.6 Shrinkage

In HP cement pastes having low w/cm ratio, the internal relative humidity decreases with the water consumption resulting in increased shrinkage especially for SF containing pastes [34]. In cement-based composites, the cement paste is the major source of shrinkage [35]. Being a volume change, it can be studied either by volumetric experimental methods, linear methods or by digital imaging techniques. These methods have their relative advantages and disadvantages. The advantage of volumetric method is that it measures shrinkage as per its true definition of a volume change. Its disadvantages include sucking-in of any entrapped air from within the membrane into the sample and thus falsely showing an increase in shrinkage. The bleeding resulting in the loss of contact of sample with the membrane is another disadvantage. The advantage of the linear method is that it is done in an apparatus of constant cross-sectional areas so that the volume change can almost be considered as a linear change in length. Disadvantage includes that an appreciable shrinkage/expansion is registered only after the onset of hardening. In this study, a modified version of German classical "Schwindrinne" meaning shrinkage channel apparatus measuring 4x6x25 cm was used at 20±1°C and RH of 31±5% with specimen in covered conditions. Calorimetiy and setting times were also done on selected specimens. Conflicting results about shrinkage found in the literature are due to interpretational differences based on concepts, definitions and measuring techniques [36]. However, it has now been shown that both techniques are valid and give almost similar results [37]. In general, for HP SCCS early age volume changes or shrinkage is of prime importance because such systems incorporate high SRM's of various types. Moreover, the literature reports measurement of various types of shrinkage by using either volumetric or linear measurements, each technique has its own plus and minus points. However very little data is available about self-compacting cementitious systems containing pozzolanic powders. Structural or construction engineers are concerned with the total amount of shrinkage and certainly not in that of its various individual parallel operating mechanisms. That's why most codes only prescribe the total amount of shrinkage. Morin et al [38] report volumetric increase of shrinkage with increase in amount of super-plasticizer and accompanying delay and reduction of chemical activity.

In controlled environmental parameters, it was not possible to assign or to distinguish between various parallel shrinkage mechanisms using the available apparatus as well as the contributions of such mechanisms could not be evaluated considering their already known and well documented definitions. Plastic shrinkage will always be present along with shying or chemical shrinkage in formulations with mixing water content greater than the system's water demand. It was also interesting to know the effect of stopping evaporation on the total early shrinkage response of various cementitious systems. The emphasis in this thesis has, therefore, been clearly on measuring the total shrinkage of various HP SCP systems in covered conditions.

Chapter 3: Experimental program

3.1 Materials

All the materials used in this research were obtained locally and stored in air tight containers to prevent any possible ingress of air or moisture. Granite powders were obtained from local industry in I-9 Islamabad. Following are the details of different materials that were part of this research work.

3.1.1 Cement

ASTM Type-1, Ordinary Portland Cement (OPC) manufactured of BESTWAY Cement Industry, confirming ASTM-C150, EN-196, CEM 1 42.5 N or Grade 53 and Pakistan Standards PS-232-2008 was used. Particle size distribution (PSD) of OPC was determined by using Mastersizer 3000, a laser granulometer, which is existing in Institute of Space Technology (IST), Islamabad. PSD curve of OPC is shown in figure 3.1 from which we can see that average particle size (D50) of OPC used is 16.4 micron. X-Ray Fluoresce (XRF) results obtained from Geoscience lab, Islamabad are showing chemical composition of OPC (see table 3.1).

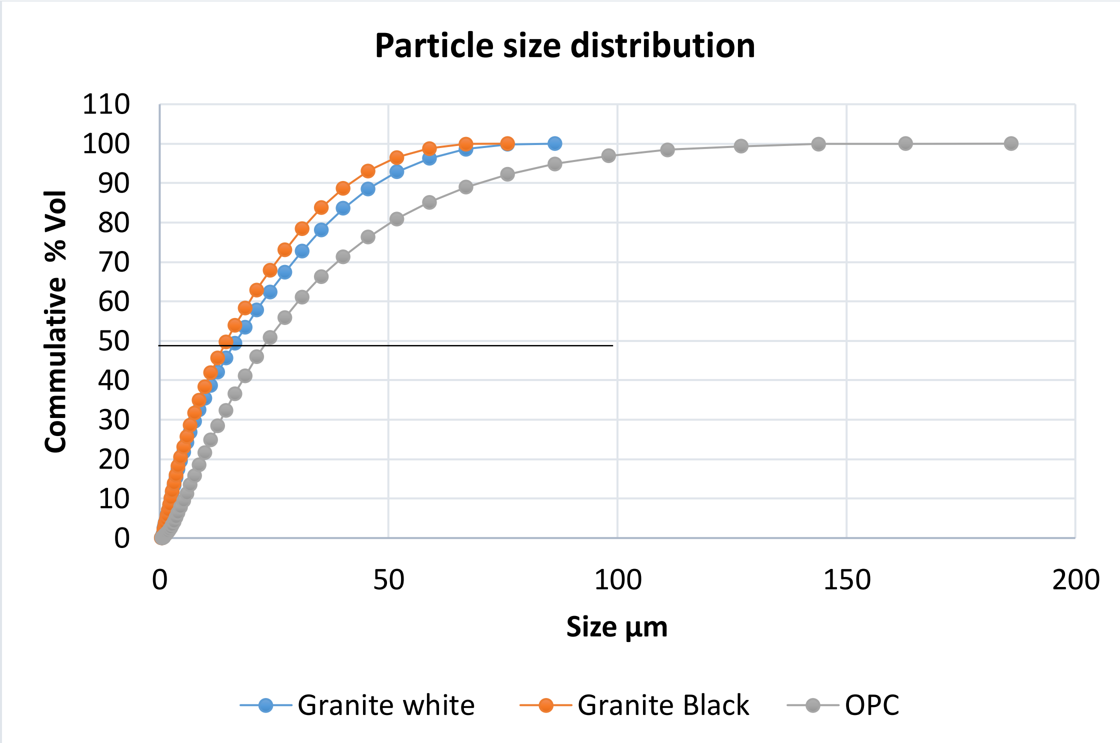


Figure 3.1 PSD of GPW, GPB and OPC

Table: 3.1 Chemical and physical properties of Powders (GPW, GPB and CEM-I)

Parameters	**CEM-I**	**GPW**	**GPB**
Particle size (D50), µm	24.4	19	16.6
specific surface area, m^2/g	0.651	2.93	3.11
Elements Mass %			
Al_2o_3	4.818	10.79	5.79
Sio_2	20.11	48.44	62.51
Fe_2o_3	3.88	23.64	16.09
Cao	67.12	12.1	9.99
Mgo	2.41	3.014	--
Tio_2	0.3	1.405	0.83
Mno	0.03	0.322	0.33
K_2o	0.48	0.289	2.60
P_2o_5	0.09		1.06
Sro	0.762		0.83

3.1.2 Secondary Raw Materials

The choice of SRMs to be used in this research work was based on previous researches conducted by Dina M. sadek et al [28] and Huajian Li et al [27] which shows improvement in terms of strength and mechanical properties of Self Compacting Paste systems. Granite powder Black and granite powder white were used as 5%, 10%, 15% replacement of cement. The properties of which are discussed below.

3.1.2.1 Granite powders

Granite Powder is a byproduct generated from the granite polishing and milling industry.
They are largely left unused and are hazardous materials to human health because they are airborne and can be easily inhaled. Their chemical composition depends upon the composition of parental rock however it mainly consists of silica, calcium, alumina and iron. Due to the presence of silicon dioxide it shows pozzolanic activity when mixed with cement in the presence of water. Its reactivity depends upon the shape and size of particle size [28]. Both the granite powders are angular in shape abrasive in nature as shown in SEM image (Figure 3.2a, b) that's why require high amount of superplasticizer contents and reduce shrinkage. Due to variability in composition I have used two types of granite powders granite black and granite white.

