

**USE OF SUPER ABSORBENT POLYMERS (SAPs) IN SELF
COMPACTING MORTAR SYSTEMS (SCMs)**



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BACHELORS IN CIVIL ENGINEERING

Year 2016

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Thesis titled

**“Use of Superabsorbent Polymers (SAPs) in Self
Compacting Mortar systems (SCMs)”**

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Has been accepted towards the requirements

For the award of Bachelor’s degree

in

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ABSTRACT

This study is a continuation of earlier study made on SCP system [25]. The project relates to a new concept regarding the prevention of self-desiccation in self-compacting mortar. The concept is based on the use of superabsorbent polymer (SAP) as an admixture in mortars. Through the use of such polymer, water-filled macropore inclusions are introduced inside the mortar, a technique known as water entrainment. Consequently, self-desiccation is mitigated due to the progressive discharge of water by SAP particles at the appropriate time during the hydration process. Nine formulations involving three different basic w/c ratios (0.38, 0.40, and 0.42) were studied at varying amounts of SAP (0%, 0.3% and 0.4%). The project rendered very promising results with some formulations showing restricted shrinkage and some showing even expansion. Overall, the shrinkage observed in mortar system was less as compared to paste system due to the dilution of cement when aggregate is introduced in it.

DEDICATION

We dedicate this thesis to our parents

ACKNOWLEDGEMENTS

We are highly grateful to professor Ole Mejlhede Jensen of Denmark Technical University for providing us with Superabsorbent Polymers (SAPs) and his research papers.

Thanks are due to the Lab staff of NICE structure lab for helping us throughout the experimentation process.

We acknowledge and appreciate our advisor Professor Dr.Syed Ali Rizwan for sparing his time for us. Working with him turned hard work into amusement.

Last but not the least, we are thankful to our friends and family, whose constant support and blessings made this work possible.

LIST OF NOTATIONS

SAPs	Super Absorbent Polymers
SCMs	Self Compacting Mortars
SCC	Self Compacting Concrete
SEM	Scanning Electron Microscopy
XRF	X-ray Fluorescence
EDX	Energy Dispersive X-Ray
SP	Super Plasticizers
w/c	water-cement ratio
HPC	High performance concrete
(w/c)_B	Basic water-cement ratio
(w/c)_T	Total water-cement ratio
RH	Relative Humidity

Table of Contents

1.Introduction	1
1.1 General	1
1.2 Self-Compacting Mortar Systems.....	1
1.3 Super-Absorbent Polymers	2
1.4 Objective of Research	2
2_LITERATURE REVIEW	3
2.1 Shrinkage of concrete system	3
2.1.1 History and Background.....	3
2.1.2 Autogenous Shrinkage	3
2.1.3 Self-desiccation	4
2.1.4 Chemical Shrinkage.....	5
2.1.5 Surface Tension Theory	6
2.1.6 Disjoining pressure Theory	6
2.2 Super Absorbent Polymers (SAPs)	7
2.2.1 Suspension Polymerized SAPs	7
2.2.2 Solution Polymerized SAPs	8
2.2.3 Absorption Mechanism of SAPs [6]	8
2.2.4 Why SAP does not dissolve in water?	10
2.2.5 The Dry State of SAP	11
2.2.6 Absorption Capacity of SAP	11
2.3 Self-compacting cementitious Systems	13
2.4 Experimental Techniques for SAP characterization	14
2.4.1 X-ray Diffraction.....	14
2.4.2 X-Ray Fluorescence.....	14
2.4.3 Scanning Electron Microscopy.....	15
2.5 Calculating the Absorption capacity of SAP	17
2.5.1) Hydrogen Bonding:.....	17
2.5.2) Osmosis:	17
2.6 Flow test	18
2.7 Shrinkage.....	18

2.8 Strength.....	18
3.Experimental Procedures.....	19
3.1 General	19
3.2 Materials	19
3.3 Super Absorbent Polymers.....	19
3.4 Test Procedures.....	20
3.4.1 Mixing Regime	20
3.4.2 Mix Formulations.....	20
3.5 Absorption Capacity of SAPs	21
3.5.1 Method of Graduated Cylinders for calculating the absorption capacity of SAP.....	21
3.5.2 Dry Density of SAP ρ_{sap}	23
3.6 Super-Plasticizer Demand of SCMs	24
3.7 Shrinkage of SCM formulations.....	24
3.8 Casting and Curing of SCM samples	25
3.9 Strength Evaluation of SCM formulations.....	25
4.Test Results & Discussions	26
4.1 Formulations Investigated	26
4.2 Dry Density of SAP ρ_{SAP}	27
4.3 Absorption Capacity of SAP's	28
4.3.1 Comparison of Absorption Capacity of SAP with Previous Research...	29
4.4 Shrinkage Response of SCM formulations	30
4.4.1 Comparison of shrinkage response in SCM and SCP	33
4.5 Compressive and flexural strength of SCM formulations	35
CONCLUSIONS.....	37
RECOMMENDATIONS	38
References	39

List of Figures

Figure (2.1) Schematic Representation of a cross-section of Hydrating Cement Paste. & Left: Low degree of Hydration.....	5
Figure (2.2) Surface of Hindered Absorption and Distribution of Disjoining Pressure.....	6
Figure (2.3) SEM image of Suspension polymerized SAP	7
Figure (2.4) SEM image of Solution Polymerized SAP	8
Figure (2.5) Diagrammatic representation of Part of a Polymer Network	9
Figure (2.6) Interaction of Ions of a solute with molecules of Solvent	9
Figure(2.7) Hydrogen Bonding of Water Molecule.....	10
Figure (2.8) Cross-linked Chain Behavior after coming in contact with water	10
Figure (2.9) Illustration of SAP particle size after absorption of liquid of different Ionic Strengths	12
Figure(2.10) Typical XRD results	14
Figure (2.11) Scanning Electron Micrograph of SAP	17
Figure (3.1) Steps to find Absorption Capacity of SAP through Graduated Cylinder method.....	23
Figure (3.2) SAP gel on a Spoon	24
Figure (3.3) Precipitated Column of SAP Gel	24
Figure (3.4) SAP of known mass immersed in Olive Oil	25
Figure (4.1) Graph of water absorption of SAPs in different liquids	29
Figure (4.2) Absorption Capacity of SAP in different liquids using sieve method by Rizwan et al [25].....	30

Figure (4.3) Line Graph of Shrinkage in Mortar with 0.38 w/c at different amounts of SAP	31
Figure (4.4) Line Graph of Shrinkage in Mortar with 0.4 w/c at different amounts of SAP	31
Figure (4.5) Line graph of Shrinkage in Mortar with 0.42 w/c at different amounts of SAP	32
Figure (4.6) Shrinkage response of SCP at $(W/C)_T=0.4$	34
Figure (4.7) Shrinkage response of SCM at $(W/C)_B=0.4$	34
Figure (4.8) Scatter plot of compression strength of mortar for 1, 3 and 24 days.....	35
Figure (4.9) Scatter plot of Flexural strength of mortar for 1, 3 and 24 days.....	35

List of Tables:

Table (3.1): Mixing Regime of Formulations	21
Table (4.1): "9" Formulations at Different w/c ratios	27
Table (4.2): Density of SAP at different trails	28
Table (4.3): Absorption Capacity of SAP in different liquids	29

Introduction

1.1 General

Concrete is a composite material prepared by the mixing of cement, fine aggregate, coarse aggregate, water and air. Cement, water, sand, and coarse aggregate are proportioned and mixed to produce concrete of desired properties suited for a particular job. Concrete is widely used construction material around the globe and a lot of research is being carried out by adding different kind of materials in it to attain desired type of mix. For enhancing the properties of concrete like strength, workability etc. some chemical and mineral admixtures can be incorporated in it. For achieving desired performance of concrete it's efficient placing is crucial, which requires intense compaction by skilled manpower and equipment. If proper compaction is not achieved then concrete reduces its strength, durability and aesthetics. For attaining maximum degree of compaction Self-compacting systems can be used which are obtained by using super plasticizers as chemical admixtures in mix. Usually in the mixes of low water cement ratio, during the hydration process shrinkage of volume occurs which leads to cracking in early age and strength reduction. Super Absorbent polymers (SAPs) can be used to mitigate early age shrinkage because they can internally cure the matrix.

1.2 Self-Compacting Mortar 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

mortars (SCMs) flow under their own weight. We can produce high performance concrete while keeping it workable at low water cement ratios by using self-consolidating systems obtained using SP. Usage of self-consolidating systems leads to reduction in cost of construction by elimination of intense manpower and mechanical equipment required for compaction. Durability of poured concrete is uniform because self-consolidating concrete flows under its own weight which ensures compaction. Reason for selecting SCMs instead of SCC is to study SCC's in different phases. After studying use of SAP in SCP and SCM systems we can easily extend its scope towards SCC systems.

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 was 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 Objective of Research

This research is mainly focused on the comparative study of early age shrinkage on both kind of samples with and without introduction of Super Absorbent Polymers (SAPs) as an internal curing agent. Different percentages of Super plasticizers (Melflux) were also used for achieving self-compaction. Effect of adding SAPs on flexural and compression strength was also studied.

LITERATURE REVIEW

2.1 Shrinkage of concrete system

2.1.1 History and Background

The modern HPC systems contain low w/c ratio, such w/c ratio is not enough for complete unrestricted hydration of cement and will cause the cement system to self-desiccate [3].

