Use of Superabsorbent Polymers (SAPs) to Mitigate Shrinkage in Self-Compacting Cement Paste Systems (SCPs) Containing Mineral Admixtures

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This is to certify that the

Thesis titled

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ABSTRACT

This thesis reports the effect of superabsorbent polymers (SAPs) on the shrinkage response of self-compacting cement paste systems (SCPs) with and without the cement replacement using Fly Ash (FA) and Marble Powder (MP) in addition to giving other information about strength and Calorimetry. Twenty formulations were studied at varying water-cement ratios (0.27, 0.30, 0.35 and 0.40) to observe the effectiveness of SAPs as internal curing agent with varying water content. 10% cement replacement was done using FA and a 50-50 combination of FA and MP to study the effects of their addition on the SAPs containing self-compacting cement pastes. The results of this pioneer study in Pakistan indicate very promising results while giving insights about SAP-super-plasticizer interaction and the possible industrial short term uses which might revolutionize the construction industry of Pakistan

DEDICATIONS

We dedicate this thesis to our parents.

ACKNOWLEDGEMENT

LIST OF NOTATIONS

SCPs	Self-Compacting Pastes
SAPs	Superabsorbent Polymers
SCMs	Self-Compacting Mortars
SCCs	Self-Compacting Concrete
SEM	Scanning Electron Microscopy
XRF	X-Ray Fluorescence
EDX	Energy Dispersive X-Ray
SRMs	Secondary Raw Materials
SP	Super-plasticizers
FA	Fly Ash
MP	Marble Powder

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1   INTRODUCTION

1.1   General

Concrete is a composite material formed by mixing cement, sand, aggregate and water. Some other chemical and mineral admixtures can also be added to enhance the properties of concrete. Concrete has become the most widely used construction material due to its strength, economy, durability and the ability to cast into any shape. The efficient placing of concrete requires heavy compaction by skilled labor and the disability to do so reduces the durability, strength and aesthetics of concrete. One way to ensure efficient compaction is to use self-compacting systems obtained using super plasticizers. During hardening a number of simultaneous phenomenons occur within the cement matrix resulting in shrinkage of the volume causing early age cracking and reducing strength, especially in the mixes with low water-cement ratios. One of the methods to mitigate the shrinkage of the concrete systems is to use Super Absorbent Polymers (SAPs) to internally cure the matrix.

1.2   Self-Compacting Paste Systems

Self-compacting concrete (SCC) as defined by ACI 237R – 07 as "a highly flow able, non-segregating concrete that can spread into place, fill the formwork, and encapsulate the reinforcement without any mechanical consolidation". The spread of SCC is purely under its own weight. Similarly the self-compacting pastes (SCPs) flow under their own weight. One of the major advantages of using SCC is that we can produce high performance concrete systems at low water-cement ratios while keeping it workable. It also reduces the cost of construction as by the using, SCC we eliminate the need for the labor required to consolidate the poured concrete using conventional mechanical equipment. As SCC flows under its own weight it also ensures that compaction and hence durability of the poured concrete is uniform.

1.3 Super-Absorbent Polymers

Super Absorbent Polymers (SAPs) are defined as "a group of polymeric material that have the ability to absorb a significant amount of liquid from the surroundings and to retain the liquid within their structure without dissolving" (1). The amount of liquid absorbed by SAPs is dependent on several factors including temperature, pH, ionic composition of the liquid and the number of cross-links in the polymers. Since the development of Super Plasticizers enabled the formation of high-performance cement systems the need for an internal curing agent is realized. SAPs can be used to incorporate water-filled packets within the cement systems in order to reduce the magnitude of overall shrinkage.

1.4 Secondary Raw Materials

1.4.1 Fly Ash

Fly Ash (FA) is used in the cement systems to help proceed toward green construction. Fly ash is collected by either mechanical or electrostatic separators in the power plants using pulverized coal. They are mainly made of silica (SiO_2) and alumina (Al_2O_3) and are used as a substitute for conventional raw materials.

1.4.2 Marble Powder

Marble is a metamorphic rock resulting from the transformation of pure limestone. A large quantity of marble powder is generated from the cutting process which is then used in construction. Marble powder is used as filler in cement paste systems which reduces the porosity in cement. Very small size of marble powder particles increases the surface area thus increases the water requirement, so its addition as secondary raw material in SCPs would increase strength and durability due to increased packing density of the system.

1.5 Objective of Research

This research focuses on the mitigation of early age shrinkage, causing early age cracking, by introduction of Super Absorbent Polymers (SAPs) as internal curing agent in self-compacting cement pastes with and without chemical (FA) and physical(MP) admixture. The effects of SAPs addition on strength, calorimetric response, setting times and super plasticizer demand was also studied.

2   LITERATURE REVIEW

2.1   Shrinkage of Cement Pastes

2.1.1   History and Background

Shrinkage of concrete refers to the reduction in volume of the concrete systems. This behavior can be attributed to various simultaneous mechanisms occurring within the cement matrix. This contraction of the cement paste can be a result of autogenous shrinkage due to cement hydration, thermally-induced shrinkage and drying shrinkage due to loss of water to the surrounding.

2.1.2   Autogenous Shrinkage

The term "autogenous", as defined by Prof. O.M. Jensen in his Phd Thesis, refers to a certain thermodynamic state: a system is under autogenous conditions when it is (1) closed (2) isothermal and (3) not subjected to external forces. Autogenous deformation refers to the deformation under autogenous conditions. To completely understand the effects and mechanism of autogenous deformation, we must first understand the process of cement hydration. This process can be divided in three major periods(2)

1- Early Period - Also referred to as the pre-induction phase which last only a few minutes. The cement grains, immediately after getting in contact with water start to react with calcium aluminate and gypsum as the main reactants. High percentage of calcium ions is observed and ettringite is formed.

2- Middle Period- CSH needles and crystalline CH is formed by the reaction of C_3S and C_2S with water. C_3A and C_4AF also react giving off high heat of hydration. This marks the end of workability of the cement systems i.e. setting.

3- Late Period- A dense micro-structure is formed within the cement grains which gives the strength to the overall matrix, also called hardening. The heat given off during this phase is lesser

owing to the slower diffusion of water molecules and ions through the increasing thickness of hydration products layer.

The core reason for autogenous shrinkage is believed to be the capillary tension in the pore fluid which strengthens the belief that drop of internal relative humidity causes self-desiccation shrinkage. Various other driving forces have also been suggested by P. Lura(3) which are discussed in detail.

2.1.3 Chemical Shrinkage and Self-Desiccation

Chemical Shrinkage refers to the shrinkage of cement paste due to hydration reactions as discussed above starting from the time that water is mixed with the cement grains. Not only the hydration of clinker causes chemical shrinkage but also the secondary reactions like ettringite formations. In fluid phase, the cement is unable to sustain the void created by the chemical reaction so reduces in volume.
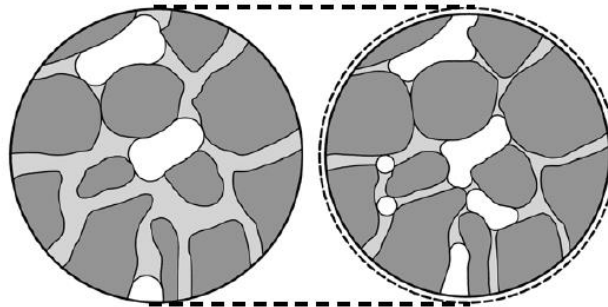
Figure 1 Schematic Representation of a Cross-Section of Hydrating Cement Paste (1)

2.1.4 Surface Tension

According to the surface tension approach, bulk shrinkage and expansion of the cement paste are results of changes in the surface tension of the solid gel particles. Adsorption of water lowers the surface tension of the cement gel particles and results in expansion. Conversely, removal of adsorbed water causes shrinkage.

2.1.5 Disjoining Pressure

The disjoining pressure is active in areas of hindered adsorption, i.e. where the distances between the solid surfaces are smaller than two times the thickness of the free adsorbed water layer. This effect should be important also at high relative humidity (RH).The disjoining pressure between the solid particles is the result of van der Waals forces, double layer repulsion and structural forces. The disjoining pressure varies with the RH and with the concentration of Ca^{2+} ions in the pore fluid. When the RH drops, the disjoining pressure is reduced, causing shrinkage.
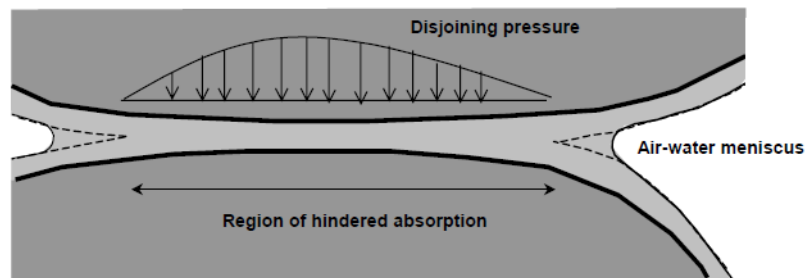
Figure 2 Surfaces of Hindered Adsorption and Distribution of Disjoining Pressure. [Lura 2001]

2.2   Self-Compacting Pastes

Development of Self compacting cementitious systems (SCCS) originated in 1980's in Japan. In mid-1980's Japanese construction industry was facing some serious challenges related to durability and serviceability requirements of the concrete structures. To make durable concrete structures proper vibration of concrete is required to place it at placements where heavy and overcrowded reinforcement is present. These places include heavily reinforced columns, deep foundations, tunnel linings, piers of bridge etc. Self compacting paste is characterized by their high flowability under its own weight such that they are able to easily fill small interstices of formwork without vibrationand can be pumped through long distances which has made casting of dense reinforcement and mass concrete convenient while minimizing the noise and improving the quality of concrete. Therefore, use of SCC in civil engineering has remarkably increased in the concrete industry over the last few years (4)

Khayat et al define SCC as "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".

This definition clearly states that SCC must have adequate flow to reach into those places where normal and conventional concrete can't reach without the help of manual vibration and it should be able to resist segregation. European guidelines (5) for self-compacting concrete define it 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". This definition also pretty much supports the same idea mentioned above.

Rizwan et al states that "as paste is the vehicle of aggregate phase, good workability can be achieved by reducing the aggregate content with an increased paste volume thus resulting in reduced internal friction". This statement suggests that by increasing the quantity of fines in the mixture, higher flow is achievable.

Rizwan et al (6) also reported that "shape, size, surface morphology and porosity of secondary raw materials play a very significant role in determining the water and super plasticizer demands of the system, but besides the physical properties, the chemical composition of the secondary raw materials is also very important". It is true because few secondary raw materials have much higher water demands as compared to others and this phenomenon is because of their texture and other physical properties.

Self-compacting concrete (SCC) has shown several advantages such as technological, environmental and economical due to its high fluidity. However, because of its particular composition, it has often resulted in a higher fine content and paste volume. It is more sensitive to cracking than traditionally vibrated concrete (TVC). Besides the effect of increased paste volume, the autogenous shrinkage is also influenced due to the presence of mineral admixtures in the capillary network. This change in pore structure of capillaries affects the magnitude of self-desiccation shrinkage.

2.3 Super Absorbent Polymers

The most fundamental property of SAPs is their ability to take up enormous amount of water from the surroundings and retain it within their structure. When fully swollen SAPs are said to be

99% water and only 1% of polymer. This unique property gives SAPs edge over all other absorbing materials in various applications.

Some specific types of SAPs can take up water up to 1500 g/g of dry material, although in cementitious environment this value is reduced to about 20 g/g due to high Ca^{+2}ion concentration in the resulting fluid which is still higher than the absorption capacity of any other absorbing material(7). It can be said that the absorption capacity of SAPs is dependent on several factors including temperature, pressure,water activity and the ionic composition of the exposure liquid.

2.3.1 The Dry State of SAPs

SAPs when exposed to atmosphere, due to their higher absorption capacity, absorb the moisture so we need a mechanism to establish an initial dry state for reliability of results.

Generally the dry state of any construction material refers to heating in an oven at 105 ℃ which results in rapid boiling away of the water leaving behind the dry material. This definition of dry state applies to SAPs but the process used is not that effective due to higher absorption capacity of SAPs which causes the release of water to be too slow. The most obvious solution is to oven dry the SAPs at a higher temperature but as we go above 180 ℃the polymeric chains of SAPs begin to break causing the deterioration of its particles. This limits the maximum possible drying temperature below which the drying process is ineffective.

The error induced due to improper drying of SAPs under normal laboratory conditions is minute, approximately 1% but this can be huge if SAPs have been exposed to a humid environment. SAPs typically contain 0.01-0.05 g/g water after commercial production(8) but if exposed to RH of about 50%, it can absorb moisture up to 0.25 g/g of dry mass(7).

To overcome this problem SAPs were kept in a desiccator with silica gel for at least 24 hours prior to the use. Silica Gel acts as a desiccant and absorbs the moisture from the air within the desiccators. This causes little or no moisture available in the air surrounding SAPs i.e. RH falls which causes the SAPs to lose the absorbed water down the potential gradient into surrounding air which again is absorbed by the silica gel ultimately keeping the SAPs particles dry.

2.3.2 Chemical and Physical Properties

The most significant physical characteristic of SAPs is their ability to take up and hold significant amount of the liquid they are exposed to.The amount of water absorbed by SAPs

depends on properties of the SAPs, and its exposure environment. SAPs geometry influences the rate of water exchange with the surroundings, whereas SAP chemistry influences both the rate of water exchange as well as the absorption capacity. Parameters in the exposure environment influencing the SAP water absorption include the temperature, pressure, the water activity and the specific ionic composition of exposure liquid (7).

With regard to chemical composition, SAPs exist in two opposite extremes: ionic and non-ionic polymers. Some SAPs are also a mixture of these extremes, they are called co-polymerized mixtures.Ionic SAPs have much higher values of absorption capacity due to presence of strong dipole-ion interaction between water and ions present on the polymer chain. Non-ionic SAPs generally work on the basis of hydrophilic groups along the polymer chain. Commercial SAPs are generally ionic due to their obvious advantage of high absorption capacity. Although, in solution with high ionic concentrations the ionic SAPs do not perform well owing to the shielding of ionic charges, significantly reducing their water holding capacity. The most common type of ionic SAP is polyacrylic acid while non-ionic SAP is polyacrylamide.The cross-linking of SAPs also greatly effects its physical characteristics along with giving SAP the ability to hold water instead of dissolving. Cross-links can be ionic, covalent or hydrogen bonded, although covalent are preferred due to their higher strength and stability.