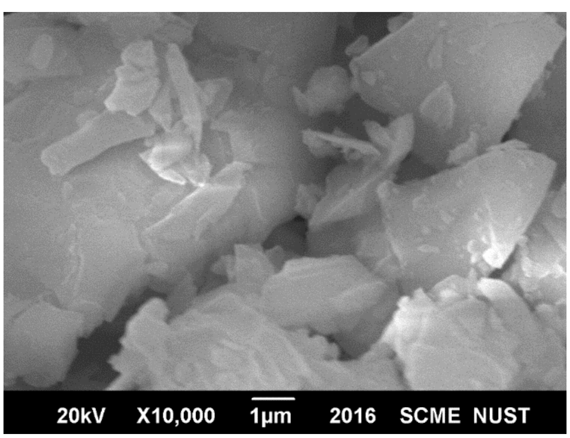


Figure 3.2 (a) Granite white SEM image

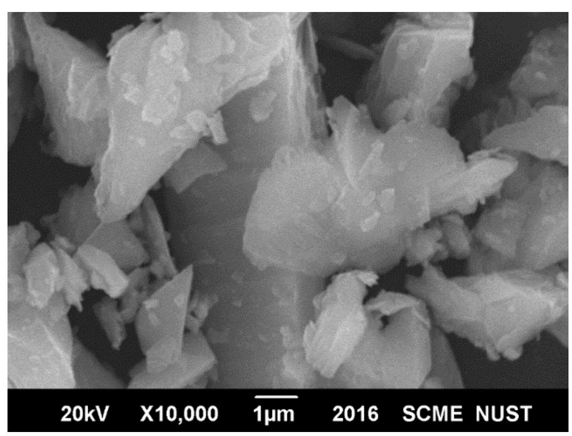


Figure 3.2 (b) Granite Black SEM image

From XRD results we can conclude that both the granite powders are crystalline in nature and mainly consist of silica, calcium, magnesium, iron which confirms the results of XRF. The graphs of XRD are as shown in figure (3.3a, b).

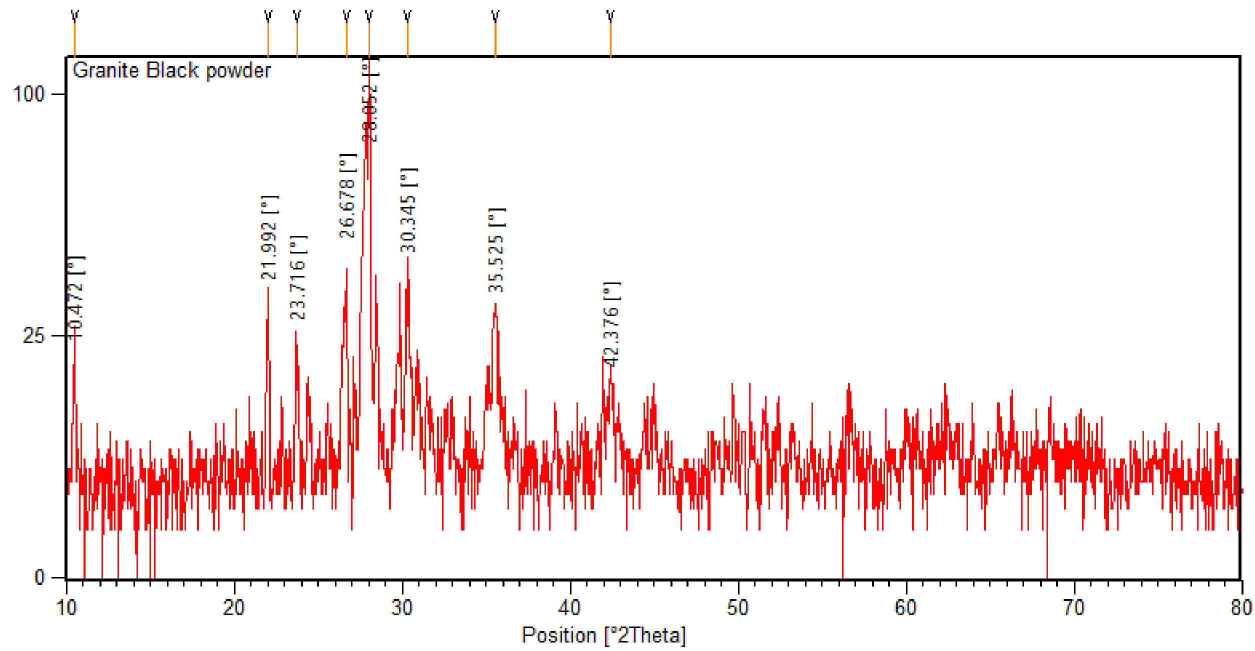


Figure 3.3 (a) Granite Black XRD

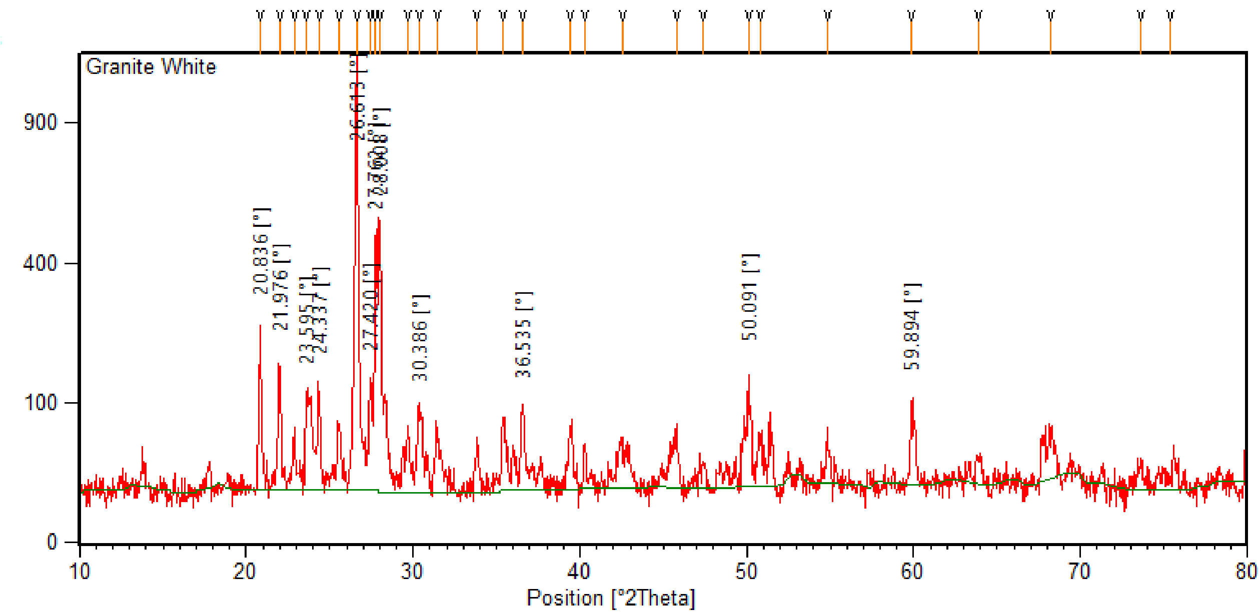
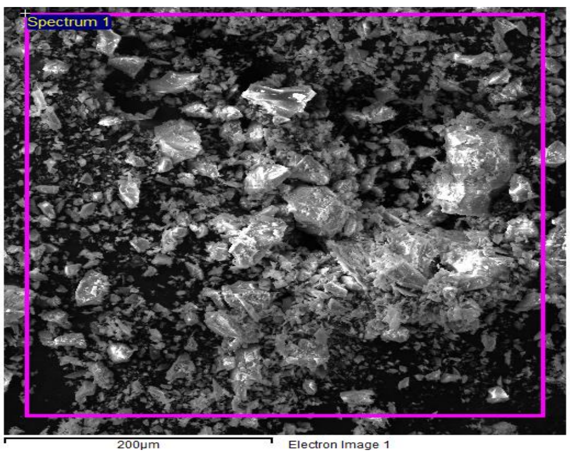


Figure 3.3 (b) Granite White XRD

From EDX graphs we can conclude that both the granite powders mainly consist of silica, calcium, magnesium, iron which confirms the results of XRF, XRD. The graphs of EDX graphs are as shown in figure (3.4a, b).