It depends a lot on the composition of a cement based system whether it shows shrinkage or expansion. Shrinkage of concrete refers to the reduction in volume of the concrete systems. With time this behavior can be attributed to various simultaneous mechanisms occurring within the matrix. There are various mechanisms of shrinkage like plastic shrinkage, chemical shrinkage, autogenous shrinkage and drying shrinkage. As civil engineers we should be able to identify such shrinkage mechanisms but in the end we are more interested in the total amount of shrinkage of a given cement based formulation.

2.1.2 Autogenous Shrinkage

Something which is fashioned individually i-e without any external influence or aid is termed as autogenous. The autogenous shrinkage refer to the shrinkage in closed isothermal conditions. There are various theories explaining the mechanism of autogenous shrinkage. There is consensus regarding the existence of a relationship between the relative humidity (RH) changes in the pores of the hardening cement and the autogenous shrinkage, but the actual mechanisms are vague yet. Among other debated principal factors, (regarding autogenous shrinkage phenomenon), are tension in capillary water, surface tension of the solid gel particles and the disjoining pressure theory. To reach a solid ground about the mechanism of autogenous shrinkage, we need to carry out intensive research to have understanding of the development of the pore volume and pore size

distribution, of the state of water in the capillary pores (free or adsorbed) and of the stiffness of the solid skeleton as hydration proceeds is needed [2].

2.1.3 Self-desiccation

Producing a drop in the internal relative humidity of the system by the removal of free water as a result of a chemical reaction so as to leave inadequate water amount to cover the surfaces of the solids. In order to fully understand the mechanism of self-desiccation, first we need to know about the different types of pores and water in a cementitious matrix. One classification of pores in cementitious matrix are gel pores (<10nm), capillary pores (10nm-10 μ m) and voids (>10 μ m) [4]. Based on Powers' comprehensive study of chemically bound water in hardening cementitious systems and the water vapour sorption isotherms, the water held in cement paste can be classified into three phases: capillary water (free water present in the capillary pores), gel water (physically bound water present in the gel pores) and chemically bound water (non-evaporable water) [1]. Powers' calculations and measurements indicate that, 1 gram of cement requires approximately 0.23 grams of water to chemically react during the hydration process. This water is non-evaporable and is termed as chemically bound water. Apart from this chemically bound water there is also some amount of water adsorbed on the surface of the solid gel formed. This adsorbed water is termed as physically bound water and it is approximately 0.19 grams for 1 gram of cement. The bonding energy of this physically adsorbed water corresponds to the internal relative humidity of the cementitious system. The third type of water present in the cementitious environment is in the coarse capillary pores. This water is not bounded and can be easily removed/evaporated. It is termed as free water and also as capillary water. **It is only this capillary water which is easily available and contribute to the unrestricted hydration of cement.**

Per gram of cement we require 0.23 grams of water as chemically bound water + 0.19 grams of water as physically bound water which gives us a total water of 0.42 grams of water per gram of cement. So for a complete unimpeded hydration a W/C ratio of ≥ 0.42 is required. When w/c drops below 0.42, the cement starts using up the physically bound water, a type of water which is necessary for volume stability of the system. Resultantly, the volume of the system decreases known as shrinkage [1].

2.1.4 Chemical Shrinkage

The shrinkage which occurs due to the chemical reactions is known as chemical shrinkage. It occurs in an open system at isothermal conditions. We know when two or more reactants chemically react with each other the resultant product have less weight or volume. Like any other chemical reaction, similar effect can be seen in the chemical hydration of cement. When the solid particles of cement come in contact with water they start reacting and form different products of hydration like ettringite, calcium hydroxide and calcium silicate hydrate gel. The products formed during hydration have less volume as compared to the reactant or parent cement particles, which causes the formation of empty spaces or voids in the cementitious system. The system when in fluid state is unable to sustain the created voids due to this chemical reaction, between water and cement, the reduction of volume occurs as the system in fluid state come together inwards to fill the voids thus reducing the bulk volume of the system.

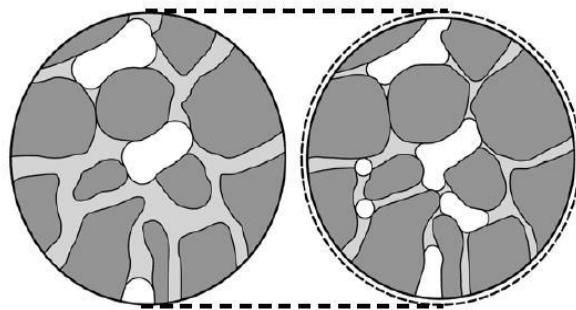


Figure-2.1 Schematic representation of a cross-section of hydrating cement paste. Left: low degree of hydration [2].

2.1.5 Surface Tension Theory

The surface tension approach declares the reasons for expansion and bulk shrinkage of cementitious systems to be the function of change in the surface tension, of the gel particles of cement, due to adsorption of water and removal of adsorbed water, respectively.

2.1.6 Disjoining pressure Theory

The disjoining pressure arises in thin liquid films due to the action of surface or colloidal forces [22]. It can be observed in the regions whenever there is a liquid (water) adsorbed between two solid surfaces, and the distance between them is less than twice the thickness of free adsorbed liquid (water) layer. This effect should be important also at high relative humidity (RH). Double layer repulsion, van der Waals forces and structural forces are the causes of disjoining pressure. It also depends upon the internal relative humidity of the system and the ionic concentration (i-e the concentration of Ca^{++} ions) of the pore fluid. **The disjoining pressure varies with the RH and with the concentration of Ca^{2+} ions in the pore fluid.** Shrinkage occurs due to the decrease in the disjoining pressure, as the disjoining pressure tends to decrease when the relative humidity drops [2].

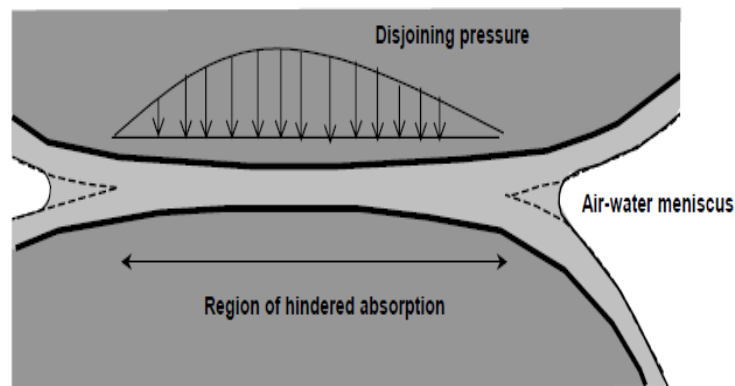


Figure 2.2 Surfaces of Hindered Adsorption and Distribution of Disjoining Pressure. [Lura 2001]

2.2 Super Absorbent Polymers (SAPs)

In simple word SAPs are material which can absorb and retain large amount of water from the surrounding environment without dissolving. SAP absorb and retain liquid by the process of osmosis and hydrogen bonding. When a SAP particle has absorbed water up to its maximum capacity it can become 99.9% liquid. Due to this exceptional ability of SAP to absorb and retain water it is commonly used in disposable hygiene products, such as baby diapers, adult protective underwear and sanitary napkins.

SAPs are classified mainly on the method of manufacturing i-e suspension polymerized and solution polymerized.

2.2.1 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 as shown in figure 2.3.

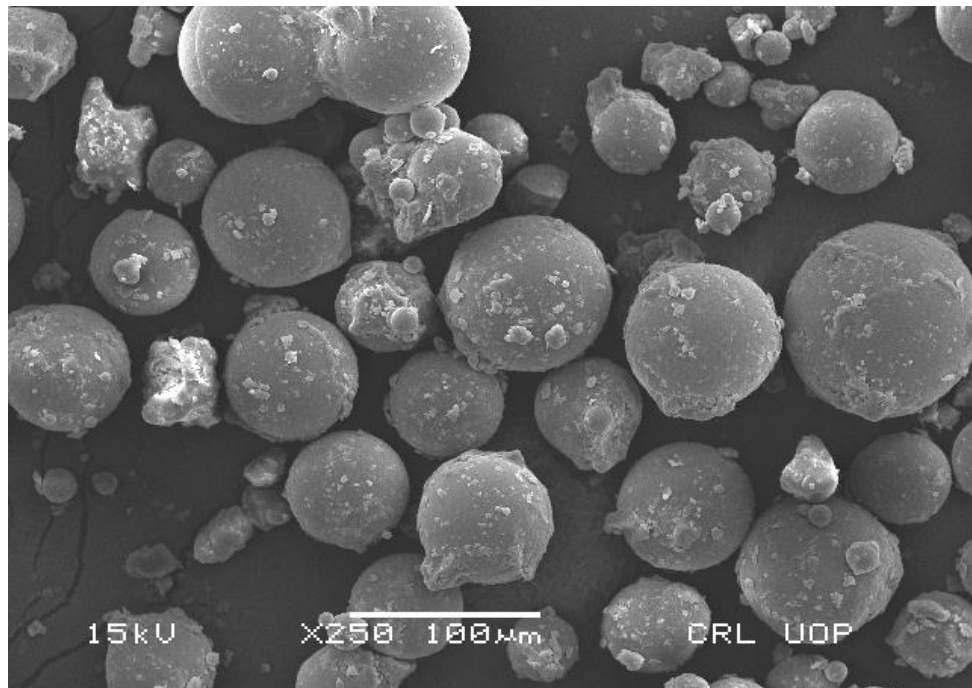


Figure-2.3 SEM image of Suspension polymerized SAP

2.2.2 Solution Polymerized SAPs

In this technique the solution is not separated into dispersed phases resulting in rough appearance of SAPs like crushed particles as can be seen in figure 2.4.