The physical appearance of SAPs depends on the method of its production which are of two basic types.

2.3.3 Suspension Polymerized SAPs

The solution, in which this type of SAP is produced, is separated into dispersed phase by means of agitation and by addition of suspension aid resulting in a spherical appearance of the final SAP particles.
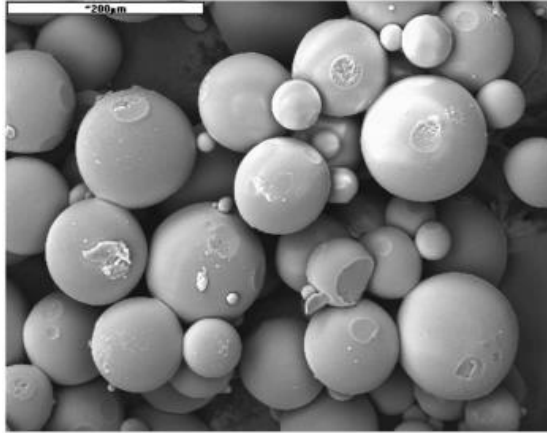
Figure 3 Spherical Suspension Polymerized SAPs (9)

2.3.4 Solution Polymerized SAPs

In this the solution is not separated into dispersed phases resulting in rough appearance of SAPs like crushed particles.
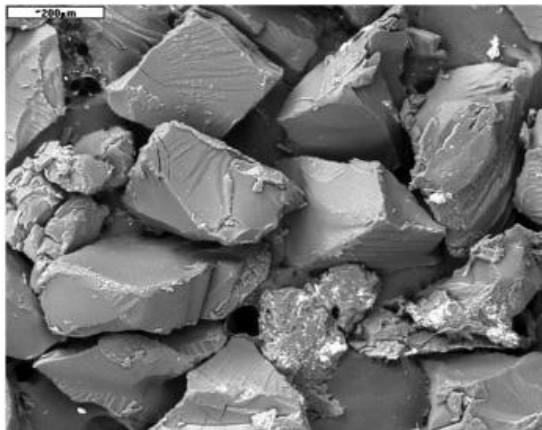
*Figure 4 Crushed Particles of Solution Polymerized
SAPs (9)*

When a dry SAP particle is exposed to water/liquid it will swell, and after a certain time reach a point of apparent equilibrium. This is referred to as "The Water Absorption Capacity of SAPs" in this particular environment. However, the equilibrium achieved is not stable for e.g. if the temperature of the exposure liquid changes the SAP will exchange water with the surrounding until a new apparent equilibrium is achieved.

The introduction of SAPs is known to reduce the compressive strength of cement pastes because the strength of material is greatly influenced by the size of largest defect present in its solid matrix. In cement pastes, the voids left by largest SAP are the largest defects which are obviously greater than the pores developed during cement hydration. In pastes with internal water curing due to SAP inclusions the initial capillary pores will be filled by hydration products and the porosity is concentrated in isolated spherical inclusions (10).

2.3.5 Applications

The unique ability of SAPs to absorb and hold enormous amount of liquid makes them useful in many industries. Traditional absorbent materials have pores within the structure of the material, which has a characteristic low bulk density. Superabsorbent polymers have cross-linked networks of flexible polymer chains: the most efficient polymer networks with dissociated, ionic functional groups. Currently these are being used in (8)

- Food Packaging

- Medicine Industry

- Diapers

- Sanitary Pads

- Horticulture Industry

It was only a matter of time before this polymer found its way to the construction industry as an additive (11). Studies have been done to study its effects on various properties of concrete including

- Mitigating autogenous shrinkage of cementitious systems (12)

- Changing the rheology of fresh concrete(13)

- Improving the freeze-thaw resistance of concrete(14)(15)

- Promoting self-healing in concrete(16)

2.4   Secondary Raw Materials

2.4.1   Fly Ash

Fly ash is a pozzolanic material. During the thermal process it melts at the higher furnace temperatures (1400-1500°C). A small part of it falls in the bottom of the boiler producing bottom ash. The main part is dragged by the exhausted gas stream, cooling quickly, and solidifying in the form of small vitreous spherical particles, which form the fly ash(17). It is a finely-divided amorphous alumino-silicate with varying amounts of calcium, which when mixed with Portland cement and water, will react with calcium hydroxide released by the hydration of Portland cement to produce various calcium-silicate hydrates (C-S-H) and calcium-aluminate hydrates. Some fly ashes with higher amounts of calcium displays cementitious behavior by reacting with water to produce hydrates in the absence of a source of calcium hydroxide. These pozzolanic reactions are beneficial for the concrete as they increase the quantity of the cementitious binder phase (C-S-H) and, to a lesser extent, calcium-aluminate hydrates, improving the long term strength and reducing the permeability of the system. Both of these mechanisms enhance the durability and strength of the cement paste systems (18).

Generally, fly ash contents used in concrete are limited to 15% to 25% of cement replacement (19) but we used 5% to 10%. Feldman et al. (20) reported that in high-volume fly ash/cement (FC) pastes, the fly ash starts reaction with Calcium hydroxide between 3 and 7 days, but significant quantities of Calcium hydroxide and fly ash still don't react, even after 91 days of hydration. Calcium silicate hydrates (CSH) that are the reaction products have lower calcium-to-silica ratios. Berry et al. (21) stated that fly ash acts as filler in the early stages and its physical properties are dominant in this period. Additionally, it is involved in the formation of ettringite. However, at the later stages they are involved in hydration reaction mainly as silico-aluminate binders. It is reported that use of fly ash can increase the slump of concrete mix without adding up extra cost. It reduces the dosage of super plasticizer to obtain similar slump compared to concrete made by Portland cement (22). Use of fly ash also improves the rheological properties of concrete and it reduces cracking in concrete by lowering heat of hydration of cement (23). Kim et al. (24) reported that replacement of cement by 30% of fly ash resulted in super flowing concrete and addition of fly ash ameliorated the flow and workability of concrete. High-strength

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self-compacting concrete production using fly ash has been a very encouraging impact to the sustainability of concrete technology. Use of fly ash decreases the demand for cement, fine fillers and sand (25). The low water to cement ratio of the concrete imparts high durability to concretealong with better mechanical integrity of the structure. More importantly, flaws due to wrong or inadequate vibration of concrete, which reduce the durability of the structure, are avoided completely(26).

2.4.2   Marble Powder

Marble as a building material has been in use for ages. However, the use was limited to as stone bricks in wall or arches, slabs in walls, or as lining of floors or roofs. This led to the wastage of high amount of unused Marble powder at quarry or at the sizing industry generally unattended in the building industry itself as filler in mortar or concrete. Recently, large amount of marble dust is generated in natural stone processing plants having significant impact on environment and human lives. The result of which is that the mass which is 40% of total marble quarried has reached as high as millions of tons. This huge mass of marble waste consisting of very fine particles is today one of the major environmental problems around the world (27). This can be reduced by utilizing them in building industry as mineral admixture. Researches are being conducted to find and assess the possibilities of using waste marble powder in mortars and concretes. Their results of strength and workability were then compared with control samples of conventional cements and mortar/concrete.

It was observed that marble powder had very high Blaine fineness value of about 1.5 - 2 m/g, with 90% of particles passing through 50 μmsieves and 50% through 7 μm sieves (28). Valeria el al also noticed that the marble powder had a high specific surface area, implying that its addition as mineral in mortars and concretes, should impart more cohesiveness especially in self - compacting concrete. Hanifi Binici et al(29) found that marble dust concrete has higher compressive strength than the corresponding limestone dust concrete having equalmix proportion and water cement ratio. The results indicated that the Marble dust concrete would probably have lower water permeability than the limestone concrete. As non pozzolanic fines, limestone and dolomite are most frequently used to increase the content of fine particles in self compacting concretes (30). Due to the advancements in concrete technology we are able to reduce the consumption of natural resources and energy sources relieving the burden of pollutants on

environment. In many countries, the effects of varying marble dust contents on the physical and mechanical properties of fresh and hardened concrete are being studied. Slump and air content of fresh concrete and absorption and compressive strength of hardened concrete were also investigated. Test results indicated that this industrial by product is capable of improving hardened cement performance up to 10%. The compressive strength of cement paste systems were measured for 1,3 and 28 days. In order to evaluate the effects of marble dust on mechanical behavior, many different mortar mixes were tested.

2.5   Experimental Techniques

2.5.1   X-Ray Fluorescence

X-ray Fluorescence is an experimental technique that involves emission of X-rays by bombarding high energy gamma rays on specific materials. Conventionally, it is used to carry out elemental analysis and chemical analysis of metal, glass, ceramic and building materials. Modern Portland cement is made by mixing substances containing lime, silica, iron oxide, alumina and then heating the mixture until it fuses. Compounds such asDi-calcium and tricalcium silicate, tricalcium aluminate, and a solid solution containing iron are formed during the heating process. X-ray fluorescence (XRF) is a standard technique which used accross the cement industry to determine metal-oxide concentrations and oxide stoichiometry.XRF spectrometer has various advantages that include the ease of sample preparation, suitability for determining of elements induced in cements, ease of calibration as well as linearity of calibration curves over extended concentration ranges for most elements(31).

2.5.2   Scanning Electron Microscopy

Use of the scanning electron microscope (SEM) with X-ray microanalysis allows study of chemical including cement and clinker; permitting measuring bulk phase abundance and surface areas of the phases, as well as bulk chemistry of constituent phases can be carried out. It has been developed using high energy electron beam rather than normal light source(32).Its multipurpose nature allows us to know the characterization of cement, concrete, aggregate, admixtures and several secondary raw material's microstructure. Direct imaging of hydraulic cements by SEM yields a more complete picture of both bulk and surface phase compositions as compared to optical methods and gives a better element analysis and imaging. It gives a very clear and fine

image of materials at very large magnifications. Mass percentages obtained by SEM imaging are in good agreement with percentages based upon XRD. Scanning electron microscopy renders quantitative chemical analysis in terms of Energy Dispersive X- ray Spectroscopy (EDX) (33). Shape and morphology of micro particles are easily assessed using scanning electron microscopy because each material has its own specific individual form. As the finer-grained phases (gypsum, tricalcium aluminate, and ferrite) show much higher surface areas per unit mass than the coarser-grained phases such as alite and belite. Such data are being applied to develop better relationships between the cement material properties and performance properties and to provide starting images for a cement hydration (34).

2.5.3 Absorption Capacity

In all its applications, the required amount of SAPs is determined using the absorption capacity of SAPs and the required amount of liquids to be absorbed (1). This renders the accurate measurement of absorption capacity of utmost significance.

Several methods have been developed by researchers to measure the absorption capacity of SAPs including Tea-bag method (precision of $\pm$ 3%), Centrifuge Method (more accurate than Tea-bag method) and Sieve Method (precision of $\pm$ 2.1%) (35).

2.5.4 Setting Time

After mixing water to cement powder there are two significant stages in process of stiffening of cement paste which is Initial setting time and Final setting time. As per codes each has been standardized in terms of time taken by cement paste to gain enough strength to resist standard amount of penetration of needle in Vicat's apparatus. Initial setting time is time taken by cement paste to stiffen enough that needle of Vicat's apparatus penetrates by 5-7 mm from bottom of mould. Whereas, the final setting time is reached when the cement shows no marks of the outer circle of Vicat's needle.

2.5.5 Flow Test

Flow test is the method to determine the consistency of fresh cement paste. The consistency of cement depends upon the w/c ratio and on various aspects of cement like fineness, flocculation and rate of hydration reactions. The test is used to determine what SP/C percentage provides the specific flow of 30 cm. If the flow did not reach the target, the test was repeated by varying the amount of superplasticizer by hit and trial method until (30±1) cm flow was obtained.

2.5.6 Shrinkage

The term "drying shrinkage" is defined as the decrease in length of the test specimen, where the decrease is caused by any factor other than externally applied forces under stated conditions of temperature, relative humidity and evaporation rate in the environment; the term includes the net effect of a variety of phenomena tending to bring about both increases and decreases in length during the period in which the test specimens under consideration are stored in the environment and in which a number of processes, including hydration of the cement, are taking place at a variety of rates. This shrinkage causes both bending and axial stresses in cement systems which results in formation of cracks. Hence, to study the effects of SAPs and other mineral admixtures shrinkage test was performed.

2.5.7 Calorimetry

Cement hydration is an exothermic reaction taking place in a series of steps. It has following stages(36):

- Rapid Initial Process

- Dormant Period

- Acceleration Period

- Retardation Period

- Long-term reactions

Calorimetry is the best procedure to find all the stages of hydration process of cement (Bensled 1987). Determination of heat of hydration is very important because it affects almost all the properties of concrete including workability, setting times, strength development rates and pore structure development. Heat of hydration affects the early age of concrete as well as the long term performance of concrete. Basically, Calorimetry is the technique used to measure the heat production of the cement paste with time and evaluate the hydration kinetics. At initial stages, heat of hydration is high due to the fast hydration of aluminate phase, C_3A, in this phase the main product formed is AFt. After the initial period, heat of hydration decreases to minimum within 2-3 hours. This phase of hydration reaction is called induction period or dormant period. This dormant period is then followed by pozzolanic reaction and mass precipitation of hydration

products, mainly Calcium silicate hydrate (CSH) gel. Then the calorimetric curve rises to a second highest value of hydration process and this happens after 15-18 hours for self-compacting paste systems. After this the hydration process slows down and smaller peaks are formed in the process (37). Rizwan et al(38) stated that superplasticizers presence in the cementitious systems delays the heap peaks produced during calorimetry of cement process. Moreover, amount of heat evolved depends upon a variety of factors which include cement type, its content and water to cement ratio because super-plasticizer acts as retarder. Self-compacting cement pastes with various mineral admixtures were tested through this technique to observe the effects on temperature changes.

2.5.8   Strength

Strength of cement is most important of all cement properties. When cement is used for important structures, compressive strength is always carried out to ascertain the quality of cement. Grades mentioned on the cement bags as 53/43 grade OPC/PPC infact represents the strength of the cement.