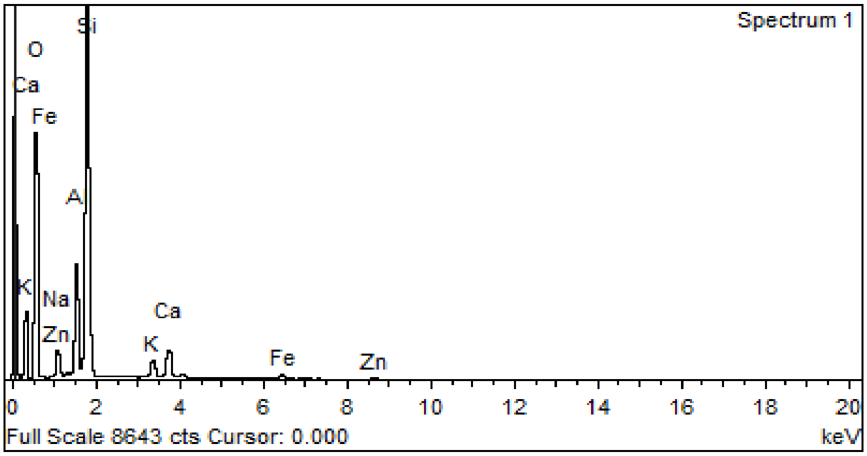


Figure 3.4 (a) Granite White EDX

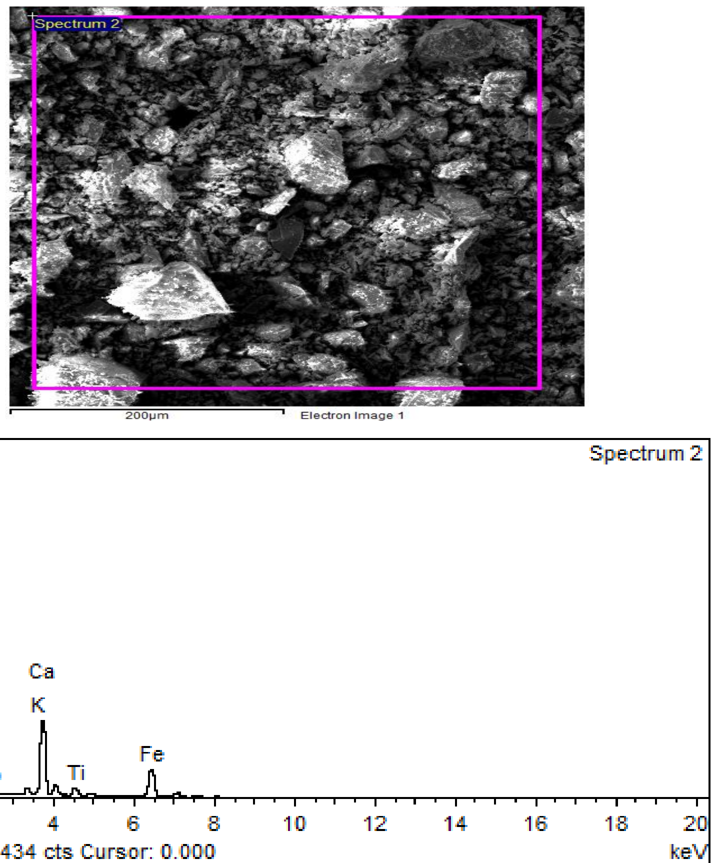


Figure 3.4 (b) Granite Black EDX

3.1.3 Chemical admixture

Super plasticizer is the chemical admixture used to increase the flow of SCC, it reduces the additional amount of water required to make the concrete flow under its weight. Thus, increasing the strength and durability of concrete. It is also known as high range water reducing agent (HRWRA). A newer type of SP, which is based on Polycarboxylate ethers (PCE) is found to be more effective and requires lesser dosage as compared to older sulfonated melamine (SMF) or naphthalene (SNF) formaldehyde. For this research work Mel flux 2651F Poly-carboxylate ether (PCE) based super plasticizer supplied by BASF Germany was used to prepare self-compacting pastes. Some of their physical and chemical properties are listed below.

Table 3.2: Physical and chemical properties of superplasticizer

Physical Form	Powder
Odor	Characteristic
Color	Yellowish to brownish
PH value	Approx. 6.5-8.5 at 20±2ºC
Bulk density	300 - 600 kg/m3
Solubility	Soluble in water

3.2 Experimental program

Experimental program was conducted with great attention to attain maximum precision. Standards procedures of DIN, ASTM and BS were followed for experiments as stated below.

Table 3.3: Tests on fresh and hardened paste

	Experiments	**Tests Standard**	**Measured Values**	**Property Assessed**
Fresh tests on cement Paste	Setting Time	EN-196	% by weight of Cement	Consistency
	Water Demand	EN-196/3	Time (mint)	Initial and Final Setting
	SP content	DIN-193-3	Time (mint)	Flowability
	shrinkage		Relative shrinkage	Shrinkage
	Calorimetry		Time in mints vs hydration	Hydration kinetics
Tests on hardened cement Paste	Strength test	DIN-196	Load (KN)	Flexure and compression
	Thermal analysis	DIN-196	Load (KN)	Flexure and compression

3.2.1 Mixing Regime and SCP Formulations

In this research total seven formulations were casted and studied as shown in the Table 3.4. Super Plasticizer content demand for each formulation was determined by performing different trials of flow test using Hagerman mini-cone slump apparatus of 6x7x10 cm^3 to achieve a target flow of 30±1 cm.

To ensure uniformity during sample preparation, the mixing regime was kept constant and DIN-193-3 Standard was followed. First, cement, granite powders and SP were dry mixed for 30 secs before adding water. Mixing water temperature was kept at 20±2 °C. Cement mixed with SP and granite powders were added to the Hobart Mixer. Then water was added according to water demand and mixed at slow rate for 30 sec. After that break of 30 second for cleaning sides and edges of the bowl. Then mixing was done for 30 secs slow at 145 rpm. At last fast mixing was performed for 90 secs at 285 rpm.

Table 3.4: Formulation casted and their demands

S.NO	Cement-Type	GPB	GPW	SP %	W/C ratio %	Formulation nomenclature
1	CEM-1	0	0	0.19	27	C1-0-27
2	CEM-1	5	0	0.221	28.6	C1-5GPB-28.6
3	CEM-1	10	0	0.224	30.4	C1-10GPB-30.4
4	CEM-1	15	0	0.227	32.1	C1-15GPB-32.1
5	CEM-1	0	5	0.198	28.5	C1-5GPW-28.5
6	CEM-1	0	10	0.2035	30	C1-10GPW-30
7	CEM-1	0	15	0.205	31.8	C1-15GPW-31.8

3.2.2 Water Demand and Setting Time of SCPs

The first stage as per European guidelines is to determine the water demand of self-compacting cementitious system. For various self-compacting paste systems, the water demand (WD) and setting times both initial and final were determined using VICAT apparatus following DIN-196 standards at 20±1ºC and 20±5 percent relative humidity.

In this experimental work water was used according to the water demand of the formulation. Initial and final setting times were determined with and without superplasticizer. Figure 3.5 show the vicat apparatus on which tests were conducted.

Figure 3.5: Vicat apparatus and formulation tested

Vicat apparatus

3.2.3 Superplasticizer Demand

The Hagerman's mini slump cone was used to find the demand of third generation powder type super plasticizer Melflux 2651 required for a target spread of 30+1 cm of self-compacting paste formulation. various trials of flow tests were conducted to determine the required super plasticizer demand of various formulations containing total water equal to respective water demand. Hagerman mini slump cone apparatus having 6x7x10 cm3 dimensions was used. For each SCP systems SP demand required is as shown in figure 3.6.

Figure 3.6: Hagerman's mini slump cone

3.2.4 Shrinkage measurements

The total shrinkage of any cementitious system is important as it affects volume stability. To assess the volume stability of SCPs with and without granite powders content total early linear shrinkage data was recorded for first 45 hours for all ordinary Portland cement based SCP formulation using modified shrinkage channel apparatus of dimensions 4x6x25 cm^3 with a sensitivity of 0.31 microns as shown in Figure. 3.7. Linear change protocols were followed to measure the linear shrinkage for each formulation covered with a plastic sheet to minimize moisture exchange with environment.