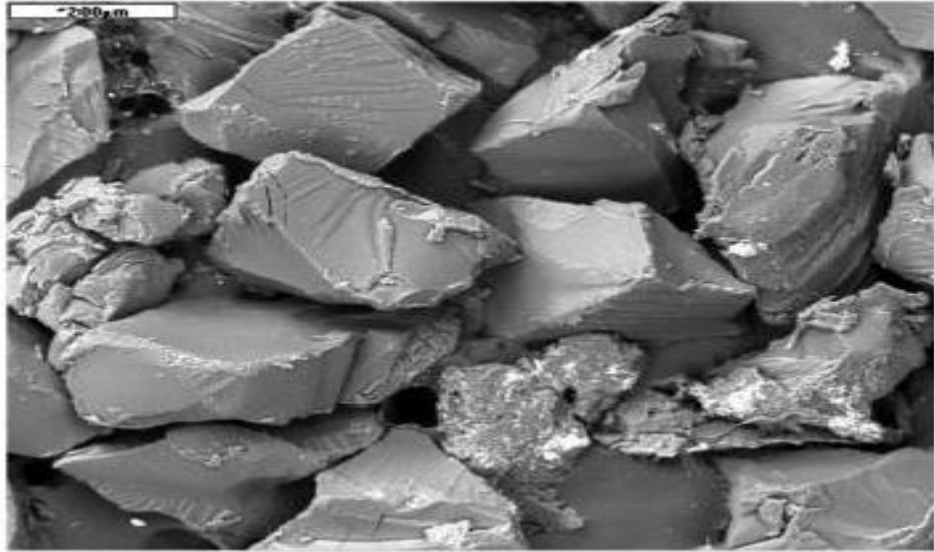


Figure-2.4 SEM image of solution polymerized SAP

2.2.3 Absorption Mechanism of SAPs [6]

There are a number of mechanisms to the process of swelling, contributing to the final swelling capacity or the CRC, which is the centrifuge retention capacity, in this a SAP is allowed to absorb a solution, which is a 0.9 wt% saline solution, under the free swelling conditions after this the surface water is drained out by means of a centrifuge, the amount of solution retained after this centrifuge process is noted [6]. Figure 2.5 shows the schematic on polymer network.

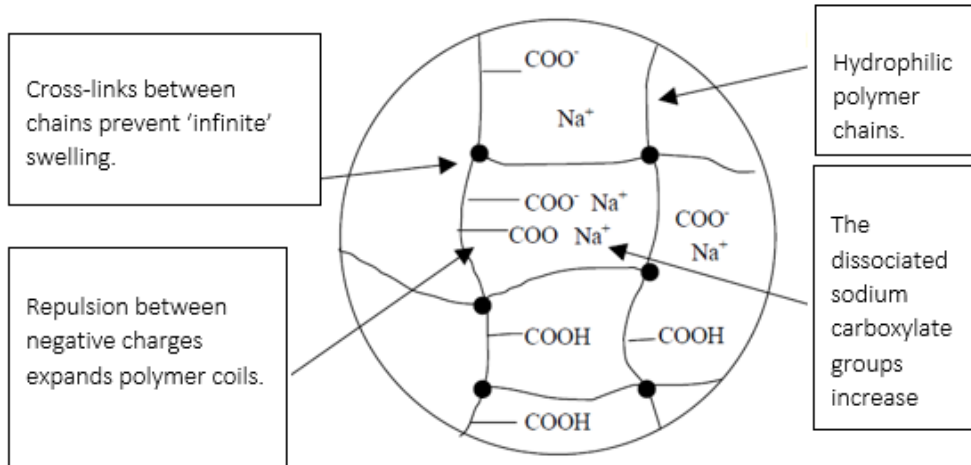


Figure-2.5 Diagrammatic representation of part of the polymer network. [6]

2.2.3.1 Hydration Reaction

The figure 2.6 shows when the hydration reaction occurs, how the interaction between the solute ions, the COO^- and Na^+ ions and the polar water molecules occurs.

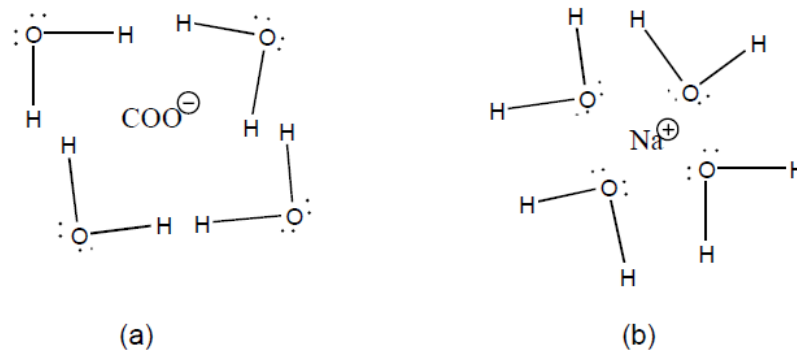


Figure-2.6 interaction of ions of a solute with molecules of a solvent. [6]

2.2.3.2 Hydrogen Bonding

Hydrogen bonding is the formation of bond in molecules having hydrogen atom attached to the high electronegative elements. Due to the electrostatic attraction forces between hydrogen and the lone pair of electrons of the small high electronegative elements like nitrogen, fluorine and oxygen. The attraction between hydrogen and the lone pair of electrons form a strong bond.

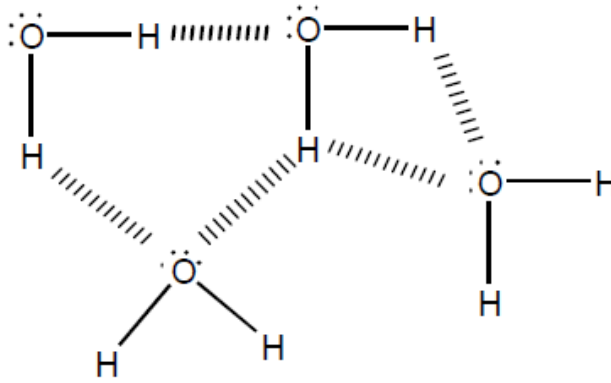


Figure-2.7 Hydrogen bonding of water molecules. [6]

Entropy is a measure of the unavailable energy in a closed thermodynamic system. As entropy of the system is increased as the energy of the system is decreased by these effects. SAP being hydrophilic the polymeric chains can spread over a wide area in a definite quantity of water, which increases the entropy also leads to a greater number of configurations for the system.

2.2.4 Why SAP does not dissolve in water?

When SAP comes in contact with water, a three-dimensional network is formed by the cross-linked chains of the SAP, which prevents its particles to be dissolved in water. The hydrated chains become stiffer than their originally coiled state, due to the decrease in entropy of the chains and the elastic retraction forces of the three-dimensional network formed.

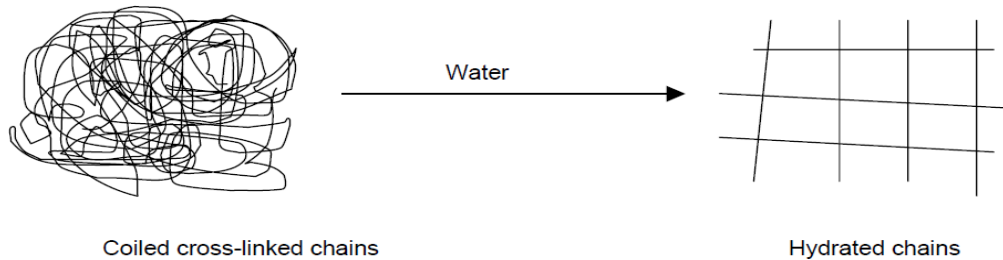


Figure-2.8 Schematic showing cross linked chains behavior after coming in contact with water.[6]

An equilibrium is formed between the affinity for the chains to swell to unlimited dilution and the retraction forces. The strength of network formed and the level of swelling is directly dependent on the degree of cross-linking.

2.2.5 The Dry State of SAP

SAPs are highly sensitive hygroscopic and hydrophilic materials and can quickly absorb moisture from the surrounding when exposed to an open environment of high relative humidity (RH). Because of their highly sensitive hygroscopic nature, SAP particles need to be stored in a closed environment of low RH to avoid any sort of error during the experiment.

For this reason SAP was stored in a desiccator, which is a glass container having silica gel as a desiccant at the base, above which there is a perforated plate and to cover the container is a glass lid which prevents any moisture movements from outside environment into the container. SAP particles, in a glass/plastic dish, were placed inside the desiccator 24hrs prior to the testing.

2.2.6 Absorption Capacity of SAP

The amount of water which a SAP particle can absorb and retain depends upon the type of SAP as well as the surrounding environment. There are specific types of SAP which can absorb water up to 1500 times their own weight. Temperature, pressure, water activity and the specific ionic composition of the exposure liquid are a few of the parameters influencing the absorption capacity of that particular liquid by SAP [5].

A SAP's capability to absorb water depends upon the ionic concentration of the aqueous solution. A certain type of SAP may absorb water 300 times its own weight in de-ionized water and distilled water, due to no/negligible ionic concentration, and can become up to 99.9 part liquid and only 0.1 part solid. But the absorption may drop to 50 times its weight, when a SAP is exposed to a 0.9% saline solution.

Even the very small amount of ions present in tap water can reduce the absorption capacity to 50g/g. In saturated Ca(OH)_2 solution the absorption capacity is further reduced to about 10g/g. The Ca^{2+} in saturated Ca(OH)_2 solution as well as the Ca^{2+} in tap water is the main reason for both the lower absorption capacity [5]. More

the ionic concentration of aqueous solution less will be the absorption of SAP in that medium.