Inert and pozzolanic mineral admixtures modify the physical and chemical properties of mortars and concretes and the compressive strengths can be separated into fractions of strength related to physical and chemical effects of mineral admixtures. Amount of mineral admixture affects the strength of cement paste system drastically. A small amount of powder having optimum efficiency results in large increase the compressive strength of cement where the use of large amount of powder has a smaller effect (39).

2.5.9   Particle Size Distribution

Particle size distribution is an experimental technique for accurate measurement of particle size and distribution in relation to size. Hence, PSD is essential for giving a complete characterization of cement powder and is closely linked to the cement performance. Since cement is a problematic material since cement particles are highly agglomerated in dry state it is very important to determine accurate particle size distribution for the computational modelling of the hydration process and to predict the performance of cementitious material. Presently, the only relevant standard method is ASTM C115-96, determining fineness (Standard Test Method for Fineness of Portland Cement by the Turbidimeter ASTM C115). a turbidimetric method for This method is limited in scope, however, with a lower size detection limit of 7.5 μm. However, the

new techniques have made it possible to the size even lower than 7.5 μm. The laser diffraction measurement is widely known for use in knowing the cement particle distribution. Because there are no standard procedures that adequately cover the broad particle size range associated with portland cement powder, the implementation of different measurement techniques varies widely within the industry(40). Cement manufacturers use PSD for quality control of cement, in association of Blaine fineness. The laser diffraction is quicker than blaine test and automated for efficient measurement. The information resulting from laser diffraction method provides an estimation of powder surface area by assuming specific gravity for the particles. Nevertheless, it is still not a standard test to measure the particle sizes and their distribution (41).

2.5.10 FTIR Spectroscopy

Infrared spectroscopy utilizes molecules or groups of atoms as large molecules which are able to absorb different wavelengths of infrared light depending on their geometry and immidiate surrounding of the atoms that constitute them. This allows it to be used to study both crystalline and amorphous samples. The sample is exposed to radiation with infrared light with a span of different wavelengths. The sample will absorb some of the light at wavelengths that have characteristic similar to its chemical composition. The intensity at each wavelength is measured with and without sample to see at which wavelengths the sample has absorbed light. IR radiation only penetrates about 1 wavelength into the sample (~10 μm for 1000 cm^{-1}), making it ideal in the study of surface processes(42).

Fourier-Transform Infrared (FT-IR) spectroscopy displays several advantages that make it interesting to study cementitious materials: from clinker or hydrated phases to the bulk or the surface of hardened concrete. The amount of material required by FT-IR analyses in transmission mode is only a few milligrams to provide its composition while other techniques (such as X-ray fluorescence, thermo-gravimetric analysis and X-ray diffraction) need a few grams. Moreover,the results provided by FT-IR analyses are rapid and are obtainedin few minutes while other methods need at least a few hours for one sample. The analyses done in Attenuated Total Reflection Mode allowsthe studying of the surface of materials without any specific sampling methods (such as cleaning with solvent or storage under vacuum), which can alter the final composition (43).
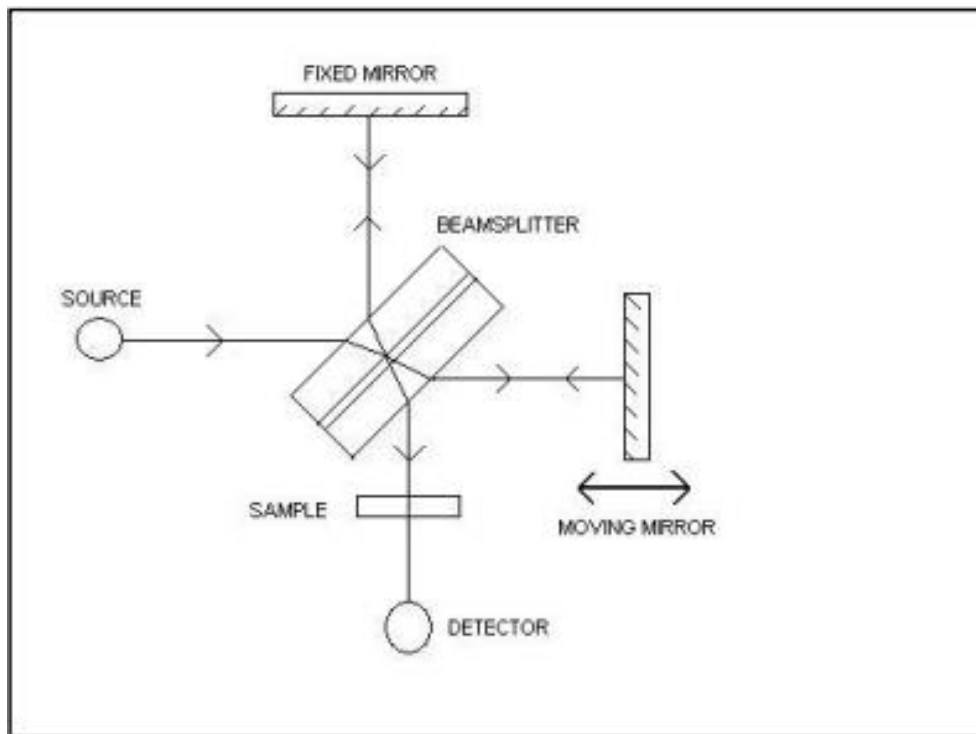
Figure 5 Schematic Diagram of Infrared Spectrometer

3   EXPERIMENTAL PROCEDURES

3.1   General

All the tests were carried out following the standards in controlled lab conditions of temperature and humidity.

3.2   Materials

3.2.1   Cement

Best Way Grade 53 cement is used during the course of study. Fresh OPC free from any lumps was obtained and kept in a sealed container to avoid any interaction with the moisture in atmosphere. Initially the physical and chemical properties of the cement were determined using XRF as shown. Figure 7 was obtained by mapping the laser granulometry results on a fifth order methematical equation using MATLAB to determine $D_{50}$of the powders. D_{50} of cement was aroung 19.54 microns.

Sample Name	CEM E-880
SiO_2	19.19
TiO_2	0.29
Al_2O_3	4.97
Fe_2O_3	3.27
MnO	0.04
MgO	2.23
CaO	65.00
Na_2O	0.58
K_2O	0.51
P_2O_5	0.08
LOI	3.84

Figure 6 XRF of Cement
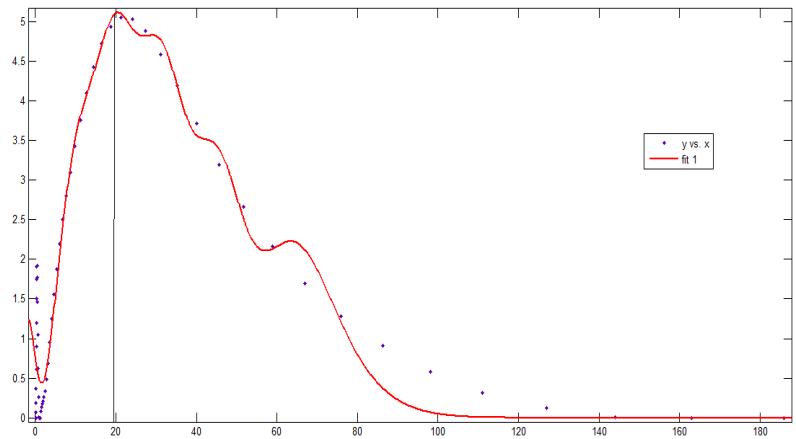
Figure 7 D50 of Cement Particles

3.2.2   Super Absorbent Polymers

SAPs were provided by Prof. O.M. Jensen (Denmark Technical University). Before introducing them into the cement pastes, their physical and chemical properties were studied. SAPs are hygroscopic in nature so immense care was required to maintain the dry state of SAPs. To avoid any errors in mass measurement SAPs were kept in a desiccator with Silica Gel as desiccant for at least 24 hours prior to use.
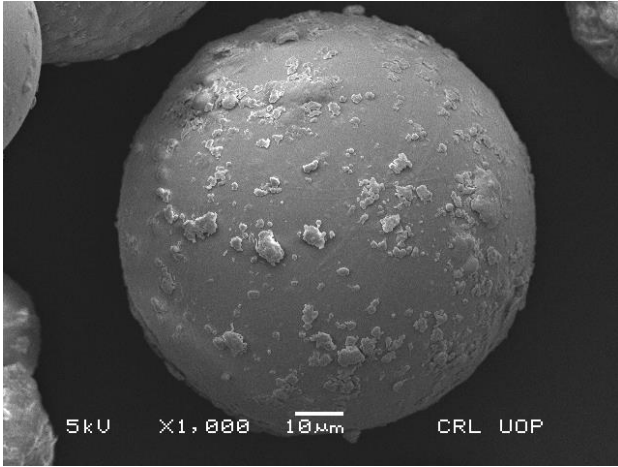
Figure 8 SEM of an Individual SAP Particle
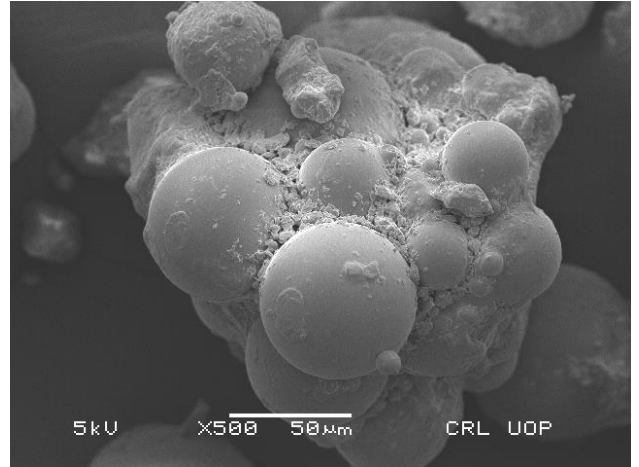
Figure 9 Agglomerated SAPs Particles

Element	Weight (%)
C	45.43
N	6.79
O	39.48
Na	8.18
S	0.12

Full Scale 2010 cts Cursor: 20.194 keV (0 cts)
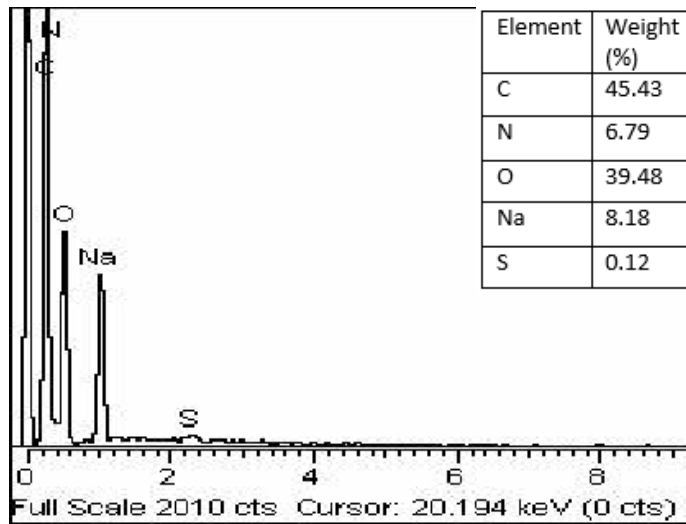
Figure 10 EDX of SAPs

The EDX results show that the most abundant element is carbon, the polymeric chain, with 8.18% sodium and Oxygen being the second most detected element. Nitrogen and Sulfur are also detected. This shows that the polymer under investigation is a copolymerized mixture of ionic and non-ionic polymer with sulfur cross links.
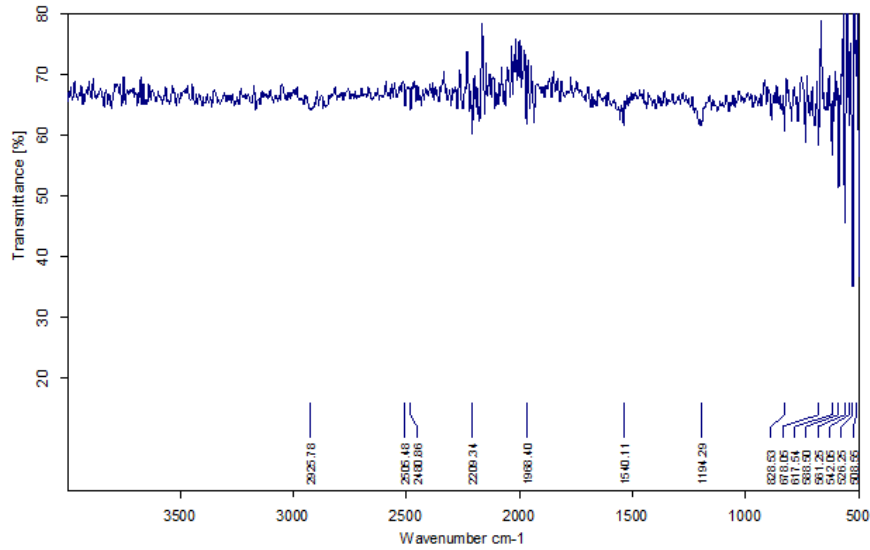
Figure 11 Infrared Spectrograph of SAPs

The peaks of IR compliment the results obtained by EDX data. The peaks of 2200 cm^{-1}, 1194 cm^{-1}, 1540 cm^{-1}, 3000 cm^{-1} proving the existence of bonds as shown in Annex A.

3.2.3 Secondary Raw Materials (SRMs)

Two basic types of SRMs were used, pozzolanic (FA) and inert (MP).

3.2.3.1 Fly Ash

Class F German fly ash was obtained and kept in a sealed container to ensure the consistency. It was made sure that it is free of lumps before addition to the cement mix. The XRF and particle size analysis was carried out to study its physical and chemical characteristics. D_{50} of FA used was around 23.78 microns.

3.2.3.2 Marble Powder

Locally available marble was ground and crushed to fine powder for use in cement mixes. The XRF and particle size analysis was carried out to study its physical and chemical characteristics. Results shown in Annex B. MP used has a D_{50} of 7.62 microns.