Figure. 3.7: Modified German Schwindrine Shrinkage Apparatus

3.2.5 Calorimetry measurements

Hydration kinetics of SCP systems is very important to be examined as it has an impact on determining curing time for a specified mix and predicts the setting times. F-Cal 8000 field calorimetry was used to investigate the hydration kinetics of cement based system for around 48 hours for each formulation. For studying the hydration kinetics of each formulation, about 750 g of SCP was placed in F-CAL 8000 Field calorimeter as shown in Fig. 3.8, and the data was logged till calorimetric curves became horizontal showing no alteration along the temperature axis.

Figure. 3.8: F-CAL 8000 Field calorimeter

3.2.6 Casting and curing

The casting and curing was carried out as per EN 196-1. After the tests for fresh properties were completed, the SCP formulations were casted into molds, at least three samples of each formulation were casted to increase reliability of results. The formulations were poured in to the prisms of 40x40x160 mm size (EN 196-1). In total 81 prisms were casted with CEM-I and varying amount and two types of granite powders in laboratory at 25± 5 C° with relative humidity of 30±2%. The samples were kept in sealed plastic bags for initial 24 hours at room temperature to ensure minimum moisture loss due to temperature changes. Then these samples were demolded, weighed and placed underwater in a closed water tank till the age of testing then they were tested in SSD conditions. Figure 3.9 show casted prisms.

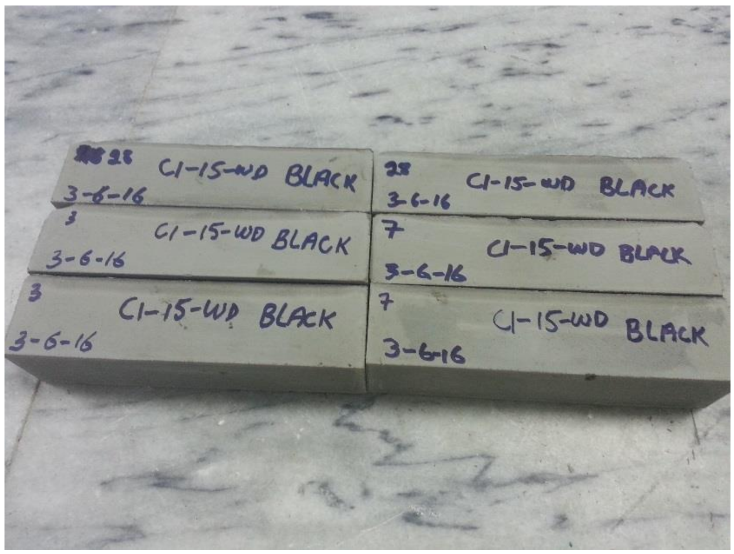


Figure 3.9 Casted prism

3.2.7 Strength tests

In case of self-compacting paste (SCP) systems the flexural strength was the average of 3 three prisms then resulting in six small portions, tested for compressive strength as shown in figure 3.10. The prisms specimen had dimensions of $4x4x16cm^3$. Compression test samples were obtained from broken pieces of flexure sample with cross-section of $40x40\ mm^2$. For this research specified ages were 3, 7, & 28 days, demolded samples were tested as shown in figure 3.10.

Figure 3.10: Assembly for compression and flexure testing

3.2.8 Thermal analysis

Thermal analysis was done at elevated temperature in electric furnace available at NICE NUST H-12 Islamabad. The samples having high strength at 28 days were tested at elevated temperatures of 100, 300, 600. After rising temperature samples were tested in compression testing machine for evaluating compressive strength in laboratory.

3.2.9 Scanning electron microscopy

Rizwan et al [39] states that scanning electron microscopy is a versatile tool for study of hydration products including calcium silicate hydrate, calcium hydroxide and ettringite. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, crystalline structure and orientation of materials making up the sample. The micro structural analysis, study of ITZ and identification of hydration products of self-compacting cementitious system can also be done conveniently with SEM in BSE and SEM modes respectively. Scanning electron microscopy was done by using JSM5910 model scanning electron microscope manufactured by JEOL, Japan in SCME at NUST H-12 Islamabad. The specimens of self-compacting paste system of maximum strength at 28 days were studied after stopping hydration with Iso-Propanol and Acetone.

3.2.10 Energy Dispersive X-Ray (EDX) Analysis

EDX is an analytical technique used for the elemental analysis or chemical characterization of a material. EDX was done in institute of space technology (IST) Islamabad.

Chapter 4: Results and discussions

4.1 Tests on fresh Self-Compacting Paste Systems

Tests conducted on fresh paste system are stated below.

4.1.1 water demand and setting times

The water demand and super plasticizer demands has a general trend to increase with addition in content of secondary raw material (SRM, s). The water demands for both granite powders increases with increase in the amount of cement replacement because of fineness and angular shape of granite powders. The change in the setting time of formulations varies due to the individual characteristics of each granite powder along with the amount of that powder incorporated in that system. The initial and final setting time was determined with and without incorporating superplasticizer contents with the help of Vicat's apparatus. From the graph, it is concluded that by introducing SP content initial and final setting time got increases. The initial & final setting time of formulations were calculated as shown in figure 4.1 and 4.2.

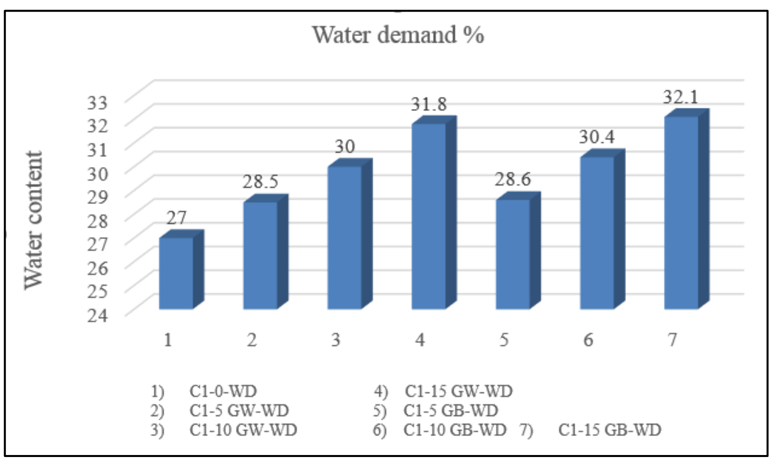


Figure 4.1: Water demand

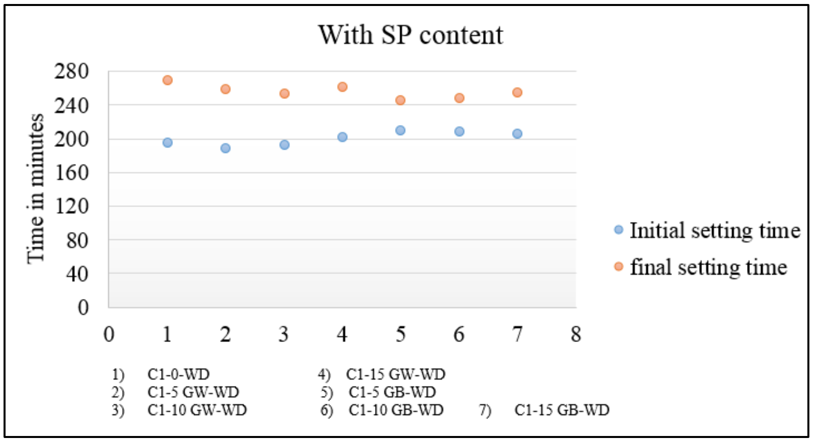
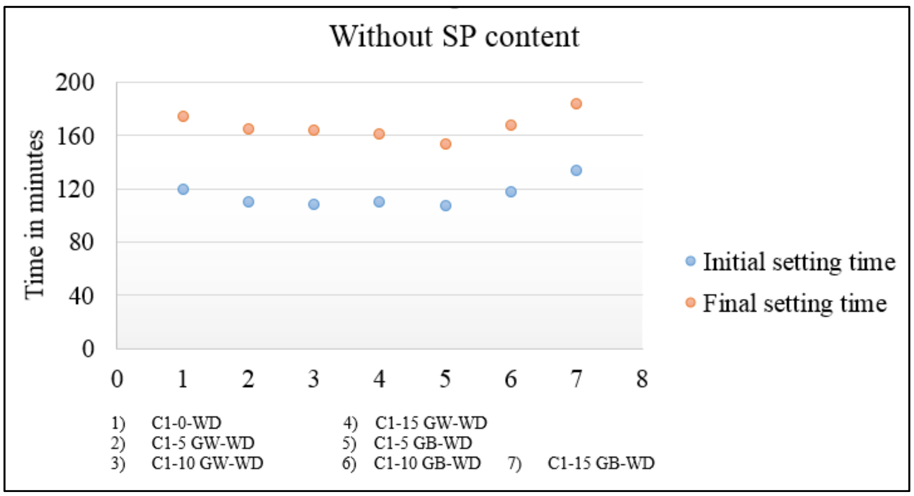