Figure 2.9 is an exaggerated illustrations of the size of a swollen SAP particle after it absorbs water in a medium with a particular ionic concentration. It can be seen that as the ionic concentration of the medium increases the size of the swollen SAP particle decreases. More ions in a medium cause hindrance in the osmosis process, thus the absorption decreases.

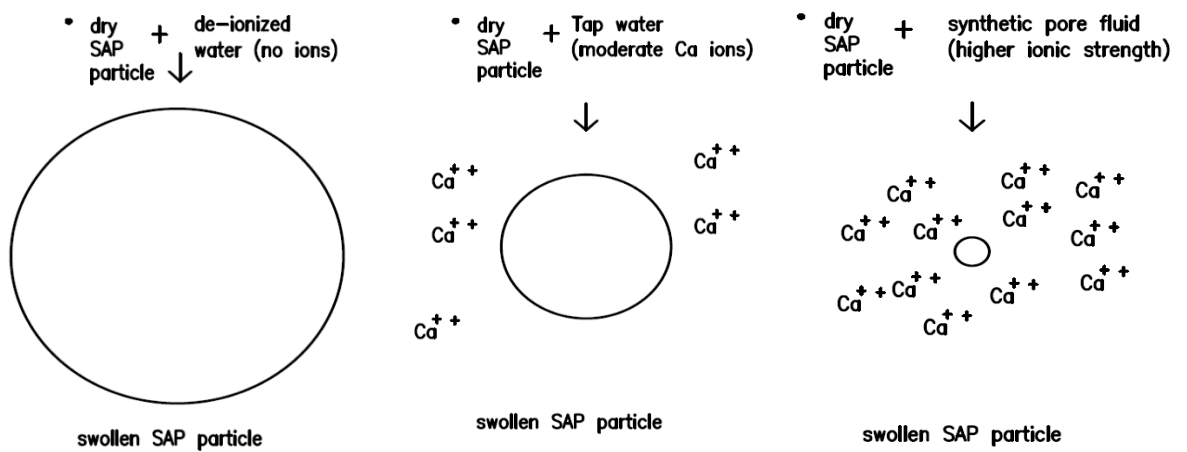


Figure-2.9 illustration of SAP particle size after absorption in liquids of different ionic strengths

2.3 Self-compacting cementitious Systems

Self-compacting concrete (SCC) is a type of concrete which does not require any sort of external mechanical vibration for its placement and compaction (ACI 237). It can completely fill the formwork as it flows under its own weight without any segregation. Such a concrete when hardened is dense, homogeneous and has the same engineering properties like traditional vibrated concrete.

Self-compacting concrete can be rapidly placed, has faster construction times and can easily flow around congested reinforcement. The segregation resistance and fluidity of SCC guarantees a high level of homogeneity, minimum concrete voids and uniform strength, providing the potential for a superior level of finish and durability to the structure. Often a low w/c ratio is used in making SCC thus providing the potential for higher early strength, earlier demoulding and quicker use of elements and structures. [7]

To achieve a better design of SCC, it is important to understand the fresh and hardened properties of SCM. Because SCM has an important role on the design of SCC as a complimentary part of concrete [8]. Thus in order to achieve SCC, we need to first know the characteristics of a SCM system as it is an inevitable milestone in achieving SCC.

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” [9]. The above statement means that in order to improve the workability of a concrete system, we need to increase the paste content so that more transport is available for aggregate flow.

2.4 Experimental Techniques for SAP characterization

2.4.1 X-ray Diffraction

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for identification of phase of a crystalline material and also provide information on the dimensions of a unit cell. The material to be analyzed is finely ground, homogenized, and average bulk composition is determined.

XRD is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of solids of unknown origin is critical to studies in biology, environmental science, geology and many other subjects [11]

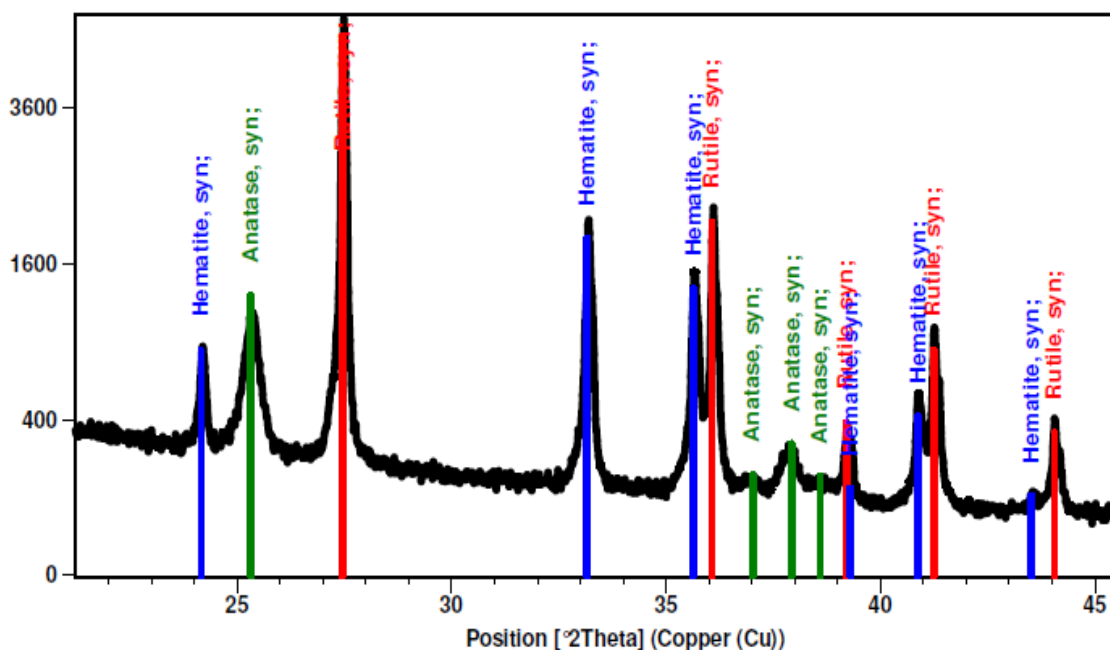


Figure-2.10 Typical XRD results [10]

2.4.2 X-Ray Fluorescence

An X-ray fluorescence (XRF) spectrometer is an instrument used for non-destructive chemical analyses of minerals, sediments, rocks, and fluids. It follows the principle of wavelength-dispersive spectroscopy. However, in general, an XRF cannot make analyses at the small spot sizes like those in the range of 2-5 microns. Thus it is typically used for bulk analyses of geological

materials of larger fractions. What makes x-ray spectrometers one of the most widely used methods for analysis of major and trace elements in minerals, rocks, and sediment is the relative ease and low cost of sample preparation, and the ease of use and stability.

The principle followed by XRF is somewhat common to the principle followed by other instrumental methods that involve interactions between electron beams and x-rays with samples like X-ray spectroscopy (e.g., SEM - EDS), wavelength dispersive spectroscopy, and X-ray diffraction (XRD) [12]

What makes XRF able to analyze major and trace elements in geological materials is the way the atoms behave when they interact with radiation. When a material is excited with high-energy, short wavelength radiation (e.g., X-rays), it becomes ionized. If the energy of the X-ray is sufficient enough to remove a firmly-held inner electron, the atom becomes unstable. To retain its stability, an outer electron replaces the missing inner electron. As a result, energy is released due to the lower binding energy of the inner electron orbital compared with that of an outer one. The radiation that is emitted has energy contents lower than the incident radiation and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample. [12]

2.4.3 Scanning Electron Microscopy

Use of the scanning electron microscope (SEM) with X-ray microanalysis allows study of chemicals 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 [23]. 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 for metallic system. However for cementitious systems they provide limited variable information. Scanning electron microscopy renders quantitative chemical analysis in terms of Energy Dispersive X-ray Spectroscopy (EDX) [24]. 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 [25]. Figure 2.11 shows SEM presentation of SAP particles.

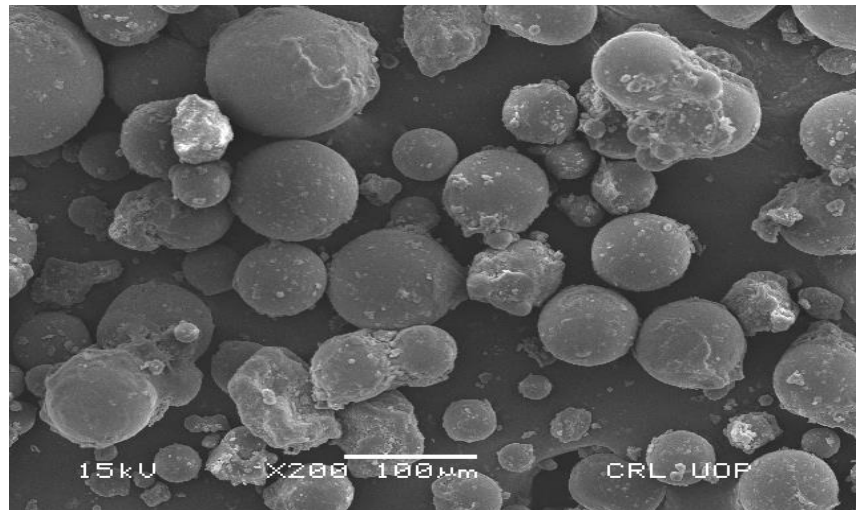


Figure-2.11 Scanning Electron Micrograph of SAP

2.5 Calculating the Absorption capacity of SAP

The absorption capacity of SAP is of utmost importance as it is the basis of all the calculations regarding the amount of SAP as well as the mixing water content required to be used in a particular formulation.