21
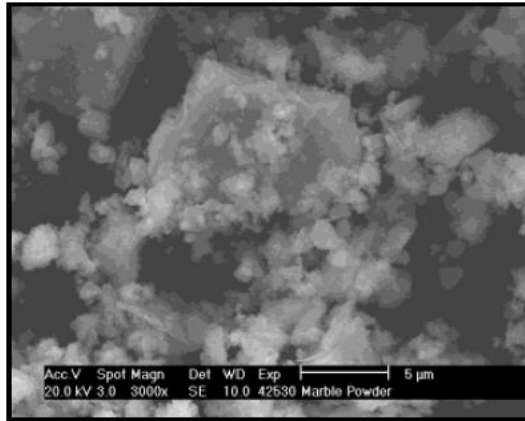
Figure 12 SEM of Marble Powder (MS Thesis NUST)
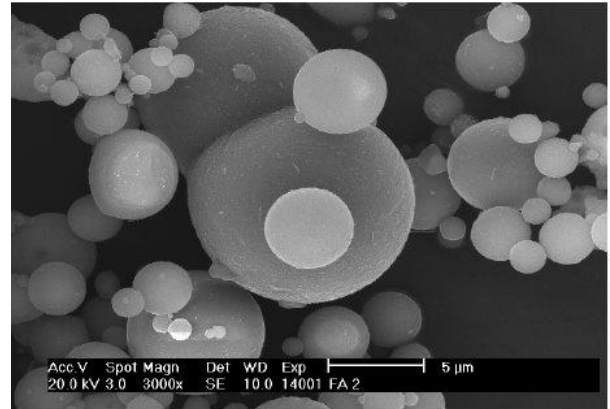
Figure 13 SEM of FA (Rizwan 2006) (44).

3.3   Test Procedures

3.3.1   Mixing Regime

The minimum time required by the SAPs to attain absorption ($> 80\%$) within the cementitious mix is 5 minutes(45) irrespective of the size of SAP particles as shown in figures 14, 15 and 16. So a 5 minute mixing regime was selected. The contents of the formulation were mixed in dry state for 1 minute before being added to the Hobart Bowl containing the mixing water. The mix then received 90 sec of slow mixing (145 rpm) followed by cleaning of the bowl using a spatula for 30 sec. lastly, the mix received fast mixing (285 rpm) of 210 sec completing the mixing time of 5 minutes.

Table 1 Mixing Regime of Formulations

Time/s	Regime
0-60s	Dry Mixing of the powders
60-150s	Slow mixing of the mix containing SRMs, SAP, SP and water
150-180s	Cleaning of the mixer walls
180-390s	Fast Mixing
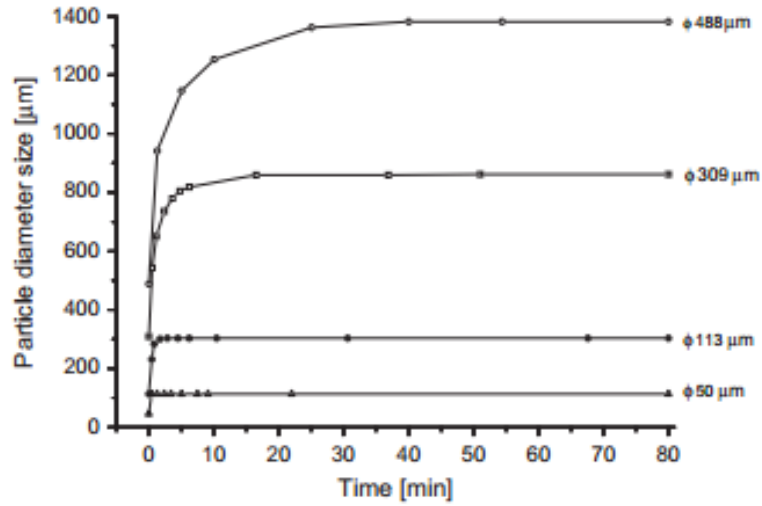
Figure 14Growth of SAP with Respect to Time
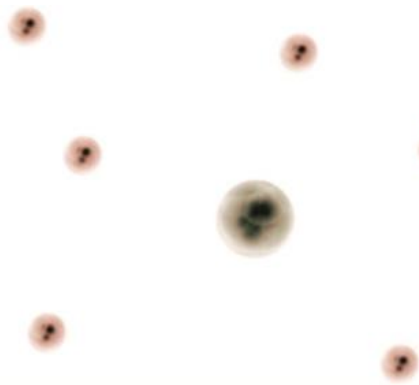
Figure 15SAP Particles at Time = 0 min
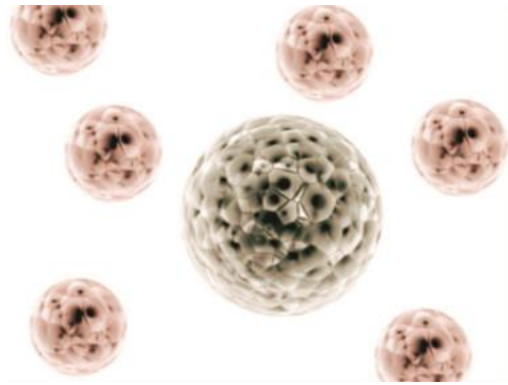
Figure 16SAP Particles at Time = 5 min

3.3.2 Mix Formulations

Mix formulations were decided on the basis of flow test (Hagerman's Cone) and Power's Theorem (1). 20 different formulations were selected for the study. Basic four water-cement ratios (0.27, 0.30, 0.35 and 0.40) were decided with each having 5 variants as listed below.

- Convention Plain Cement Paste

- Self-Compacting Paste

- SAPs containing Self-Compacting Paste

- SAPs and FA containing Self-Compacting Paste

- SAPs, FA and MP containing Self-Compacting Paste

The individual formulation name also has five segments each representing a different characteristic of formulation following the below stated description.

CEM type - % replacement by SRMs – W/C ratio – SP demand – SAP %

But for simplicity we'll refer to the formulations by their serial number given in the extreme left column of the table while discussing the results.

3.3.3 Absorption Capacity

Sieve Method was used to measure the absorption capacity of SAPs using three different liquids (de-ionized water, tap water and cement slurry) to study the results of ionic composition variation and pH on the absorption capacity of SAPs. The cement slurry was obtained by adding 400 g of water to 40 g of cement and subsequent filtration(46). 1g of SAP was added to 200 g of liquid and stirred magnetically for 30 minutes. The resulting mixture was filtered through sieve 100 (150 microns). The excess of liquid was removed by rubbing a soft sponge at the bottom of the sieve until, when held vertically, no flow of the gel was observed(35).

Absorption Capacity was calculated by

$$St = \frac{(At + B) - (B + W1)}{W1}$$

Where St = swelling at time t (g/g)

At = Weight of swollen SAP at time t (g)

B = Weight of sieve (g)

W1 = Weight of dry SAP (g)

3.3.4 Water Demand

Water demand of the samples with and without SRMs was determined using the standard of DIN-EN 196-3. The contents were mixed following the above stated mixing regime and the resulting fresh paste was placed in a vicat mould. The w/c ratios at which the penetration was 3-7

mm from the bottom were recorded against the formulations. This signifies the minimum amount of water required to ensure consistency in the mixes.

3.3.5 Super-plasticizer Demand

The Super Plasticizer demand was determined using Hagerman's Cone measuring 6x7x10 cm3. SP dosage was adjusted by trial and error until the target flow of (30 ± 1) cm was achieved. To further asses the flow characteristics of the cement pastes T_{30} cm was recorded using a stopwatch with accuracy of 0.01s. Where T_{30} cm represents the time taken for the fresh paste to flow till the 30cm mark.

Figure 17 Hagermann's Cone Apparatus
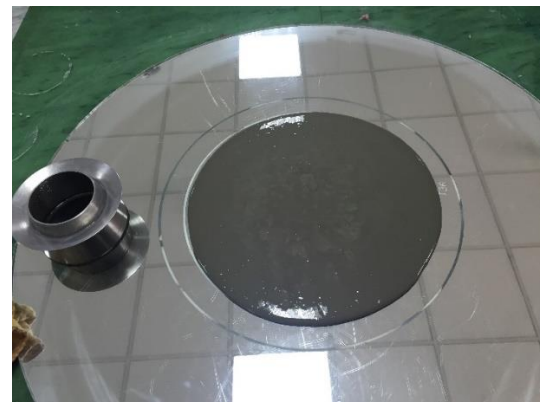
Figure 18Paste with 30 cm Flow

3.3.6 Setting Times

The setting times of the cement mixes are used to assess the workable duration of cement mix, although these can be delayed, if required, using retarders or agitation of the fresh pastes. Initial setting represents the time when the cement paste begins to stiffen considerably i.e. loses its elasticity whereas final setting demarcates the time when the cement has hardened to the point at which it can sustain some load i.e. it loses its plasticity and the skeleton is formed. Setting time of cement is measured by ASTM C191-01 using Vicat needle Apparatus.

Figure 19 Vicat Initial Set Needle *Figure 20 Vicat Final Set Needle* *Figure 21 Vicat Apparatus Being Used for Final Setting Time*

3.3.7   Shrinkage

The fresh mixes were placed in a modified version of German Classical "Schwindrinne" channel apparatus measuring 4x6x25 cm interfaced with computer software at 20-25 ^{o}C. The edges of the moveable plate were carefully greased so that the bleeding is avoided, yet the movement is not hindered. The measuring probe was pressed to around 50% of its maximum compression so that it can record both, expansion and contraction of the cement paste. The recording of the shrinkage response was started after 10 minutes of mixing for all the formulations and was carried out for the first 72 hours. The resulting shrinkage response of the formulations was plotted against time.

Figure 22 Shrinkage Apparatus (Empty)   *Figure 23 Shrinkage Apparatus (filled)*

3.3.8   Casting and Curing

To evaluate the flexure and compressive strength of the formulations 160x40x40 mm prisms were casted and tested upon. The sides of the moulds were greased to avoid bleeding and the inside were oiled so that the hardening cement paste may not stick to its walls. The fresh cement pastes were poured in to the moulds and were allowed to set for 24 hours after which they were de-moulded and placed in a sealed curing tank which contained water at the controlled room temperature.

Figure 24 160x40x40 mm moulds (Empty)

Figure 25 Fresh SCP filled in the moulds

3.3.9 Strength Evaluation

The day 1 tests were performed on the prisms as soon as they were demoulded i.e. without curing while other samples, after being removed from the curing tank, were dried in air for 30 min before any prior testing.The dried prisms were tested in flexure and compression using dual chamber apparatus. Strength tests were done for day 1, 3 and 28. Initially three prisms were tested in flexure at 0.02KN/s load application rate, this resulted in 6 samples for compressive tests. Out of these 3 were selected for compression test and load application rate was increased to 0.2KN/s as per the standards. The reported flexural and compressive strength are the mean of these three tests, this was done to increase the reliability of the results.

Figure 26 Flexure Testing   *Figure 27 Compression Testing*

3.3.10 Calorimetry

F-CAL 8000 was used for calorimetric measurement in order to observe the heat kinetics of the mixes. The apparatus was switched on and was allowed to log temperature data for at least one hour prior to the addition of sample so that it can get acclimatized. Time zero of each respective column was established at the time when mixing water was added to the dry mixed ingredients of the formulation. The fresh paste was then added to the container having poly-ethene bag and temperature of the paste was recorded for 72 hours.

Figure 28 F-Cal 8000

4 TEST RESULTS & DISCUSSIONS

4.1 Water Demand

Water demand increases with the addition of both FA and MP due to their higher absorption of water compared to the cement particles.

Table 2 Water Demand of Mixes

Formulation	Water Demand (%)
C1-0	27.0
C1-FA10	29.5
CA-FA5MP5	30.0

4.2 Super Plasticizer Demand of SCPs Formulations

The mix formulations and the amount of SP required to achieve the target flow were measured and recorded in the table given in Annex B.
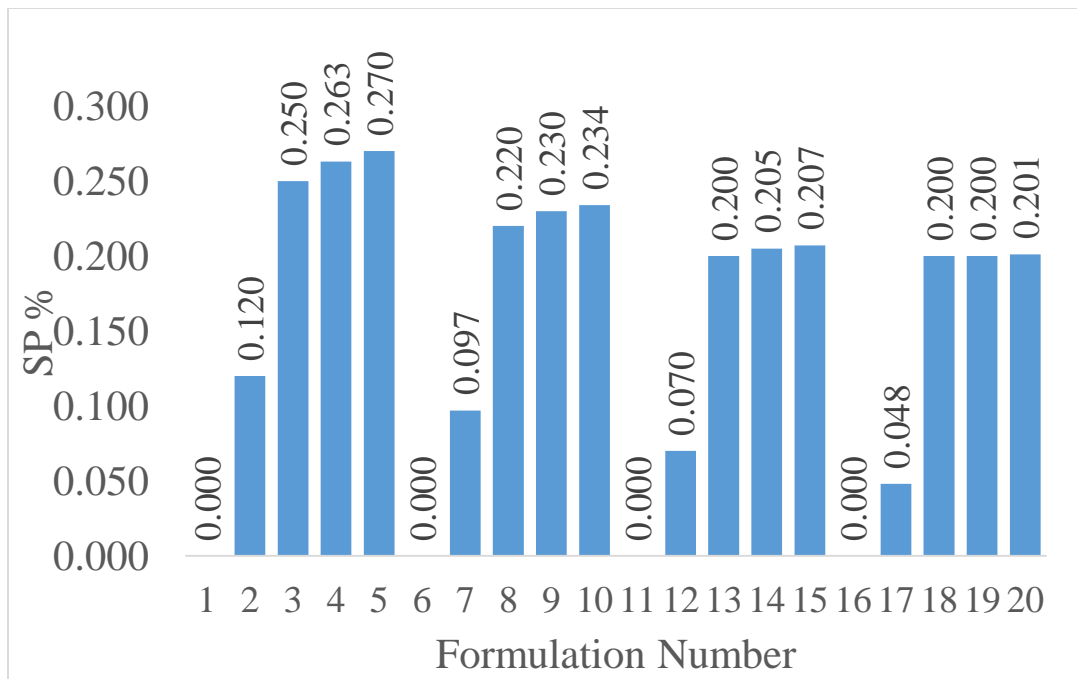
Figure 29 SP Demand of Formulations