Figure 4.2: initial and final setting times



4.1.2 super plasticizer demand

The Hagerman's mini slump cone was utilized to find Superplasticizer requirement for the target flow of 30±1. From the graph, it can be con concluded that percentage of granite powder is directly proportional to the amount of super plasticizer content due to angular shape of their particles. Percentage of SP demand by weight of cement is shown in Figure 4.3.

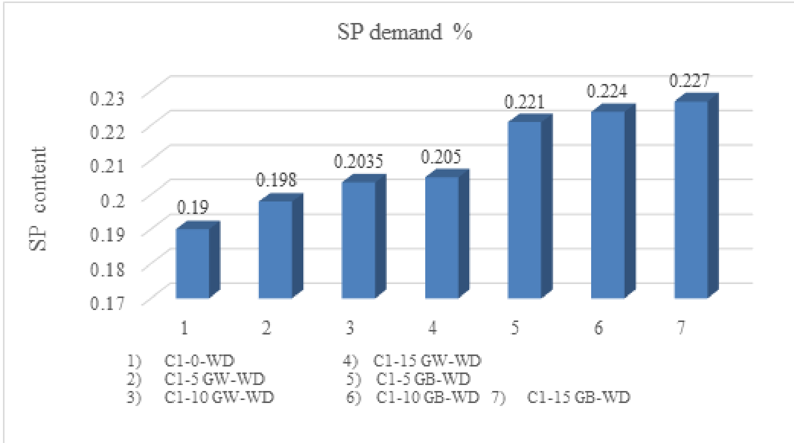


Figure 4.3: Super plasticizer demand

4.1.3 Shrinkage Response

To measure total early age linear shrinkage response, Modified German Schwindrine apparatus of 4x6x24 cm^3 dimensions with a sensitivity of 0.31 microns was used for first 46 hours. Schwindrine channels were filled with the fresh SCP, s containing granite powders, the channel was then sheltered with plastic sheet to avoid moisture loss. Control sample of pure OPC was casted to compare with formulations containing granite powders. Two types of granite powders, granite white and granite black at 5%, 10%, 15% replacements are used. From the graphs of granite black, it can be summarized that shrinkage got reduced as the replacement percentage got increased. It is due to angular particles shape which enhance internal friction and act as internal restrain. The second reason is formation of ettringite which are expensive in nature, its formations can be seen in image of SEM. While in case of granite white it can be seen that up to 10% replacement of cement shrinkage got reduced but after that it got increases because up to 10% internal friction works but after that excessive formation of CH occurs which can be confirmed from SEM images. Total linear early shrinkage response of casted formulations is shown in Figure (4.4a, b).

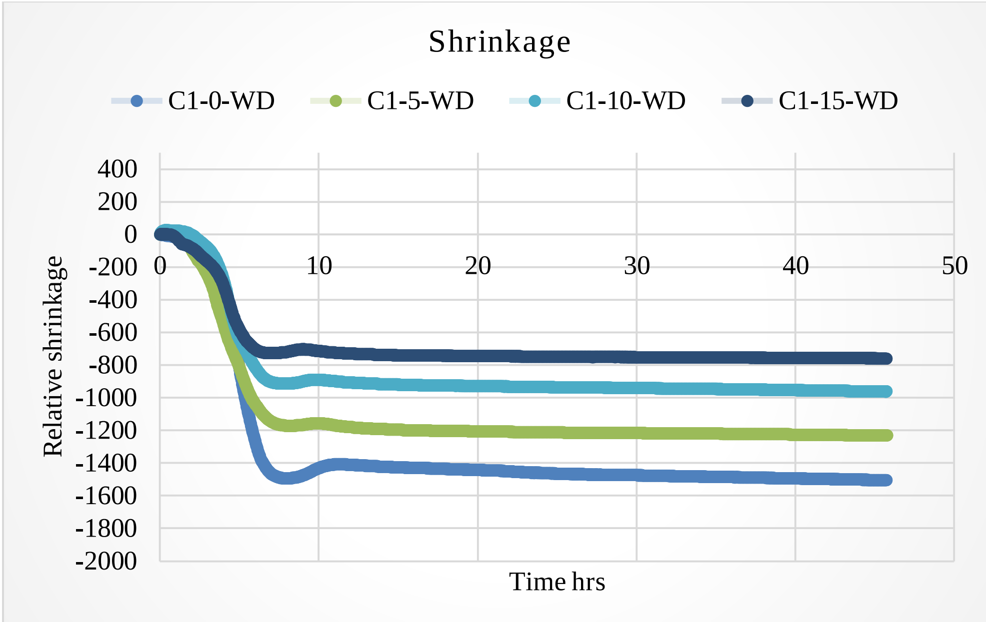


Figure 4.4a: granite Black shrinkage

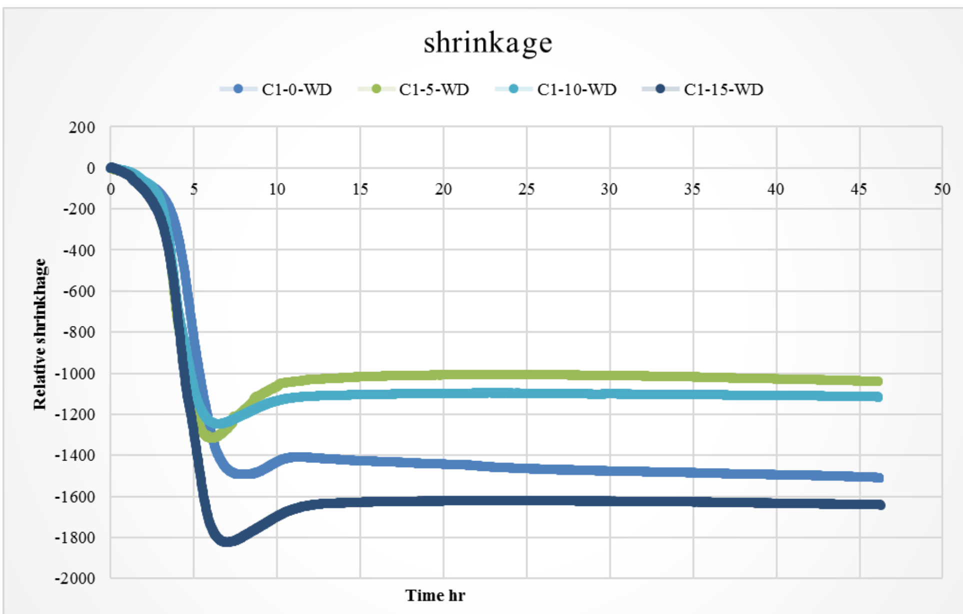


Figure 4.4b: granite white shrinkage

4.1.4 Calorimetry

Hydration kinetics of SCP formulations were studied with the help of F-CAL 8000 field Calorimeter and the calorimetric curves were drawn from the data obtained are shown in Figure 4.5 (a, b). Formulations were placed in plastic bag for initial 50 hours and data was recorded.