There are two processes responsible for the absorption of liquids by SAP. They are:

2.5.1) Hydrogen Bonding:

The bond between partial positive hydrogen atom and a highly electro-negative atom like Oxygen, fluorine and nitrogen

2.5.2) Osmosis:

It is the transfer of molecules from a solvent with high concentration to a solvent with low concentration through a semi-permeable membrane

The absorption capacity of SAP depends upon several factors:

- 1) preparation method of SAP(solution polymerized or suspension polymerized SAP)
- 2) ionic concentration of the liquid being absorbed:
- 3) PH of the liquid
- 4) Relative humidity
- 5) Crosslink density of SAP
- 6) Temperature of the liquid

Several methods are used for measuring the absorption capacity of SAP. Some of them are:

- 1) Tea-Bag method
- 2) Sieve method
- 3) CT scanning
- 4) Graduated cylinder method
- 5) Gravimetric Technique

6) Optical microscopy [5]

2.6 Flow test

The flow test is used to determine whether the mortar is a self-compacting one or not. The test is performed on Hagerman's cone apparatus consisting of a truncated cone with base diameter of 100mm, top diameter of 70mm, height of 60mm and a circular mirror with 20cm, 25cm, 30cm diameter marks. 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.

2.7 Shrinkage

It is the volumetric change in concrete due to loss of moisture by evaporation. It is a time dependent process and does not take into account the impact of external forces. The term shrinkage includes both expansion as well as contraction. Shrinkage causes both bending and axial stresses in cement systems which results in the formation of cracks. In order to study the effects of SAP on mortar, shrinkage tests were performed using a German "shwenderine" apparatus.

2.8 Strength

The strength of concrete is one of the most important property of concrete which is effected by numerous factors like PH, Temperature of water as well as the environment, impurities in water, cement properties, aggregate properties and several other factors. Strength of concrete can be flexural, compressive, torsional etc. however in his project only flexural and compressive strengths were performed.

The strength of concrete can be effected through different means like partial replacement of cement with SRM's like flyash, internal curing of concrete etc. In this project internal curing of mortars was performed using SAP and its effects on strength were studied.

Experimental Procedures

3.1 General

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

3.2 Materials

Bestway Grade 53 cement was used for this project which was kept in air tight container for avoiding lumps formation and moisture interaction. SAPs used were solution polymerized covalently cross-linked acrylamide/acrylic acid copolymer which were provided by Prof. O.M. Jensen of Denmark Technical University, Denmark. Locally available sand with the fineness modulus of 2.5 was used to prepare SCM formulations. Melflux – 2651 was used as Super plasticizer. Olive oil was used as a non-polar medium in calculating the dry density of SAP.

3.3 Super Absorbent Polymers

SAPs were provided by Prof. O.M. Jensen (Denmark Technical University). Before introducing them into the mortar, their physical and chemical properties were studied. SAPs are actually hygroscopic in nature, in other words they are water loving. As they are expose to open environment they start absorbing moisture very rapidly. So immense care is required to keep SAPs in dry condition. Before using SAPs, they were kept in desiccator for at least 24 hours. For studying the chemical and physical properties of SAPs XRF (X-Ray Fluorescence) and SEM (Scanning Electron Microscopy) are done, results are as follows.

3.4 Test Procedures

3.4.1 Mixing Regime

SAPs take almost five minutes to attain maximum absorption, thus a mixing regime of 5min wet mixing was selected.

Table-3.1 Mixing Regime of Formulations

Time	Regime
30sec	Slow Dry Mixing
30sec	Slow mixing by adding 80% Water
60sec	Fast Mixing
5min	Fast Mixing after cleaning container walls, adding remaining 20% water and Super Plasticizer

3.4.2 Mix Formulations

As self-compacting mortar has been used so all of the mix formulations were decided on the basis of flow test (Hagerman's Cone). Three different water cement ratios were used, 0.42, 0.40 and 0.38. The amount of SAPs selected were 0.3% and 0.4% by weight of cement. Percentages of Super Plasticizer were selected on the basis of flow test. Two kinds of samples were casted, with SAPs and without SAPs so that comparative study can be done. All water cement ratios have following variants:

- Self-Compacting Mortar containing Super Plasticizer.
- Self-Compacting Mortar containing SAPs and Super Plasticizer.

3.5 Absorption Capacity of SAPs

Absorption capacity is actually the fundamental property of SAP which actually defines its performance in cementitious environment. When dry SAP is exposed to polar mediums like water or methanol it starts absorbing them mainly due to hydrogen bonding and osmosis. Correct value of absorption capacity is necessary for performance of SAP. For calculating absorption capacity there are several methods, some of which are the following:

- (a) X-Ray Computed Tomography
- (b) Method of Graduated Cylinders
- (c) T-Bag Method [5]

X-Ray computed tomography is accurate method available for the finding absorption capacity of SAP, but it is very expensive to practice and involves complex calculations through software. For calculating correct absorption capacity of SAPs method of Graduated Cylinders has been used.

3.5.1 Method of Graduated Cylinders for calculating the absorption capacity of SAP

Method of graduated cylinders is mainly based on volume change of known mass of dry SAP after absorption. In this method initially the relation between mass and volume of dry SAP is calculated. For this, the graduated cylinder of 10ml volume (V_1) is completely filled and mass m_1 of SAP is noted. Then a known mass m_2 of SAP is filled into the cylinder (in our case, a beaker). Three types of fluids has been used Tap Water, Distilled Water and Cement Slurry. Each fluid is poured into the beaker containing mass m_2 of SAP and magnetic stirring is applied for 30 minutes. After stirring, mixture was allowed to settle for one hour. Till that the gel settled in the bottom and volume v_2 of gel was noted [5]. Figure 3.1 shows three images, in the fig-3.1 (1) a cylinder in filled with dry SAP particles up to its maximum graduation. Fig-3.1 (2a) a known mass of dry SAP is added in the cylinder. Fig-3.1 (2b) shows the volume of swollen SAP after the addition of synthetic pore fluid.

While figures 3.2 and 3.3 shows swollen SAP gel and precipitated swollen SAP gel, respectively.

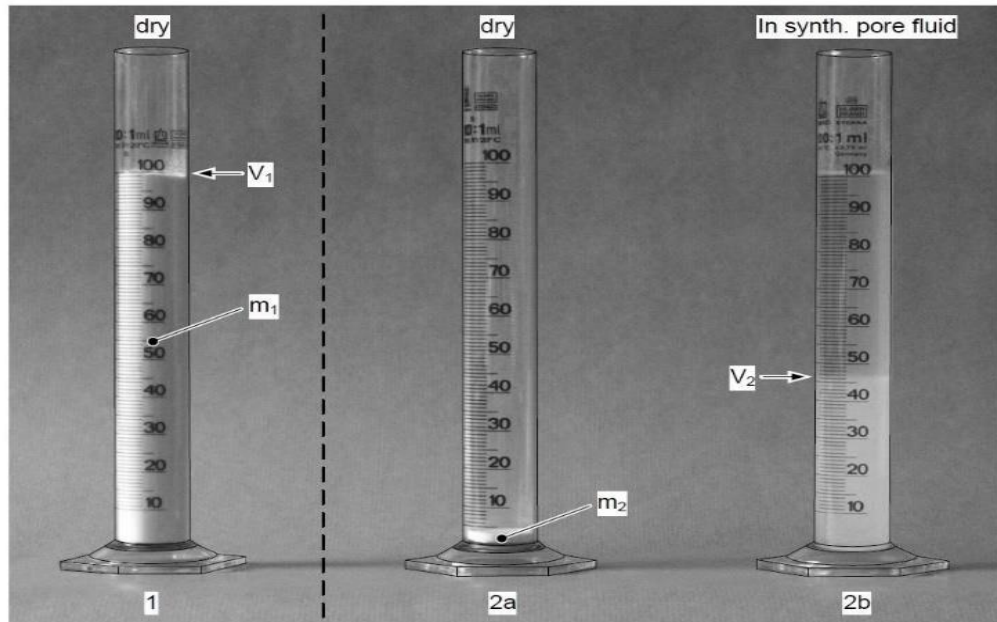


Figure-3.1 Steps to find the absorption capacity of SAP through graduated cylinder method [5]



Figure-3.2 SAP gel on a spoon

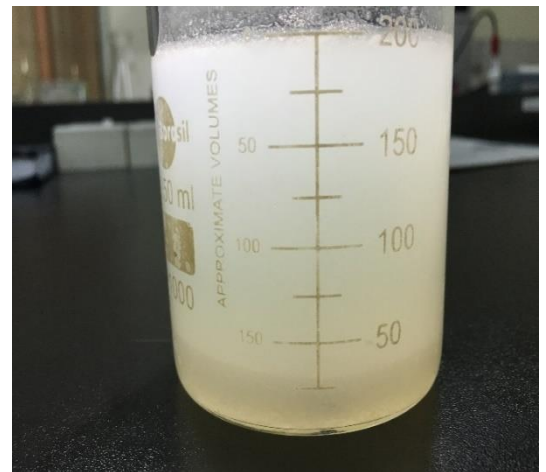


Figure-3.3 Precipitated Column of SAP gel

Following expression was used for calculating absorption capacity

$$k = \frac{\rho_{water}}{\rho_{sap}} \left[\frac{V_2}{V_1} \times \frac{m_1}{m_2} - 1 \right]$$

Where,

- k is the absorption capacity in g/g.
- ρ_{water} is the density of water 1g/cm^3
- ρ_{SAP} is the dry density of SAP
- V_1 is the volume of dry SAP completely filling the cylinder.
- m_1 is the mass of dry SAP completely filling the cylinder.
- m_2 is the known mass of dry SAP placed in the cylinder.
- V_2 is the volume of swollen SAP.(after pouring liquid in the cylinder, apply 30min magnetic stirring, allowing it to settle for 1hr)

ρ_{sap} is dry density of SAP, which was calculated by following method.