It was observed that more SP was required in formulation with lower w/c ratios because of lesser water availability for lubrication of cement particles. This idea can also be extended to explain the increase in SP demand caused by introduction of SAPs in the cement pastes as the SAP particles take up water resulting in lesser basic water/cement ratio or free water available to lubricate the cement grains. The addition of FA and MP slightly increases the SP demand at lower w/c ratios due to water absorption but at higher w/c it has no effect due to abundant availability of water, even after the absorption by SAPs, FA and MP, within the cement mix.
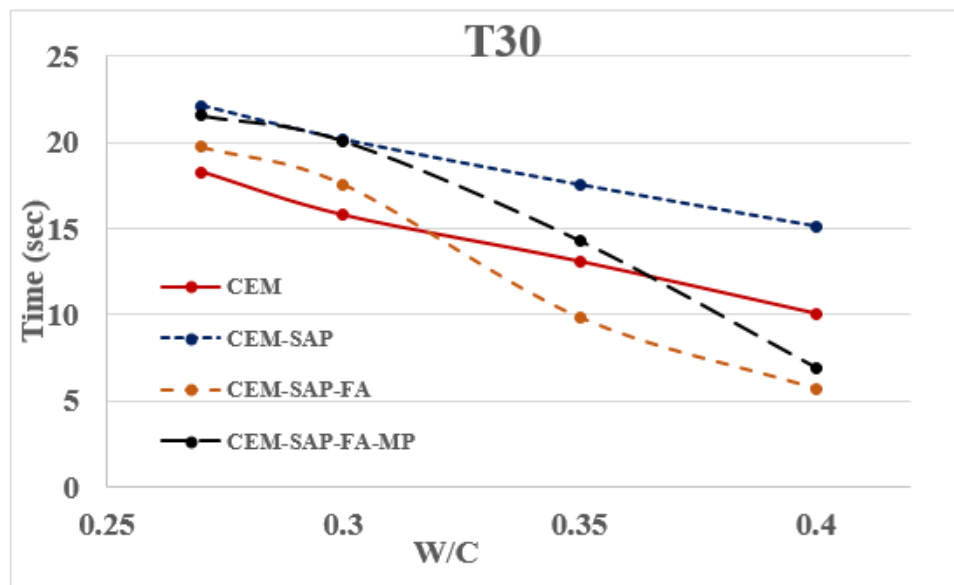
Figure 30 Variation of T30 cm of Formulations

It was observed that at a given w/c ratio the addition of SAP significantly increases T_{30}cm although the trend of decrease in T_{30}cm with and without SAPs is same against increasing w/c ratio. The higher T_{30}cm values can be due to the gel type nature of SAPs when fully saturated, thus increasing the viscosity of fresh cement pastes and resisting flow. SAPs are therefore recommended to modify the rheology of fresh pastes(13). The addition of SRMs also increase the T_{30}cm time specially MP because of its high calcium content which stiffens the cement paste even in its initial hours of mixing but at higher w/c ratios this effect is nullified owing to the abundance of available water.

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4.3 Absorption Capacity and Required Percentage of SAPs

The absorption capacity determined by the sieve test described in Chapter 3 can be approximated to 22 g of water / g of dry SAPs in cementitious environment. The following figure shows the absorption capacity of SAPs in three different liquids (de-ionized water, tap water and cement slurry).

It is observed by O.M. Jensen that the further addition of admixtures like FA does not affect the absorption capacity of SAPs. So the same value i.e. 22 g/g was assumed in mixes with mineral admixtures(46).
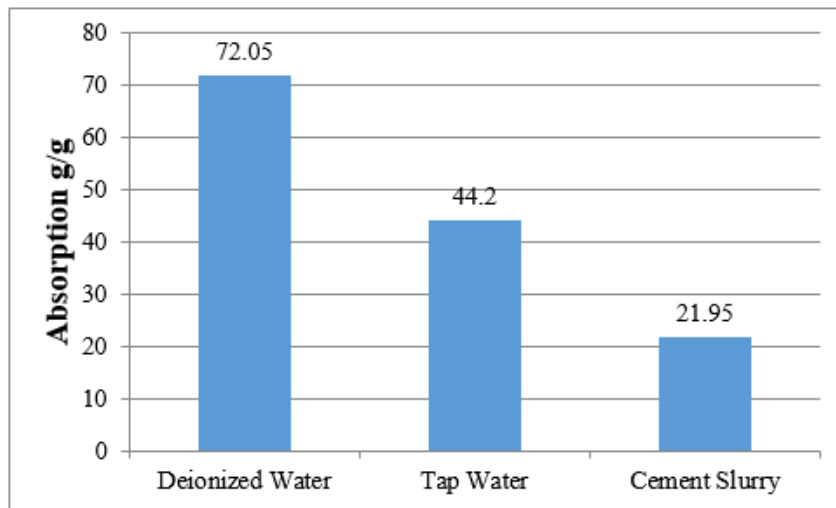
Figure 31 Absorption Capacity of SAPs in Various Liquids

It can be seen that at roughly constant temperature, by increasing the pH and varying the ionic composition of the liquid, the absorption capacity of SAPs is significantly reduced falling from 72 g/g in deionized water to only 22 g/g in the cement slurry. The major specie responsible for this reduces absorption capacity is Ca^{+2} ion(7) which develops a cross link in SAP particles resulting in release of water from SAP.

SAP demand was calculated using the following equations.

$$(W/C)e = K(SAP/C)$$

Where

(W/C)e is the effective water-cement ratio

K is the absorption capacity of SAPs in g/g

SAPs/C is the ratio of required SAPs to cement

$$\left(\frac{W}{C}\right)e = 0.18 \left(\frac{W}{C}\right) \qquad \text{W/C} < 0.36$$

At basic w/c ratios greater than 0.40 the desired degree of hydration can be attained with lesser effective water-cement ratio as described by Power (45).

$$\left(\frac{w}{c}\right)e = 0.42 - \left(\frac{w}{c}\right) \quad 0.36 < \text{W/C} < 0.42$$

The required percentages of SAPs with respect to various water cement ratios are listed below.

Table 3 W/C Ratios and SAPs Demand of Formulations

(W/C)total	(W/C)b	(W/C)e	SAP/C
0.27	0.229	0.041	0.186
0.30	0.254	0.046	0.200
0.35	0.300	0.050	0.230
0.40	0.340	0.060	0.270

4.4 Setting Time

Initial and Final Setting times were determined using Vicat Apparatus. The results are presented in tabular form in Annex C.
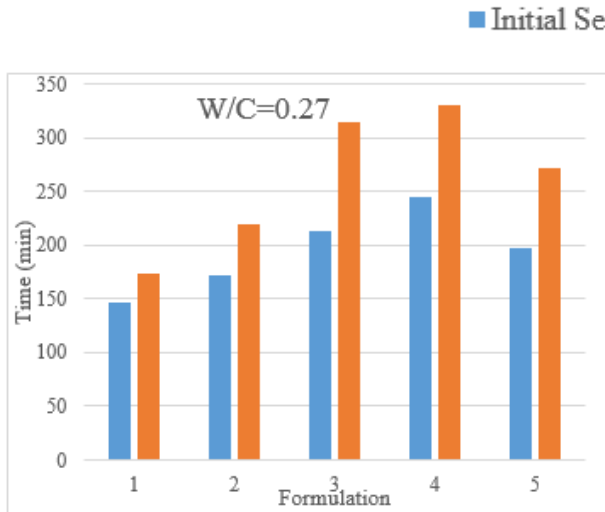
Figure 32 Setting Time of SCPs @ 0.27 w/c
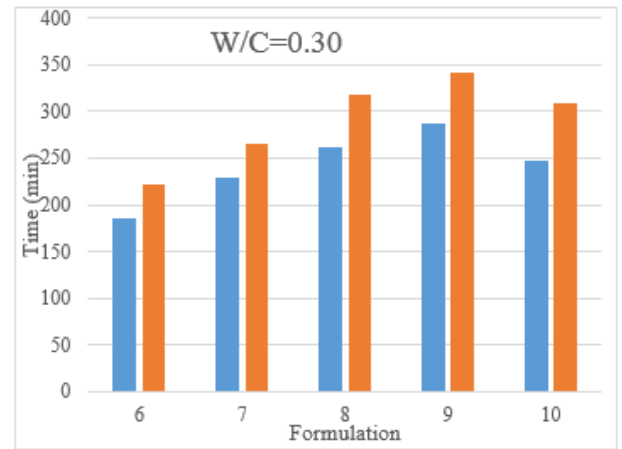
Figure 33Setting Time of SCPs @ 0.30 w/c
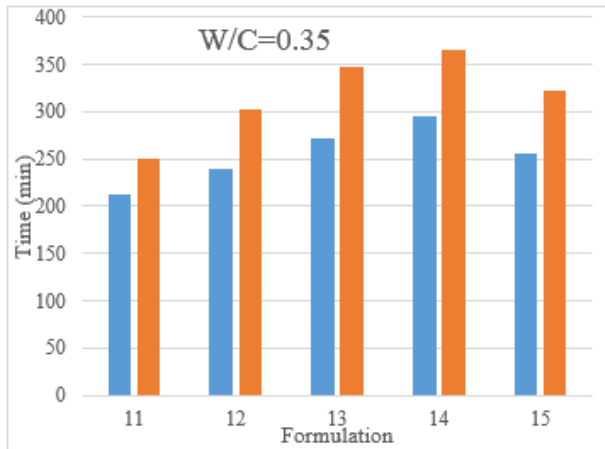
Figure 34 Setting Time of SCPs @ 0.35 w/c
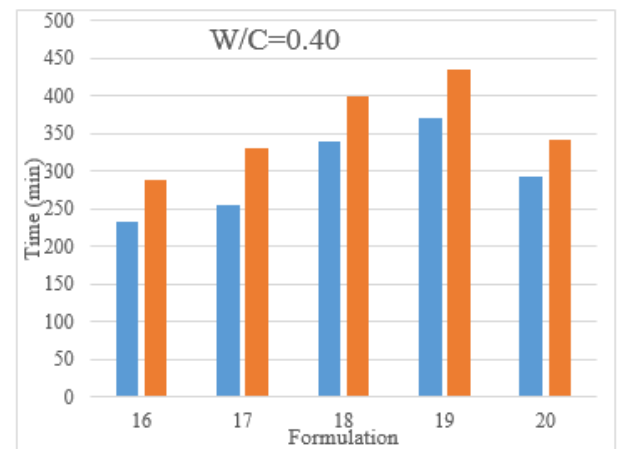
Figure 35 Setting Time of SCPs @ 0.40 w/c

The addition of SP in the cement mix delays the setting process as these are well known retarders. Both initial and final setting times are also delayed by the introduction of SAPs in the formulations because they, while absorbing water, also absorb Ca^{+2} ions from the pore fluid(7) resulting in slow building up of their concentration, thus delaying the hydration process. The same effect is observed with FA introduction in the cement formulation and can be explained using the same chemistry because FA is a well-known Ca^{+2} ion sink, depressing its concentration in initial hours of cement hydration thus delaying the process (44). However, with the addition of marble powder the setting has accelerated in all the mixes. This is because of the rough particles of MP and their cohesive nature which stiffens the fresh cement pastes in its initial hours.
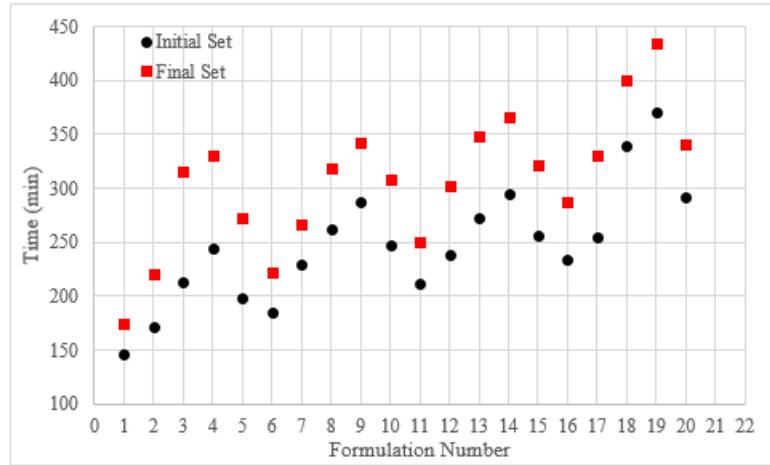
Figure 36 Setting Times of all SCPs Formulations