Two types of granite powders were used and were compared with control samples. From the graphs obtained drop-in of liberation in heat occurs. It is due to dilution effect.

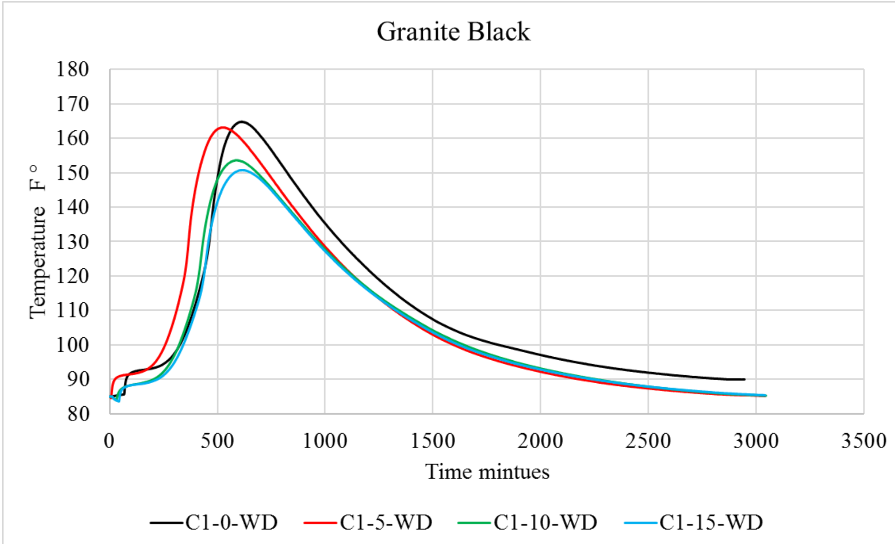


Figure 4.5a: Calorimetric curve of granite powder black

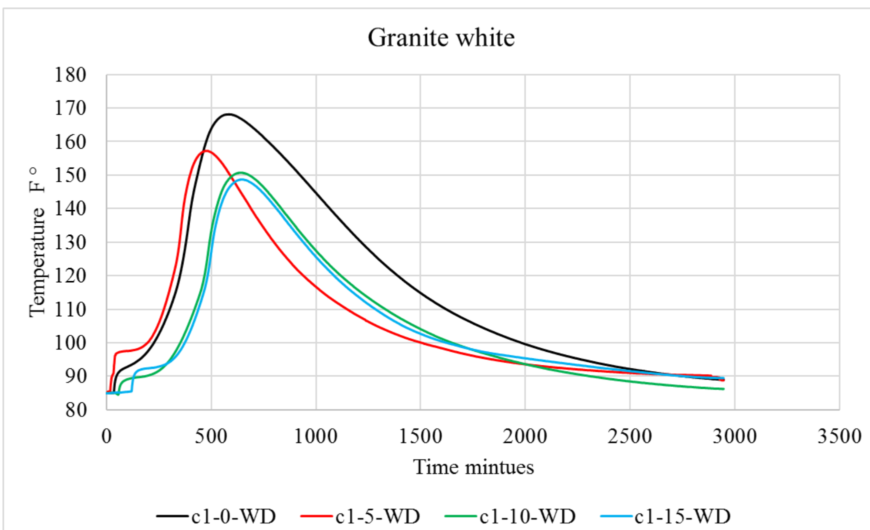


Figure 4.5b: Calorimetric curve of granite powder white

4.2 Tests on Hard specimen of Self-Compacting Paste Systems

Various tests were conducted explained as under

4.2.1 Strength tests

Standard Prisms of 4x4x16 cm of Self Compacting paste system (SCPS) containing varying amounts of granite black and white powders were tested for strength evaluation at ages of 3, 7 and 28 days. Figure (4.6 a, b) show compressive and flexural strength of granite powder black. While Figure (4.7 a, b) show results for granite powder white.

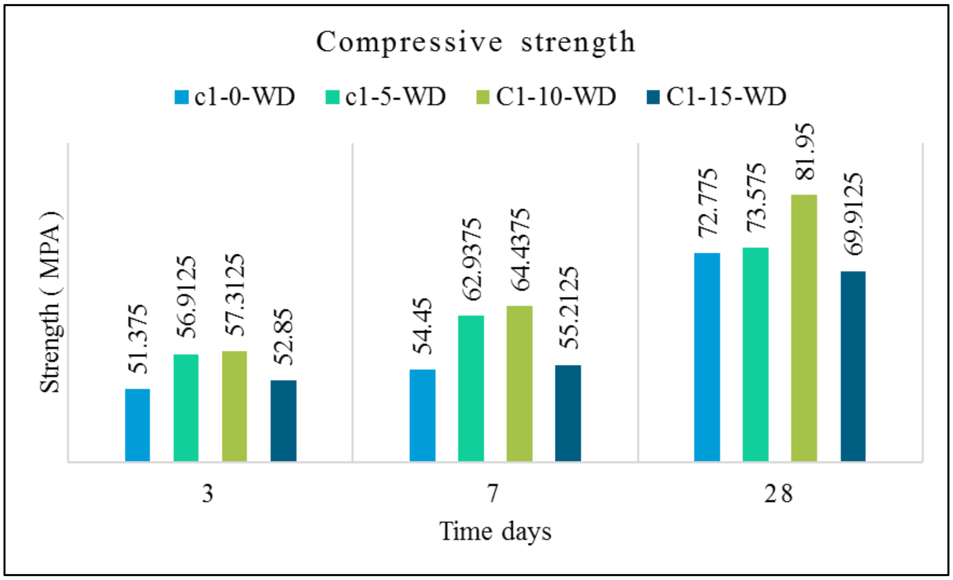


Figure 4.6 a: compressive strength of granite powder black

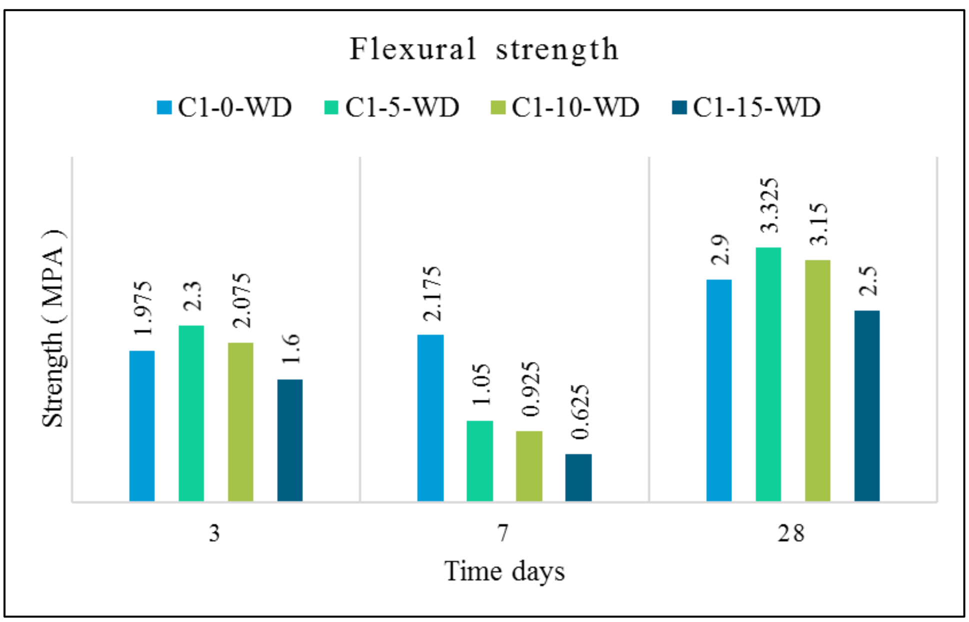


Figure 4.6 b: Flexural strength of granite powder black

From the above figures, it is reflected that formulation having 10 % replacement gives the maximum compressive strengths as compared to other replacement percentages. It is due to filler and pozzolanic effect of granite black powders.