3.5.2 Dry Density of SAP ρ_{sap}

Dry density of SAP was calculated on the base of volume displaced/increment of a non-polar fluid by the solid SAP particles. A non-polar liquid, (in our case olive oil), was used because SAP being ionic compound neither interact with nor have any absorption in a non-polar medium as no hydrogen bonding is developed between SAP and non-polar liquid. Figure 3.4 shows a graduated cylinder having olive oil in it settled SAP particles can also be observed on the bottom of the cylinder.

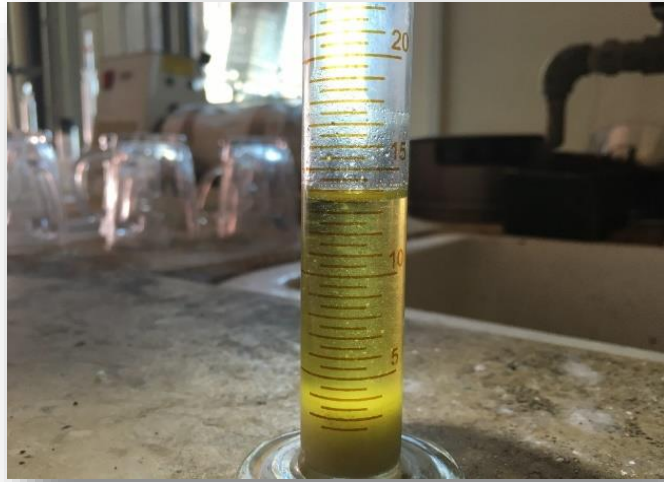


Figure-3.4 SAP of known mass immersed in Olive Oil

3.5.2.1 Procedure for determining the dry density of SAP

A graduated cylinder was filled with a non-polar liquid, olive oil, up to a certain volume “V1”. A known mass of SAP “m” was put in the cylinder containing olive oil. The SAP particles, being heavier than olive oil, start to settle at the bottom of the cylinder thus raising the level of oil in the cylinder to level “V2”. The difference between the raised levels of oil and the initial level is the volume of the SAP particles in the cylinder “V_{SAP}”. Dry density was calculated by following expression.

$$\rho_{\text{sap}} = m_{\text{SAP}} / V_{\text{SAP}}$$

Where,

ρ_{SAP} is the dry density of SAP

m_{SAP} is the mass of dry SAP particles

V_{SAP} is the volume of SAP particles.

3.6 Super-Plasticizer Demand of SCMs

Demand for super plasticizer has been determined using Hagerman’s Cone measuring 6 x 7 x 10 cm³ by hit and trial. Super-Plasticizer demand has been decided on the basis of hit and trial method.

3.7 Shrinkage of SCM formulations

The fresh mixes were placed in a modified version of German Classical “Schwindrinne” channel apparatus measuring 4x6x25cm interfaced with computer software. To avoid bleeding of freshly prepared mortar, edges of the

moveable plates of shrinkage apparatus were greased carefully. Shrinkage response was started after ten minutes of pouring of mortar and was carried out for 24 hours. The resulting shrinkage response of the formulations was plotted against time.

3.8 Casting and Curing of SCM samples

Samples for testing under compression and flexural loading were casted in 160 x 40 x 40 mm steel moulds. In order to avoid bleeding, edges of steel moulds were greased and there sides were properly oiled, by this sticking of hardened mortar on sides were also avoided. Freshly prepared mortar paste were poured into the steel prisms and allowed to set for 24 hours while being covered with plastic sheets. All the samples were de-moulded after 24 hours and allowed for curing. All formulations were cured in curing tank for three different spans of time 1 day, 3 days, 21 days after which flexure and compression testing was done.

3.9 Strength Evaluation of SCM formulations

For strength evaluation flexural and compression testing was done on all the samples (at day1, day3 and day28 of casting). For compression a uniform loading rate of 0.25kN/sec and for flexure a uniform loading rate of 0.025kN/sec was adopted. First of all flexure testing was done, due to which all the samples breaks into two parts. Then compression loading was applied on all the pieces.

Test Results & Discussions

4.1 Formulations Investigated

Three different water cement ratios were selected and the amount of SAP required by them to attain a flow of 30 ± 1 cm are listed in Table-4.1

Table-4.1 “9” Formulations at three different basic w/c ratios

Serial No.	Formulation	(W/C) _B Ratio	SP (%)	SAP(%)	Total W/C
1	C1-38-0.35-0	0.38	0.35	0	0.38
2	C1-38-1.3-0.3		1.3	0.30	0.407
3	C1-38-1.5-0.4		1.5	0.40	0.416
4	C1-40-0.31-0	0.40	0.31	0	0.4
5	C1-40-1-0.3		1	0.3	0.427
6	C1-40-1.3-0.4		1.3	0.40	0.436
7	C1-42-0.29-0	0.42	0.29	0	0.42
8	C1-42-1-0.3		1	0.30	0.447
9	C1-42-1-0.4		1	0.40	0.456

4.2 Dry Density of SAP ρ_{SAP}

Several trials were performed and the average of all the density values excluding the outlier values was taken. On average, the dry density of SAP was equal to 1.5 g/cm³ which is the equal to the one mentioned by Professor O.M.Jensen. The results are shown in Table-4.2

Table-4.2 Density of SAP at different trials

TRIALS	MASS OF SAP (g)	VOLUME (ml) or (cm ³)	DENSITY (g/ml) or (g/cm ³)
1	1.5	1	1.5
2	0.8	0.5	1.6
3	1.8	1.2	1.5
4	1.6	1.15	1.4
			$\rho_{sap} \text{ (dry)} = 1.5 \text{ g/cm}^3$

4.3 Absorption Capacity of SAP's

Table-4.3 Absorption capacity of SAP in different liquid

The results in Table-4.3 and Figure-4.1 show that the absorption capacity of SAP is maximum in distilled water followed by tap water and then cement slurry.

LIQUID	pH	TRIAL-1 (g/g)	TRIAL-2 (g/g)	ABSORPTION CAPACITY (g/g)
DISTILLED WATER	7.22	38.33	36.33	37.33
TAP WATER	7.67	26.12	21.83	24
CEMENT SLURRY	12.89	9.33	9	9.165

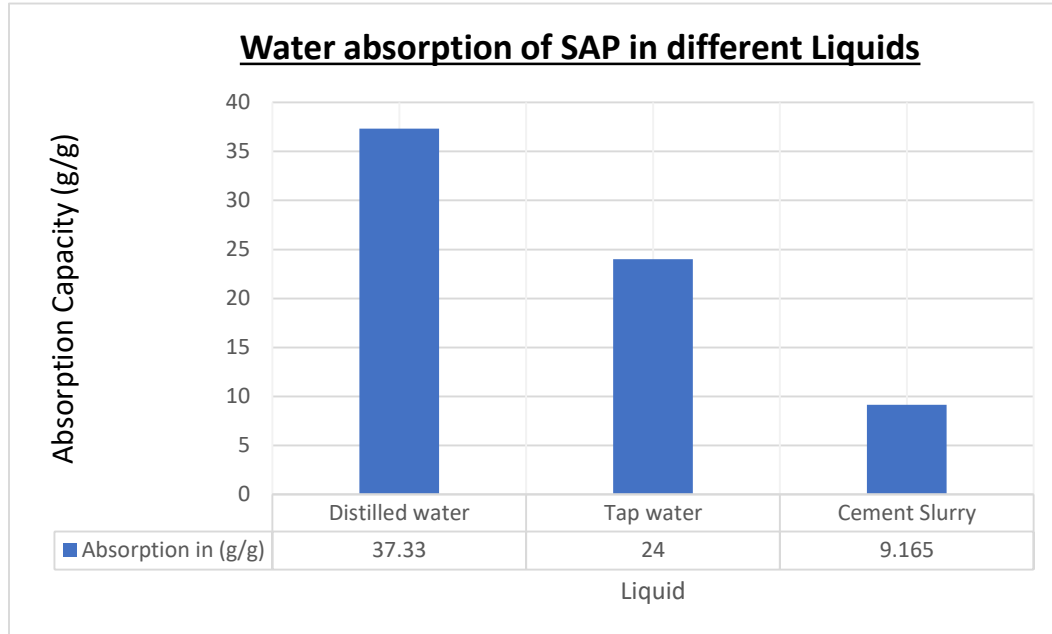


Figure-4.1 Graph of water absorption of SAPs in different liquids

This is due to the difference in ionic concentration of the three fluid. Cement slurry has the greatest amount of Ca^{+} ions followed by tap water which has lower and then distilled water which has the least. Multivalent cations like Ca^{+} diffuse into SAP particle and slowly establish cross-links between the acrylic acid polymer chains. As the results of increase in polymer chains, the SAP particles release a considerable amount of water and their absorption capacity is reduced [5].