4.5 Early Age Shrinkage

The shrinkage responses of SCPs formulations were plotted against time and the values of final set was added as a point on all graphs to compare the response before and after setting.
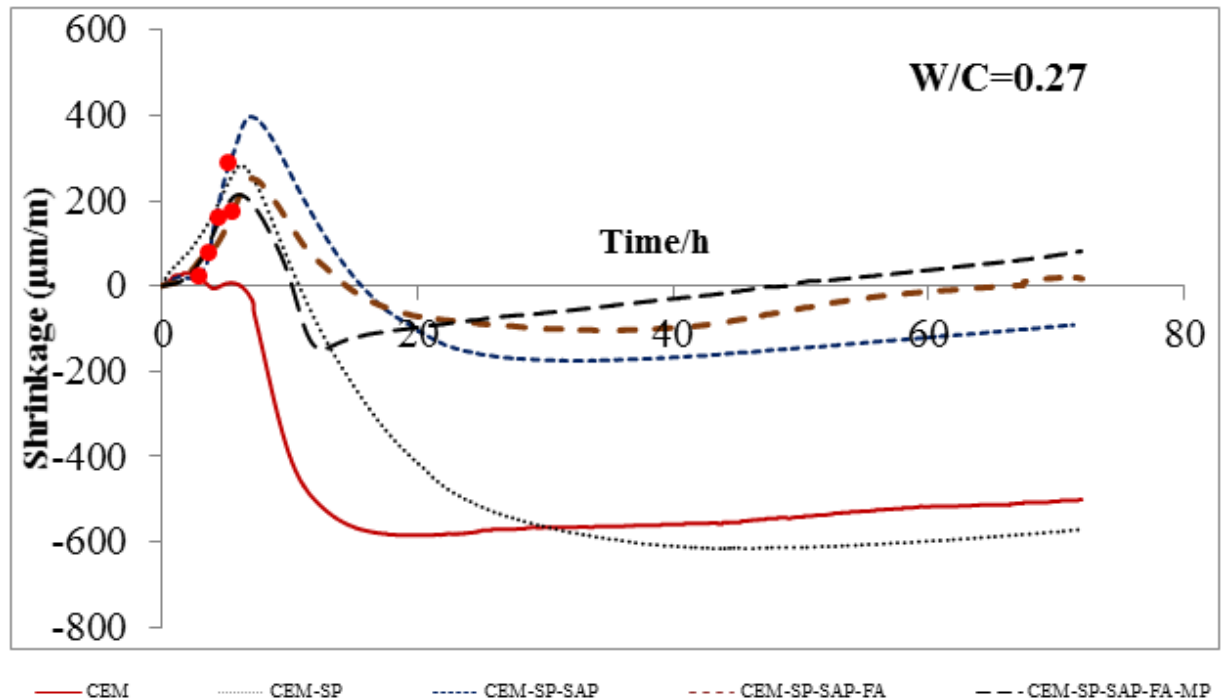
Figure 37 Shrinkage Response of SCPs Formulations @ 0.27 W/C
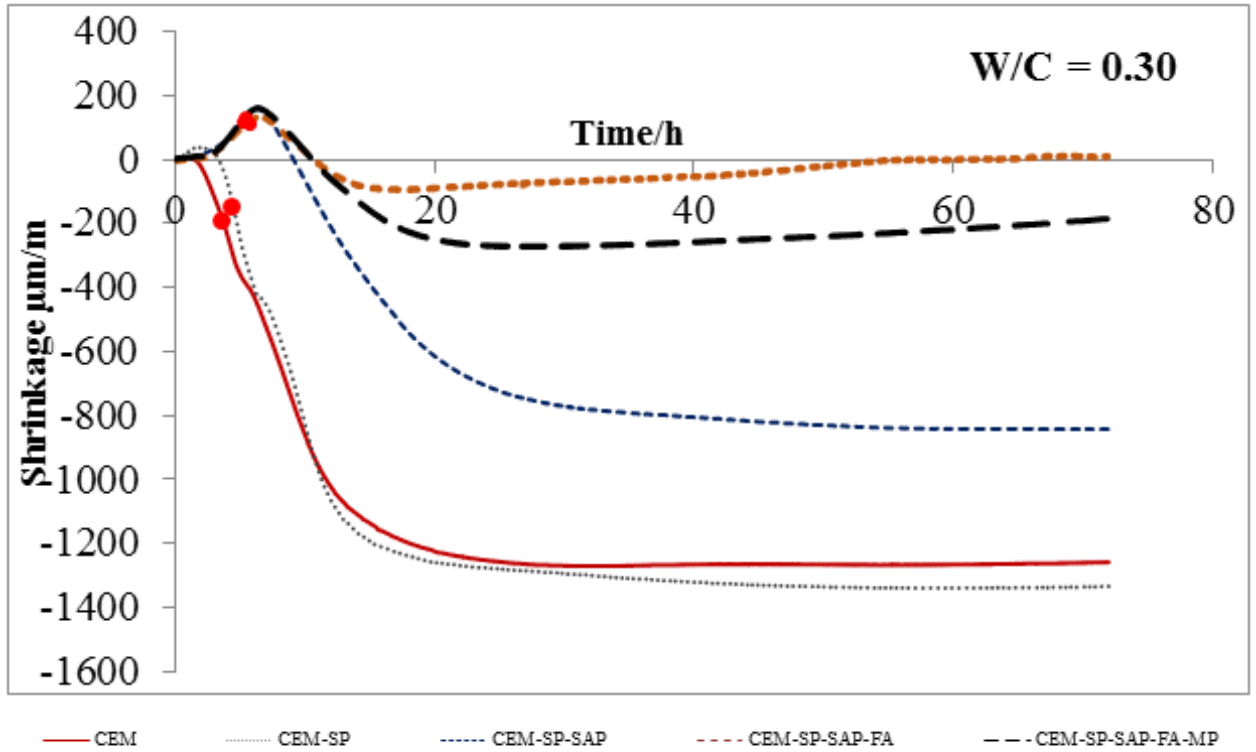
Figure 38 Shrinkage Response of SCPs Formulations @ 0.30 W/C
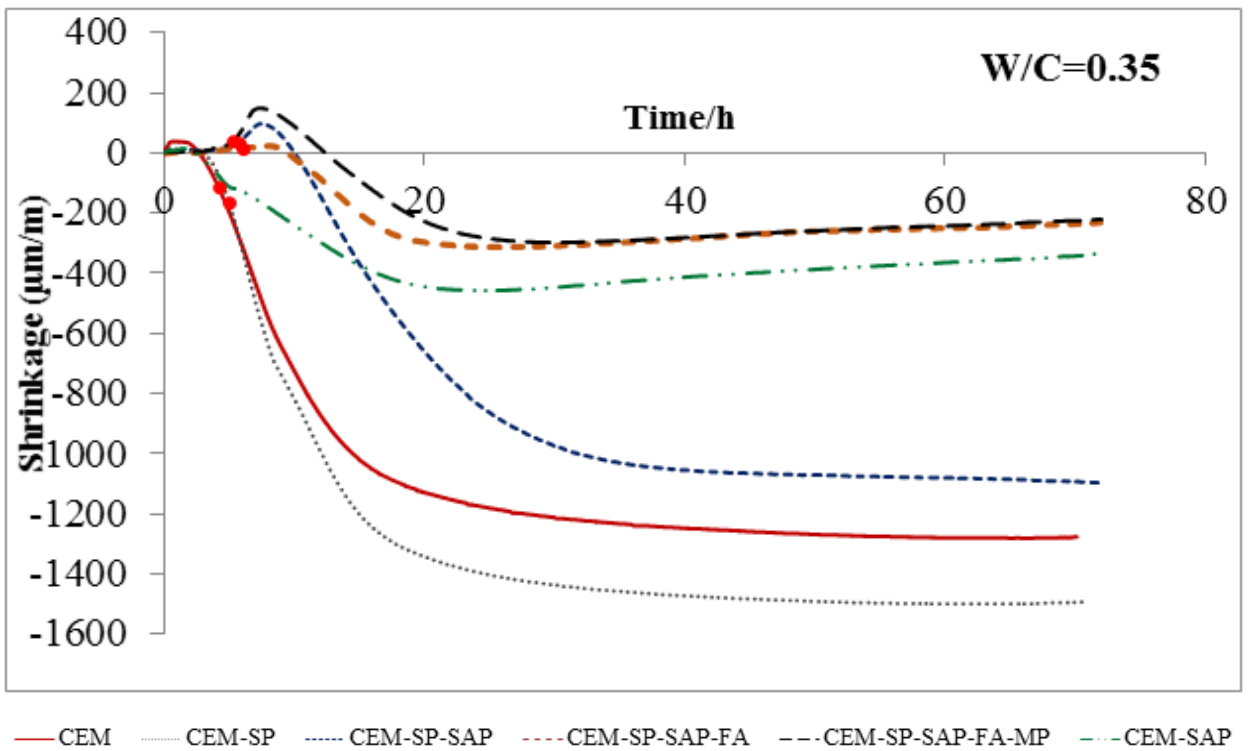
Figure 39 Shrinkage Response of SCPs Formulations @ 0.35 W/C

36
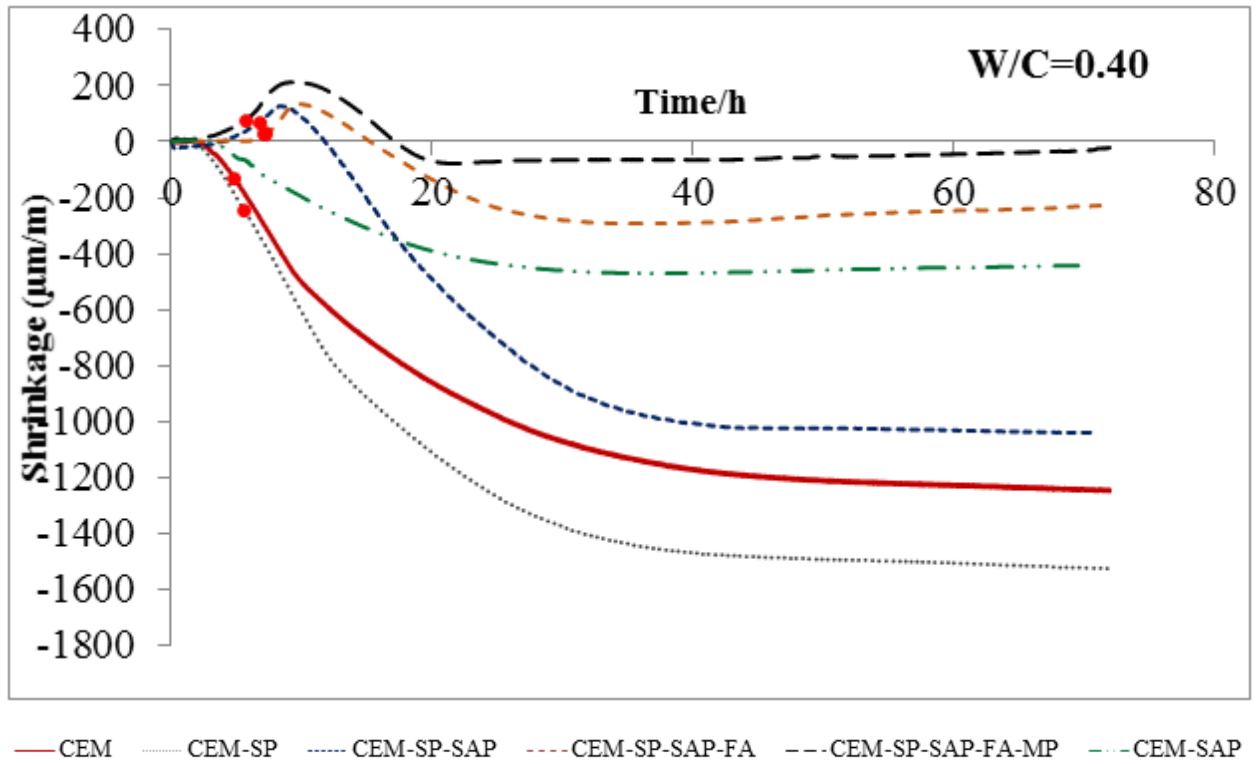
Figure 40 Shrinkage Response of SCPs Formulations @ 0.40 W/C

Cement pastes experience self-desiccation shrinkage in formulations with lower w/c ratios because the spaces between the cement particles are filled by hydration products causing the remaining water to form menisci and exert hydrostatic suction forces. These forces cause the cement mass to shrink and early age cracking is observed. By addition of SP to the cement, the overall shrinkage increases because of higher heat of hydration causing greater loss of water to surroundings.

Internal curing by means of SAPs has been found to be successful in all the formulations. Although, the effects are more prominent at lower water-cement ratios (84% reduction of shrinkage at 0.27 w/c compared to only 31% reduction of shrinkage at 0.40 w/c). This is because we are using internal curing technique to arrest shrinkage, which is most effective against the autogenous/self-desiccation shrinkage than any other form of shrinkage and autogenous shrinkage is the governing force only in the formulations having lower w/c ratios. In such mixes when the RH drops, the cement grains take water from swollen SAP particles following the desorption isotherm(47), instead of using up the water in capillaries. Hence, mitigating the

generation of hydrostatic forces which caused the self-desiccation shrinkage. Different phases of SAPs in the cement mixes are shown in the following figures.
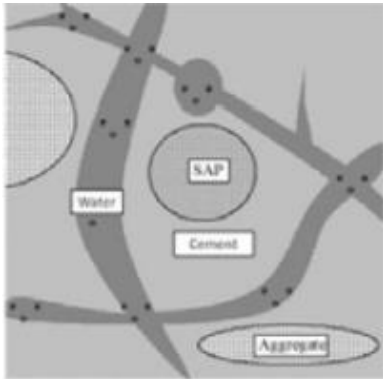
Figure 41 SAPs in Fresh Mix
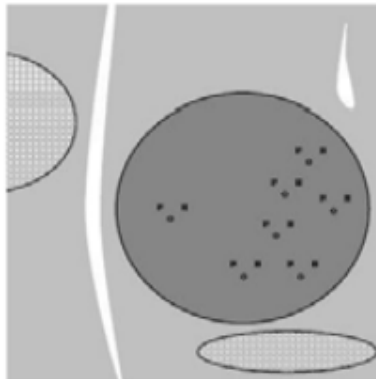
Figure 42 SAPs Until Setting

Figure 43 SAPs After a Long Time

By the addition of FA the shrinkage is further reduced in all the formulations and is almost 100% mitigated in the formulation number 9 (C1-FA10-30-0.23-0.20). This is because by delaying the hydration process FA encourages the growth of expansive species like calcium hydroxide(44) which act against the reduction in volume and aid SAPs in the shrinkage mitigation process. It can be said that in such cases shrinkage is mitigated chemically i.e. by CaOH and by internal curing agent (SAPs).

The addition of MP show very little deviation from the CEM-SP-SAP-FA graph in all formulations except at w/c of 0.40. This might be because of the higher ettringite formation in this sample owing to higher water and Ca content.

Early age expansion is observed in all the samples containing SAPs especially in formulations with 0.27 w/c ratio of around 400 µm/m. This can be due to the reabsorption of bleeding water in the cement mix by SAP particles and subsequent swelling or due to the crystallization pressure of calcium hydroxide (48). Although, some authors claim that this expansion is dependent on the size of SAP particles used. Generally greater the size of the particle, higher is the expansion observed with the exception of 125-160 µm fraction which shows higher expansion than 160-250 µm fraction. Generally the use of SAP particles greater than 200 microns in dry state is avoided because of excessive early expansion (49).