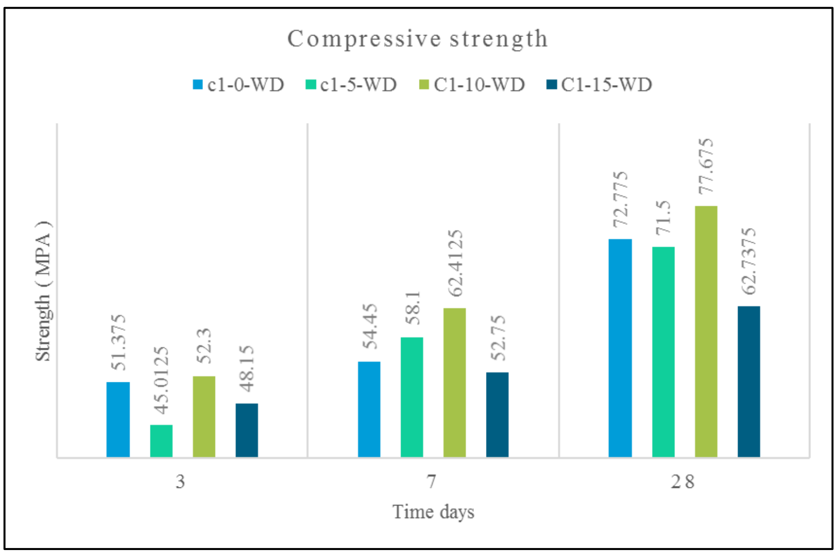


Figure 4.7 a: compressive strength of granite powder white

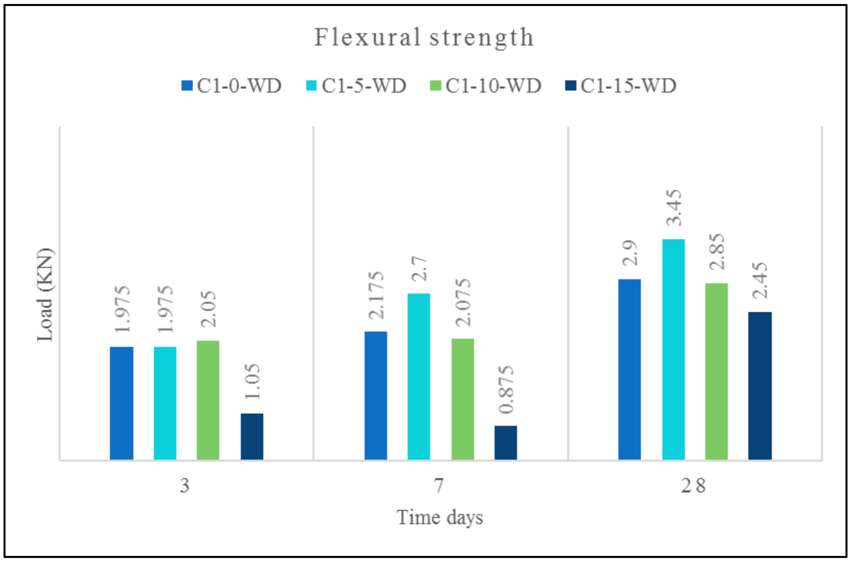


Figure 4.7 b: Flexural strength of granite powder white

From the above figures, it is reflected that formulation having 10 % replacement gives the maximum compressive strengths as compared to other replacement percentages. It is due to filler and pozzolanic effect of granite white powders. But to camper granite white and black, then Black give high strength.

4.2.2 Thermal analysis

In thermal analysis, the casted formulation with maximum strength were subjected to compressive strength after elevated temperature of 100C°, 300C°, 600C°. it can be seen in the graph that granite powder white show maximum strength. Figure 4.8 show thermal response of self-consolidating pastes system containing two types of granite powders.

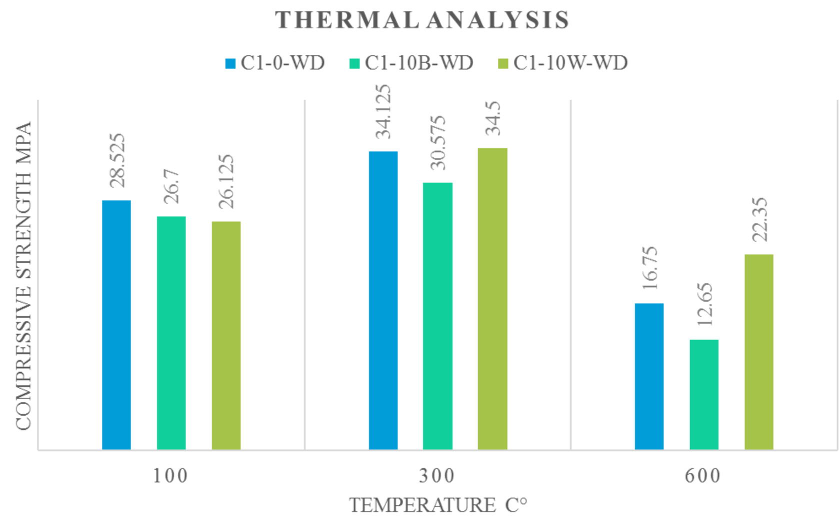


Figure 4.8: Thermal response of granite powders

4.2.3 Scanning electron microscopy for microstructure

Microstructure and hydration products were studied using SEM images obtained from Scanning Electron Microscope available at SCME NUST H-12 Islamabad. Figure 4.9 (a, b) shows the hydration products of SCP formulations at 28 days age developed due to the hydration reaction. Granite with maximum strength at 28 days were subjected for SEM analysis as shown.

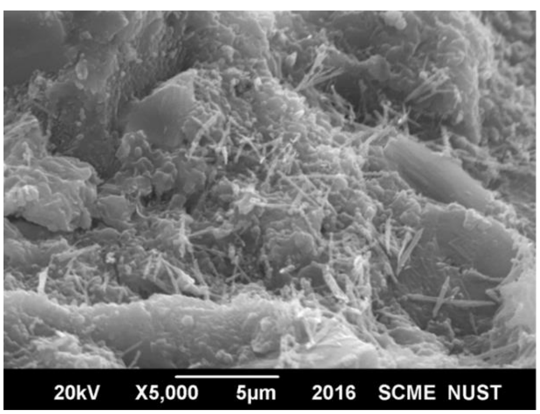


Figure 4.9a: Granite black

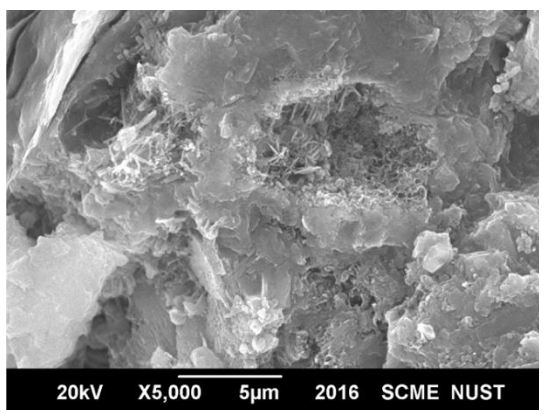


Figure 4.9b: Granite white

From the above figure, it can be concluded that in granite black formation of ettringite is dominant while in granite white formation of CH hexagonal plates are dominant which confirm the results of shrinkage and strengths.

Chapter 5: Conclusions and recommendations

5.1 conclusions

Based on this research work following conclusion can be drawn

- Granite powders can be used as a successful mineral admixture in self-consolidating pastes systems.
- Both the granite powders increase the water and superplasticizer demand due to its angular shape and fineness.
- Both the granite powders have marginal effect on the initial and final setting time so it can be used in practical fields where normal OPC can be used.
- One of the main defect in SCP is early volume shrinkage so, granite powder black play vital role and can be used to compensate early volume shrinkage. While granite white can compensate to marginal level.
- The heat of hydration produced is being lowered by introducing both types of granite powders which reflects its practical use in mass concreting.
- The main objective obtained is that by using granite powder black compressive strength increases to a significant level which is the need of the hour.
- Granite powder white does not play significant role in strengths however results are comparable to that of control sample.
- At elevated temperatures, the compressive strengths were maintained as compared to control sample which makes its use more attractive in case of fire in a building.