4.3.1 Comparison of Absorption Capacity of SAP with Previous Research

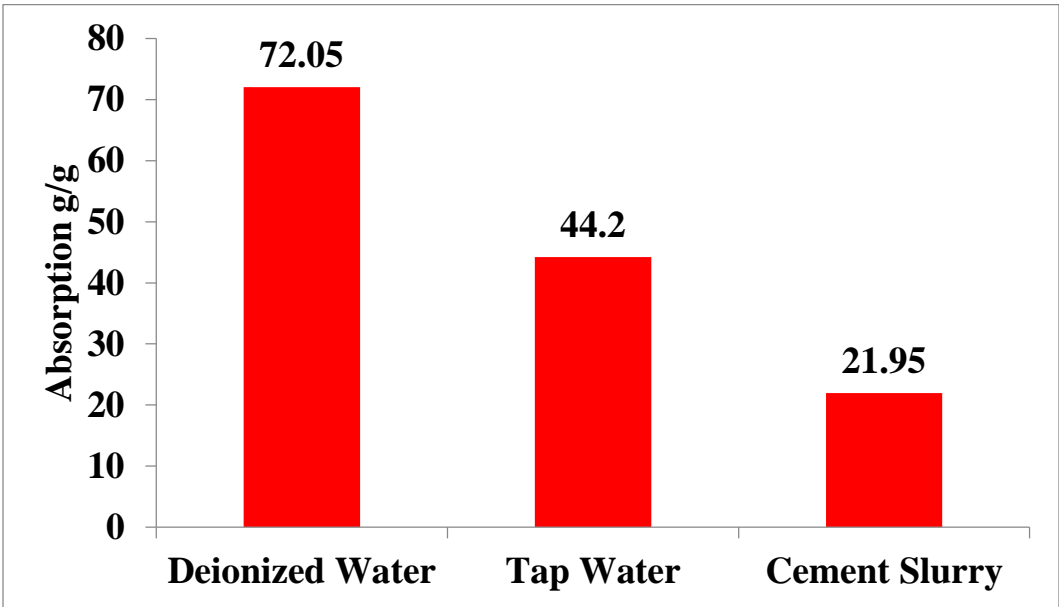


Figure-4.2 Absorption Capacity of SAP in different liquids using sieve method by Rizwan et al [26]

The results obtained by a previous research conducted by Rizwan et al suggests a high absorption capacity for the same SAP. “Sieve method” was used for finding the absorption capacity in this case. The reason for such high values compared to those obtained from Graduated cylinder method is due to the less efficiency of sieve method. A part of the mass gained by SAP in sieve method is due to the liquid held by capillary forces in between the SAP particles; interparticle, unabsorbed liquid. The water absorbed by the SAP particles in sieve method can be referred to as the “retention capacity” rather than the absorption capacity. And that is why we are getting higher values compared to the graduated cylinder method.[5]

4.4 Shrinkage Response of SCM formulations

Figures 4.3, 4.4 and 4.5 show the response of SCM formulations with and without SAP at W/C_(basic) of 0.38, 0.4 and 0.42 respectively.

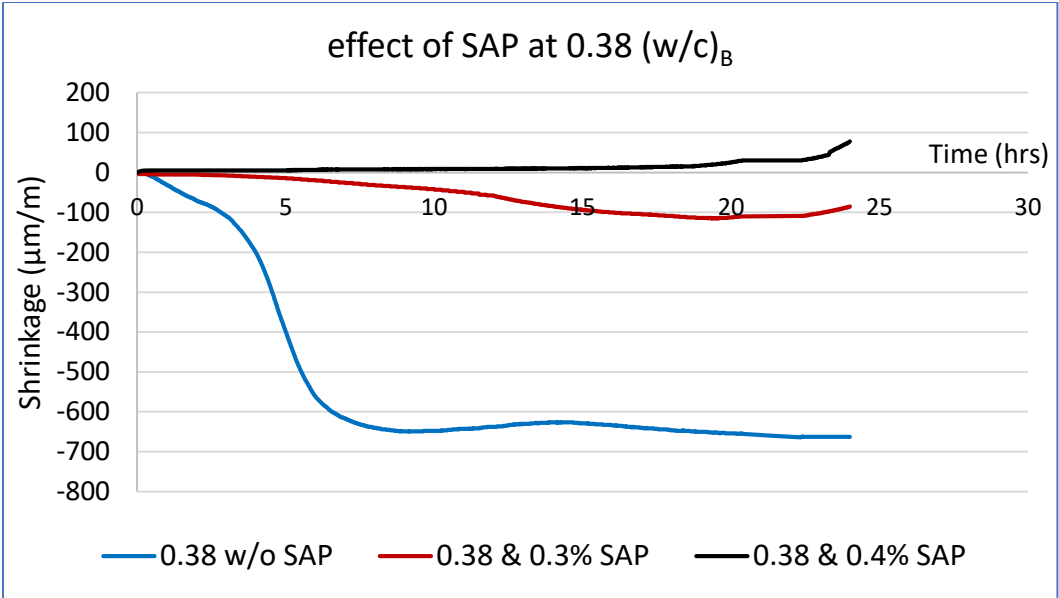


Figure-4.3 line graph of shrinkage in mortar with 0.38 w/c (basic) at different amounts of SAP

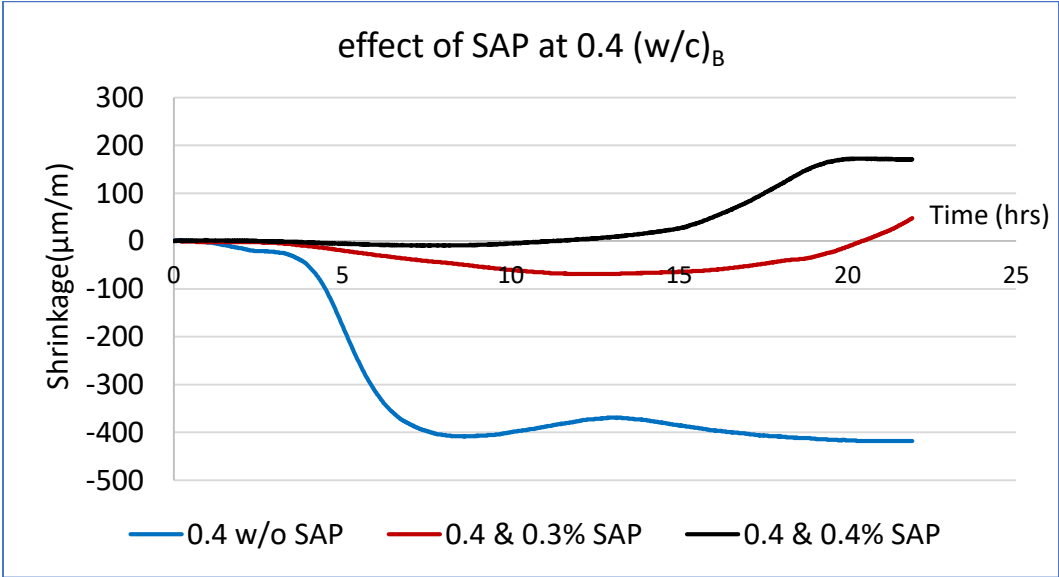


Figure-4.4 line graph of shrinkage in mortar with 0.4 w/c (basic) at different amounts of SAP

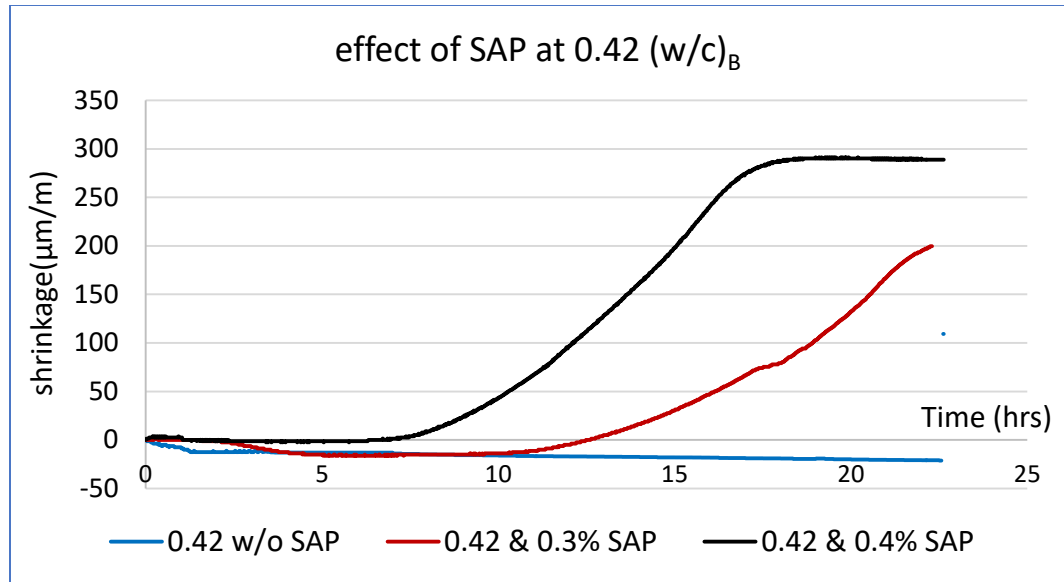


Figure-4.5 line graph of shrinkage in mortar with 0.42 w/c(basic) at different amounts of SAP

The SCM formulation without SAP and W/C of 0.38 and 0.4 shows early age shrinkage due to self-desiccation, the most probable cause of this is the absence of sufficient capillary (free) water and the use of physically bound water (which is for the volumetric stability of the system) by the cement for hydration. This causes the destabilization of volume and hence self-desiccation occurs, which leads to early-age cracking. The SCM formulation with w/c ratio of 0.42 and without SAP show very little total linear shrinkage which also confirms that to prevent the effect of self-desiccation we need a w/c ratio of 0.42 or greater.