4.6   Strength Tests

CEM-SP ■ CEM-SP-SAP ■ CEM-SP-SAP-FA ■ CEM-SP-SAP-FAMP
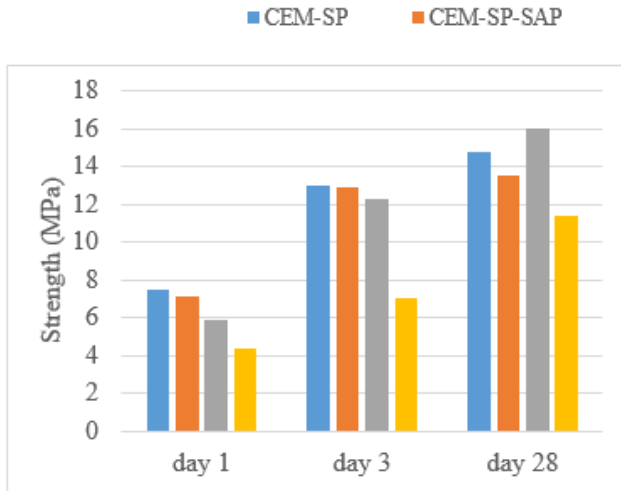
Figure 44 Flexure Strength of SCP Formulations at 0.27 W/C
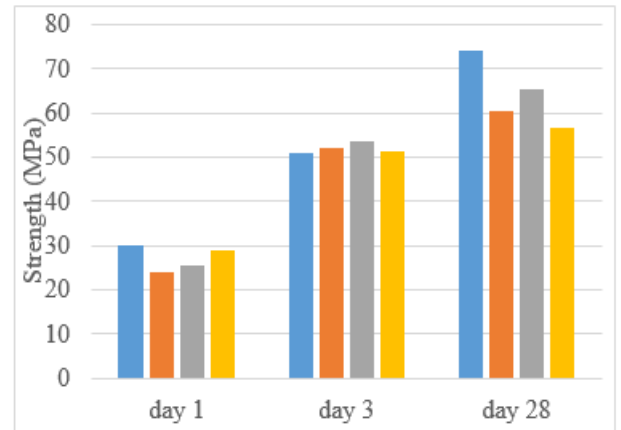
Figure 45 Compressive Strength of Formulations at 0.27 W/C
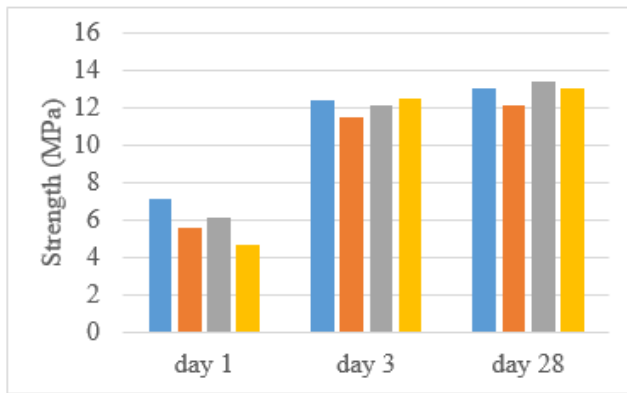
Figure 46 Flexure Strength of SCP Formulations at 0.30 W/C
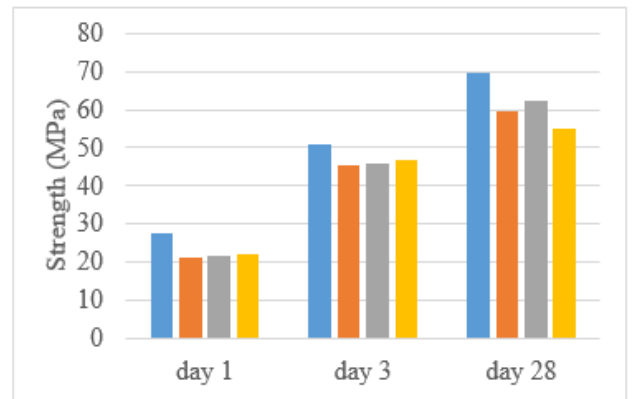
Figure 47 Compressive Strength of Formulations at 0.30 W/C
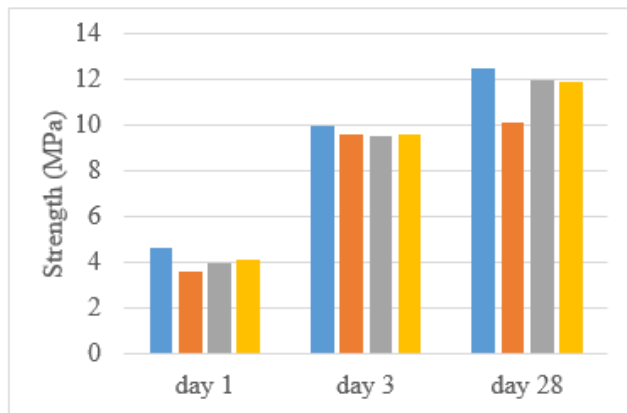
Figure 48 Flexure Strength of SCP Formulations at 0.35 W/C
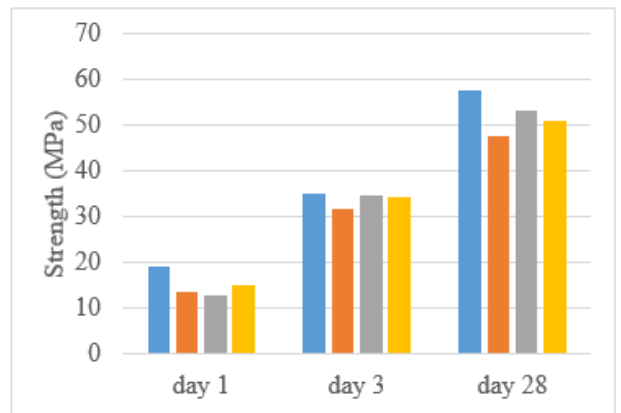
Figure 49 Compressive Strength of Formulations at 0.35 W/C

All the samples show reduction in both flexure and compressive strength of SCPs formulations with the addition of SAPs. On average the reduction in flexure strength is around 12% while in compressive strength is around 15%.This is because SAPs shift the porosity of the hardening paste from micro/meso-pores to macro inclusions thus increasing the size of the largest defect in the matrix which directly effects the strength of the pastes (50). It is suggested that the use of SAP of dry particle size less than 100 microns must avoid this loss of strength (51). Although, this might make the dispersion of SAPs difficult (52).

With the addition of FA some of the lost strength is regained in all the samples at later ages (day 28) and on average the reduction in compressive strengths of these samples is around 10% of the reference mix.This is owing to the conversion of weak CH crystals in to C-S-H and densification of cement matrix by FA. The samples containing FA-MP showed greater early age strength (day 1 and 3) compared to mixes containing FA only, due to the accelerated stiffening by MP coupled with delayed hardening by FA. Although at day 28 samples with only FA showed greater strength.

The results of strength are presented in tabular form in Annex C.

4.7   Calorimetery
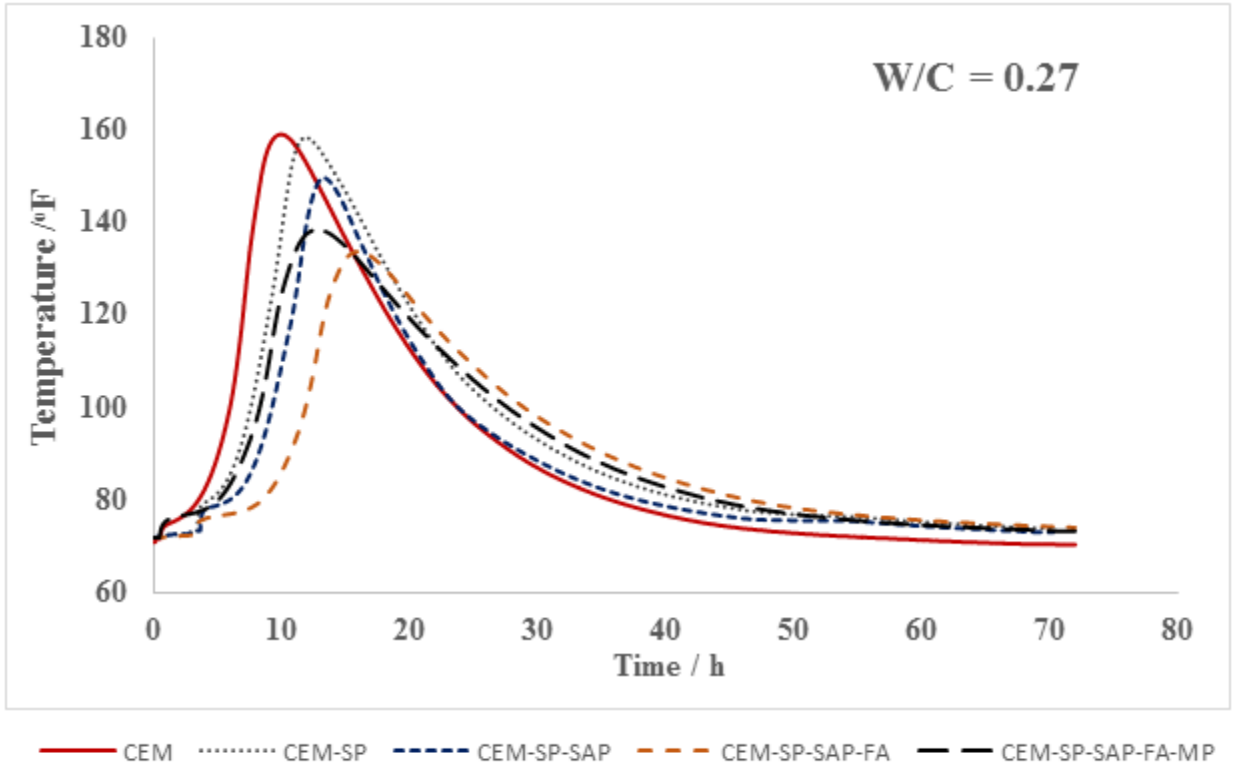
Figure 50 Calorimetric Response of SCPs Formulations @ 0.27 W/C
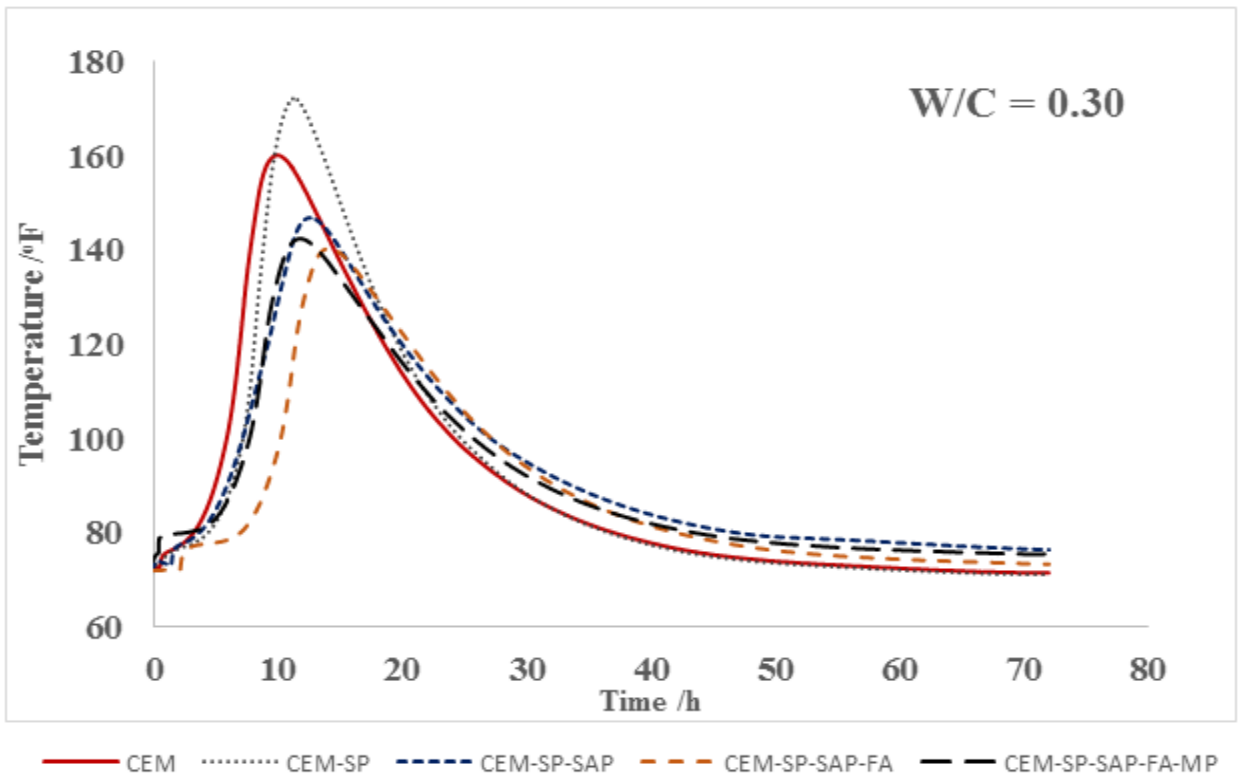
Figure 51 Calorimetric Response of SCPs Formulations @ 0.30 W/C
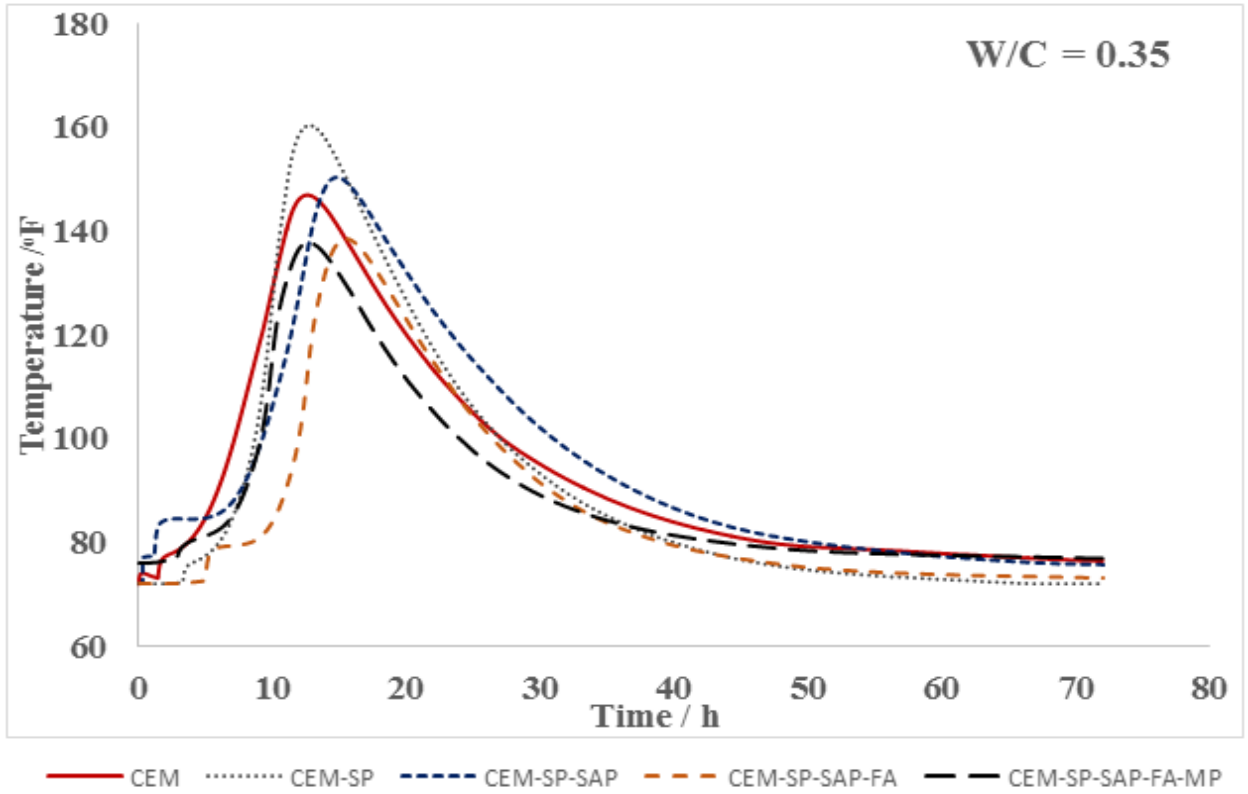
Figure 52 Calorimetric Response of SCPs Formulations @ 0.35 W/C
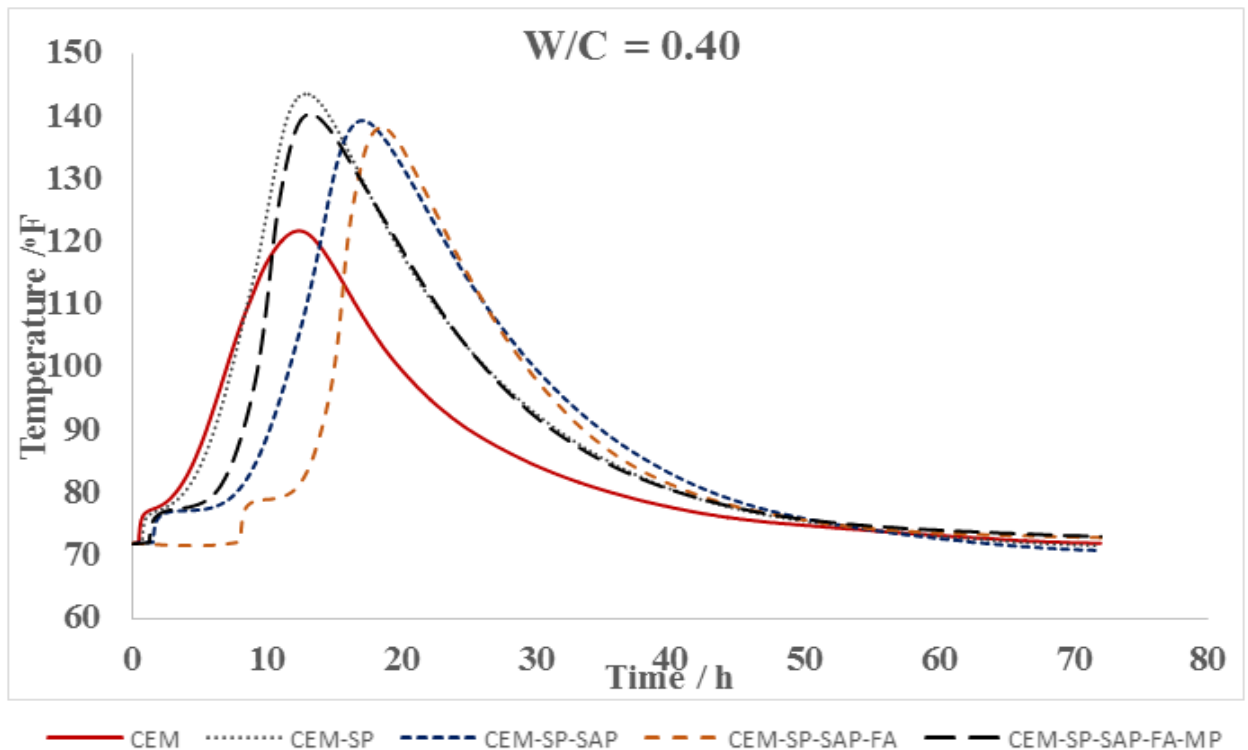
Figure 53 Calorimetric Response of SCPs Formulations @ 0.40 W/C