5.2 Recommendations

Based on this research following points needs to be addressed

- Dumping of granite wastes from industries are increasing day by day causing live threats so its need of the hour to explore alternative methods of disposition.
- Granite powder proved that it can be practically used so this project should be industrialized to avoid pollution.
- More research is required specially on using granite powder as a sand replacement.

References

[1] Fly Ash, Silica Fume, Slag, and other Mineral By-Products in Concrete, SP 79, American Concrete Institute, Detroit, pp. 1196, 1983.

[2] Eriksen, Kirsten, and Nepper-Christensen, Palle, "Experiences in the Use of Superplasticizers in Some Special Fly Ash Concretes", Developments in the use of Superplasticizers, SP-68, American Concrete Institute, Detroit, pp. 1- 20, 1981.

[3] S. A. Rizwan and T. A. Bier, "Ecological, Economical and Environmental Aspects of Self Compacting Concrete–Present and Future," International Journal of the Society of Materials Engineering for Resources, vol. 20, no. 1, pp. 12-16, 2014.

[4] ACI Committee 237R-07. Self-Consolidating Concrete. ACI Manual of Concrete Practice; American Concrete Institute: Farmington Hills, MI, USA, 2007; p. 30.

[5] Nehdi, M., Pardhan, M., Koshowski, S., 2004. Durability of self-consolidating concrete incorporating high-volume replacement composite cements. Cem. Concr. Res. 34, 2103e2112

[6] H. Okamura, "Self-Compacting High-Performance Concrete – Ferguson Lecture for 1996," Concrete International, Vol. 19, No. 7, pp. 50 - 54, 1997.

[7] Ozawa, K. Maekawa, and H. Okamura, "Development of the High Performance Concrete," Proceedings of JSI, Vol. 11, No. 1, pp. 699 - 704, 1989.

[8] H. Okamura and M. Ouchi, "Applications of Self-Compacting Concrete in Japan," Proceedings of the 3rd International RILEM Symposium on Self-Compacting Concrete, RILEM Publications, pp. 3 - 5, 2003.

[9] Roskovic, R., Bjegovic, D., "Role of mineral additions in reducing CO2 emission". Cement and Concrete Research, Vol. 35, No. 5, pp. 974 - 978, 2005.

[10] Chandra, S., "Waste materials used in concrete manufacturing", Elsevier, 1st Edition, chapter 3, pp 142 - 183, 1996.

[11] "Historical Analysis of Cement Production", All Pakistan Cement Manufacturer Association, 2016.

[12] ACI committee 116R-00, "Cement and Concrete Terminology." Reapproved 2005.

[13] ASTM C 125-00, "Standard Terminology Relating to concrete and concrete aggregate", Annual book for ASTM Standards, American Society of Testing and Materials, Vol. 04.02, pp. 150 - 155, 2004.

[14] S. A. Rizwan, T. A. Bier, "Self-Consolidating Mortars Using Various Secondary

Raw Materials", ACI Material Journals, Vol. 106, pp. 25 - 32, 2009.

[15] H. Okamura, M. Ouchi, "Self-Compacting Concrete-development, present and future", RILEM Proceedings, 1st International RILEM Symposium on Self-Compacting Concrete, pp. 3 – 14, 1999.

[16] S. A. Rizwan, T. A. Bier, "Blends of limestone powder and fly-ash enhance the response of self-compacting mortars", Construction and Building Materials, Vol. 27, pp. 398 - 403, 2012.

[17] S. A. Rizwan, A. W. Safdar, I. Ahmed, I and T. A. Bier, "Optimum replacement of OPC by fly ash and limestone powder and their blends in self-consolidating paste systems prepared at variable mixing water temperatures", International Symposium of Self-Compacting Concrete, 8th proceeding, pp. 255 - 265, 2016.

[18] ASTM C1017 / C1017M - 07 "Standard Specification for Chemical Admixtures for Use in Producing Flowing Concrete", 2007.

[19] Harrison J., Sustainability for the cement and concrete industry Part 1 , ZKG International, Vol. 59, No. 11, 83-86 (2006)

[20] Thomas A. Bier and S. A. Rizwan, "Sustainable Construction and the European CEM II Approach" International Conference on Advanced Concrete Technology and its Applications (ACTA-2012) Islamabad-Pakistan, November 6-7, 2012 pp 1-7

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

[22] U.S. Federal Highway Administration (14 June 1999). "Admixtures". Retrieved 25 January 2007

[23] ASTM C 125 – 00, "Standard Terminology Relating to concrete and concrete aggregate", Annual Book for ASTM Standards, American Society of Testing and Materials, Vol. 04.02, 2004, pp.150-155

[24] I. Marmol a, P. Ballester a, S. Cerro b, G. Monros b, J. Morales c, L. Sanchez, Use of granite sludge wastes for the production of coloured cement-based mortars

[25] Abd Elmoaty Mohamed Abd Elmoaty, Mechanical properties and corrosion resistance of concrete modified with granite dust

[26] Telma Ramos a,⇑, Ana Mafalda Matos a, Bruno Schmidt c, João Rio a, Joana Sousa-Coutinho a,b, Granitic quarry sludge waste in mortar: Effect on strength and durability

[27] Huajian Li ⇑, Fali Huang, Guanzhi Cheng, Yongjiang Xie, Yanbin Tan, Linxiang Li, Zhonglai Yi, Effect of granite dust on mechanical and some durability properties of manufactured sand concrete.

[28] Dina M. Sadek a, *, Mohamed M. El-Attar b, Haitham A. Ali b, Reusing of marble and granite powders in self-compacting concrete for sustainable development

[29] Jillavenkatesa A, Dapkunas S J, Lin-Sien Lum, Particle Size Characterization, NIST Special Publication 960-1, 2001

[30] Wang Aiqin and Zhang Chengzhi, "Study of the influence of the particle size distribution on the properties of cement", Cement and Concrete Researh-27(1997), pp. 685-695.

[31] Rizwan, S. A. *et al*, "Application of Packing Concepts to High Performance Self-Consolidating Mortar (SCM) Systems", ACI Materials Journal, SP-289.22, pp. 299-316

[32] Cabrera, J. G. *et al*, "Mechanism and kinetics of hydration of C3A and C4AF, extracted from cement", Cement and Concrete Research 14 (1984), pp. 238-248.

[33] P. Kumar Mehta, Paulo J. M. Monterio, Concrete: Microstructure, Properties and Materials, 2nd edition, October 2001.

[34] Jiang, Z., Sun, Z., and Wank, P.," Autogenous Relative Humidity Change and Autogenous Shrinkage of High Performance Cement Pastes", Cement and Concrete Research, 35 2005 1539-1545.

[35] Tazawa, E and Miyazawa, S.," Experimental Study on Mechanism of Autogenous Shrinkage of Concrete", Cement and Concrete Research, Vol. 25, No 8, pp 1633-1638, 1995.

[36] Jensen, 0. M and Hansen, P. F.," Autogenous Deformation and R-H Change in Perspective", Cement and Concrete Research, 31(2001) 1859-1865.

[37] Lura, P., Durand, F., and Jensen, O.M.,"Autogenous Strain of Cement Pastes with Superabsorbent Polymers", Proceedings, International RILEM Conference on Volume Changes of Hardening Concrete; Testing and Mitigation", 20-23 August 2006, .(Editors: O.M.Jensen,Pietro Lura and Konstantin Kovler),Technical University

of Denmark, Lyngby,Denmark.pp 57-65.

[38] Morin, V, Tenoudji, F. C, Feylessoufi, A and Richard, P.," Supelplasticizer Effects on Setting and Structuration Mechanisms of Ultra High-Performance Concrete", Cement and Concrete Research, 31 (2001) 63-71.

[39] Rizwan, S. A. and Bier, T. A.; "A Discussion on the Essential Issues for the Successful Production of Self – Compacting Concrete (SCC)", Proceedings of 8th International Symposium on Brittle Matrix Composites, BMC – 8, Warsaw, Poland, October 23-25, 2006, pp. 149 – 159