F CAL – 8000 was used for calorimetric measurement to understand the hydration kinetics of the SCPs formulations. It is observed that addition of SP the calorimetric peak because they are well known retarders. It also increases the peak value by uniform dispersion of cement grains making greater surface area available for reaction. The addition of SAPs further delays the peak hence reducing the peak value. This is because SAPs while absorbing water from the mix, also take up Ca^{+2} ions which form cross-links with the structure of SAP particle and are bound there. This causes the delay in building up of calcium ions - delaying the setting time and peak value. FA addition also delays the peak using almost the same chemistry as FA particles are well-known Ca^{+2} ion sink(44). The peak value is also reduced by dilution effect. MP acts as accelerator due to the cohesive nature and rough texture of its particles stiffening the cement pastes and causing the peak value to be slightly higher than FA alone. Almost the same trend was observed in formulations at all w/c ratios. This must also be noted that as the w/c ratio increases, the peak value of SCP formulations decreases due to the obvious dilution effect.

5   CONCLUSIONS

- Internal curing by means of SAPs has been found to be successful in all the formulations. Although, the effectiveness of shrinkage reduction by internal curing is more at lower w/c ratiosbecause autogenous shrinkage is dominent only in such mixes (84% reduction of shrinkage at w/c ratio of 0.27 compared with only 32% shrinkage at w/c ratio of 0.40).

- Mitigation of early age total shrinkage is much more effective in the mixes containing both fly ash and superabsorbent polymers because FA encourages the growth of expansive species like calcium hydroxide which aids SAPs in attaining volume stability (Shrinkage greater than approximately 200 microns/m was not observed for the first 72 hours in such mixes).

- Early expansion is observed in all the formulations containing SAPs. Although, further studies are required to fully understand its mechanism.

- The addition of SAPs to the SCPs results in reduction of both, flexure and compressive strengths by 12% and 15% respectively. This is because SAPs increase the size of the largest defect in the matrix which directly controls the strength of formulations.Although, only 10% cement replacement by FA helped us regain 33% of the lost strength by conversion of weak CH in to CSH and densification of the matrix by pozzolanic reactions.

- SAPs act as retarders in the self-compacting paste systems by taking up Ca^{+2} ions while absorbing water from the mix. These Ca^{+2} ions form cross links with SAP particles thus slowing down their building up process in the mix and delaying hydration.

RECOMMENDATIONS

- The use of SAPs to mitigate early age shrinkage must be extended to the SCMs and SCCs.

- Determination of an optimum percentage replacement by suitable SRM which help us nullify the negative effect of reduction in strength caused by addition of SAPs, without increasing the overall shrinkage.

- Smaller SAPs (dry particle size of < 50 microns) must also be tested as these would ensure better internal curing by reducing the distance to be cured by a single SAP particle. These might also help us solve the strength reduction problem due to their smaller size.

- The effectiveness of using fibrous SAPs to make fire resistant concrete must also be tested. As these would leave elongated pores which might help reduce the damage caused in case of fire attack.

- Concrete healing bacterias can also be embedded in the mixes using SAPs. Their potential in this area must also be determined through experimentation.

ANNEXURES

ANNEX A

Table 4 Characteristic IR Absorption

Table of Characteristic IR Absorptions

frequency, cm^{-1}	bond	functional group
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH$_2$X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

Table 5 Absorption Capacity of SAPs

Liquid	Temperature /C°	pH	Trial 1 (g/g)	Trial 2 (g/g)	Absorption Capacity g/g
DE-IONIZED WATER	22.1	6.10	72.1	72.0	72.05
TAP WATER	22.3	7.08	43.9	44.5	44.20
CEMENT SLURRY	23.3	11.58	22.1	21.8	21.95

Table 6 XRF of Powders

Sample Name	MP E-879	CEM E-880	E-878 (FA)
SiO_2	8.32	19.19	59.06
TiO_2	0.00	0.29	1.58
Al_2O_3	0.05	4.97	27.58
Fe_2O_3	0.02	3.27	5.14
MnO	0.00	0.04	0.05
MgO	0.28	2.23	1.27
CaO	55.64	65.00	1.66
Na_2O	0.30	0.58	0.54
K_2O	0.01	0.51	1.59
P_2O_5	0.11	0.08	0.15
LOI	43.27	3.84	1.38

ANNEX B

Table 7 SP Demand of Formulations

Formulations	SP (%)	Spread (cm)	T30 (s)
Plain Cement @ 27% WD	0.120	30.7	18.25
Cement + 0.186% SAP @ 27% WD	0.250	30.4	22.10
Cement + FA + 0.186% SAP @ 27% WD	0.263	30.7	19.73
Cement + FA + MP + 0.186 % SAP @ 27 WD	0.27	29.5	21.56
Plain Cement @ 30% W/C	0.097	30.1	15.76
Cement + 0.20 % SAP @ 30% W/C	0.220	30.0	20.13
Cement + FA + 0.20% SAP @ 30% W/C	0.230	30.3	17.56
Cement + FA + MP + 0.20% SAP @ 30% W/C	0.234	29.8	20.08
Plain Cement @ 35% W/C	0.070	29.7	13.08
Cement + 0.23% SAP @ 35 % W/C	0.200	30.2	17.52
Cement + FA + 0.23% SAP @ 35% W/C	0.205	30.10	9.82
Cement + FA + MP + 0.23 % SAP @ 35 W/C	0.207	30.30	14.29
Plain Cement @ 40% W/C	0.048	30.1	10.07
Cement + 0.27% SAP @ 40 % W/C	0.200	29.2	15.12
Cement + FA + 0.27% SAP @ 40% W/C	0.200	30.50	5.68
Cement + FA + MP + 0.27 % SAP @ 40 W/C	0.201	30.80	6.90

Table 8 Details of The Studied Formulations

Serial	Formulation	W/C	SP (%)	SAP (%)	FA (%)	MP (%)
1	**C1-0-27-0-0**		0.0	0.0	0	0
2	**C1-0-27-0.12-0**	0.27 (WD)	0.120	0.0	0	0
3	**C1-0-27-0.25-0.186**		0.250	0.186	0	0
4	**C1-FA10-27-0.263-0.186**		0.263	0.186	10	0
5	**C1-FA5MP5-27-0.27-0.186**		0.27	0.186	5	5
6	**C1-0-30-0-0**	0.30	0.0	0.0	0	0

7	C1-0-30-0.097-0		0.097	0.0	0	0
8	C1-30-0.22-0.20		0.220	0.200	0	0
9	C1-FA10-30-0.23-0.20		0.230	0.200	10	0
10	C1-FA5MP5-30-0.234-0.20		0.234	0.200	5	5
11	C1-0-35-0-0		0.0	0.0	0	0
12	C1-0-35-0.07-0		0.070	0.0	0	0
13	C1-0-35-0.20-0.23	0.35	0.200	0.230	0	0
14	C1-FA10-35-0.205-0.23		0.205	0.230	10	0
15	C1-FA5MP5-35-0.207-0.23		0.207	0.230	5	5
16	C1-0-40-0-0		0.0	0.0	0	0
17	C1-0-40-0.048-0		0.048	0.0	0	0
18	C1-0-40-0.20-0.27	0.40	0.200	0.270	0	0
19	C1-FA10-40-0.20-0.27		0.200	0.270	10	0
20	C1-FA5MP5-40-0.201-0.27		0.201	0.270	5	5

ANNEX C

Table 9 Vicat Setting Times of Formulations

Serial	Formulation	W/C	Initial Set (min)	Final Set (min)
1	C1-0-27-0-0	0.27 (WD)	147	174
2	C1-0-27-0.12-0		172	220
3	C1-0-27-0.25-0.186		213	315
4	C1-FA10-27-0.263-0.186		245	331
5	C1-FA5MP5-27-0.27-0.186		198	272
6	C1-0-30-0-0	0.30	185	222
7	C1-0-30-0.097-0		229	266
8	C1-30-0.22-0.20		262	318
9	C1-FA10-30-0.23-0.20		287	342
10	C1-FA5MP5-30-0.234-0.20		247	308
11	C1-0-35-0-0	0.35	212	251
12	C1-0-35-0.07-0		239	302
13	C1-0-35-0.20-0.23		272	348
14	C1-FA10-35-0.205-0.23		295	366
15	C1-FA5MP5-35-0.207-0.23		256	322
16	C1-0-40-0-0	0.40	234	288
17	C1-0-40-0.048-0		255	330
18	C1-0-40-0.20-0.27		339	400
19	C1-FA10-40-0.20-0.27		371	435
20	C1-FA5MP5-40-0.201-0.27		292	341

Table 10 Flexure and Compressive Strengths of Formulations

Serial	Formulation	W/C	Flexural Strength (MPa)			Compressive Strength (MPa)		
			1	3	28	1	3	28
2	C1-0-27-0.12-0	0.27	7.5	13	14.75	30.25	51.13	74

50

3	C1-0-27-0.25-0.186		7.125	12.8	13.5	23.89	52.15	60.57
4	C1-FA10-27-0.263-0.186		5.875	12.2	16	25.55	53.6	65.25
5	C1-FA5MP5-27-0.27-0.186		4.375	10	11.375	28.9	51.2	56.62
7	C1-0-30-0.097-0		7.125	12.37	13	27.75	51.05	69.7
8	C1-30-0.22-0.20	0.30	5.625	11.5	12.125	21.1	45.47	59.71
9	C1-FA10-30-0.23-0.20		6.125	12.12	13.375	21.67	46.05	62.23
10	C1-FA5MP5-30-0.234-0.20		4.625	12.5	13	22.2	46.57	54.92
12	C1-0-35-0.07-0		4.625	10	12.5	19.1	35.1	57.6
13	C1-0-35-0.20-0.23	0.35	3.625	9.625	10.15	13.7	31.59	47.76
14	C1-FA10-35-0.205-0.23		4	9.5	12	12.9	34.75	53.12
15	C1-FA5MP5-35-0.207-0.23		4.125	9.625	11.875	14.98	34.12	50.92

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