The SCM formulation containing SAP show expansion. The following can be the reasons behind this:

- 1) First, the expansion may be due to the re-absorption of bleed water.
- 2) Second, in the SCM formulation containing SAP we have more water contributing to hydration due to internal curing by means of water filled SAP particles, the increase in hydration will cause increase in the formation of hydration products like calcium hydroxide. Now due to the crystallization pressure of calcium hydroxide the expansion occurs. [18]

3) The third reason is, that for equilibrium, the chemical potential of co-existing water phases (Gel and capillary water) in paste should be equal both before and after a temperature change. The entropy (degree of disorder) of gel water is lower than that of capillary water [19]. Thus a sudden increase in temperature during hydration can lead to a higher chemical potential in gel water as compared to capillary water setting up a driving force for an internal redistribution of water from gel to capillary pores, As a result, shrinkage is expected to occur. On the other hand when the temperature would drop, water will flow from capillary pores to gel pores causing expansion [20]. An important thing to mention here is that the former phenomena involving shrinkage of paste phase is only possible when the capillary pores are not completely filled i.e. $RH < 100\%$. In our case, due to internal curing, the RH is almost equal to 100%. Thus, the reason for absence of shrinkage in our case may be due to the unavailability of empty capillary pores for water to move to from the gel pores

It is also observed that by increasing the basic w/c ratio and also the entrained water by means of SAP particles, the total linear shrinkage reduces this may be due to the dilution effect. [21]

4.4.1 Comparison of shrinkage response in SCM and SCP

Figure 4.6 shows the shrinkage response of SCP, a study which was done previously by Shozab Mustafa at NICE, NUST. While figure 4.7 shows the response of SCM formulation done in this research.

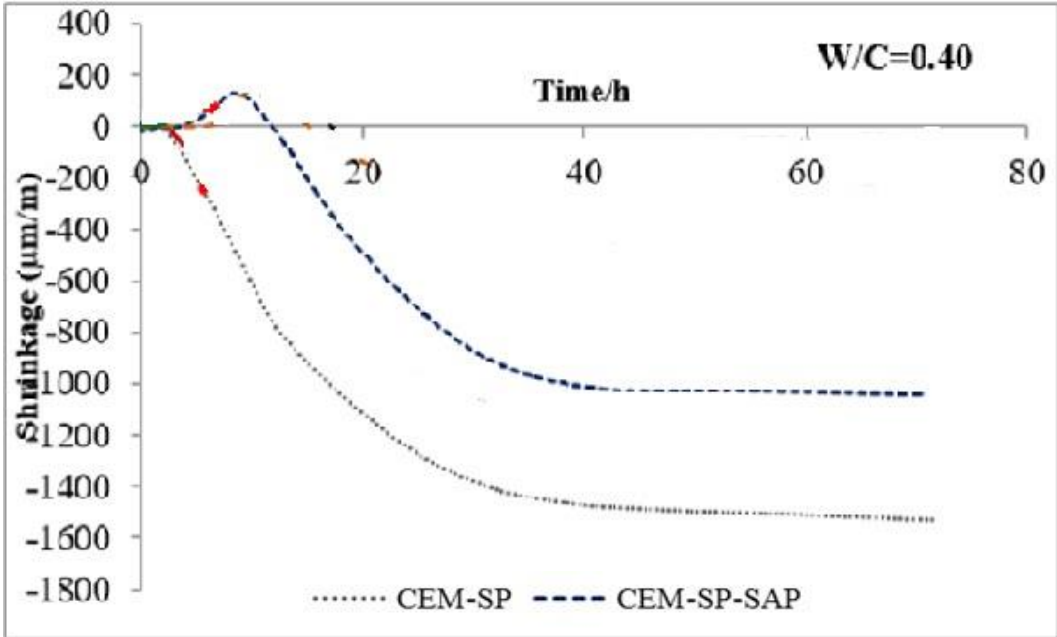


Figure-4.6 Shrinkage response of SCP at (W/C)T =0.4 [26]

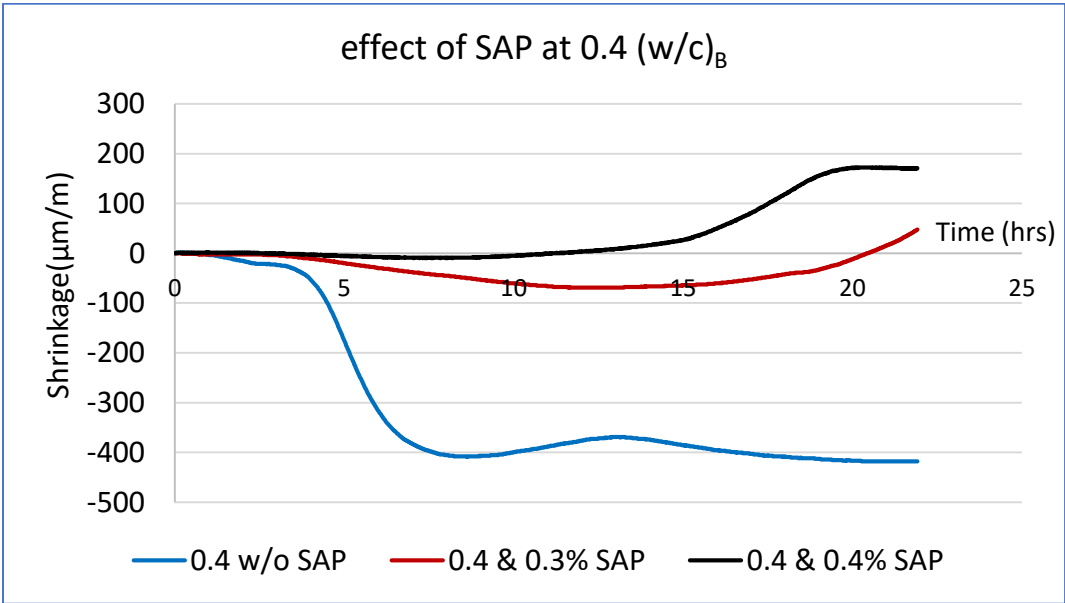


Figure-4.7 Shrinkage response of SCM at (W/C)B =0.4

By comparing the shrinkage response of SCM and SCP at $W/C=0.4$, we observe shrinkage in both the formulations involving cement and SP only. However the shrinkage in mortar is less as compared to that in paste. This can be due to the dilution of cement in mortar. As we know that shrinkage occurs in the paste phase, therefore if the paste phase is diluted, there will be less shrinkage.

Moreover, we also observe that in those formulations which involve SAP in addition to SP, the mortar is showing less shrinkage as compared to paste. In fact in some cases, some expansion is observed in mortar. This is due to the fact that in the mortar formulations 0.4 is the effective w/c whereas in the paste system, 0.4 is the total w/c . Extra water known as entrained water is added in the mortar formulation for SAP to absorb thus taking the total w/c above 0.4.

4.5 Compressive and flexural strength of SCM formulations

Figure 4.8 and figure 4.9 show the scatter plot of compressive and flexure strength, respectively for day 1, 3 and 28 of casting.

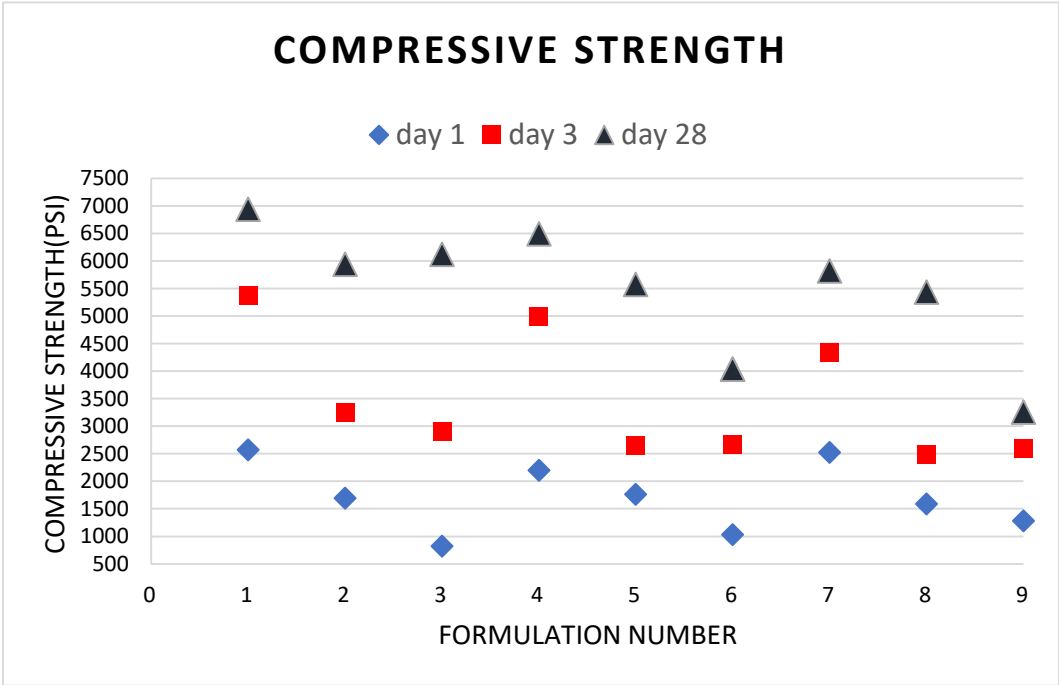


Figure-4.8 Scatter plot of compressive strength of SCM formulations for 1, 3 and 28 days

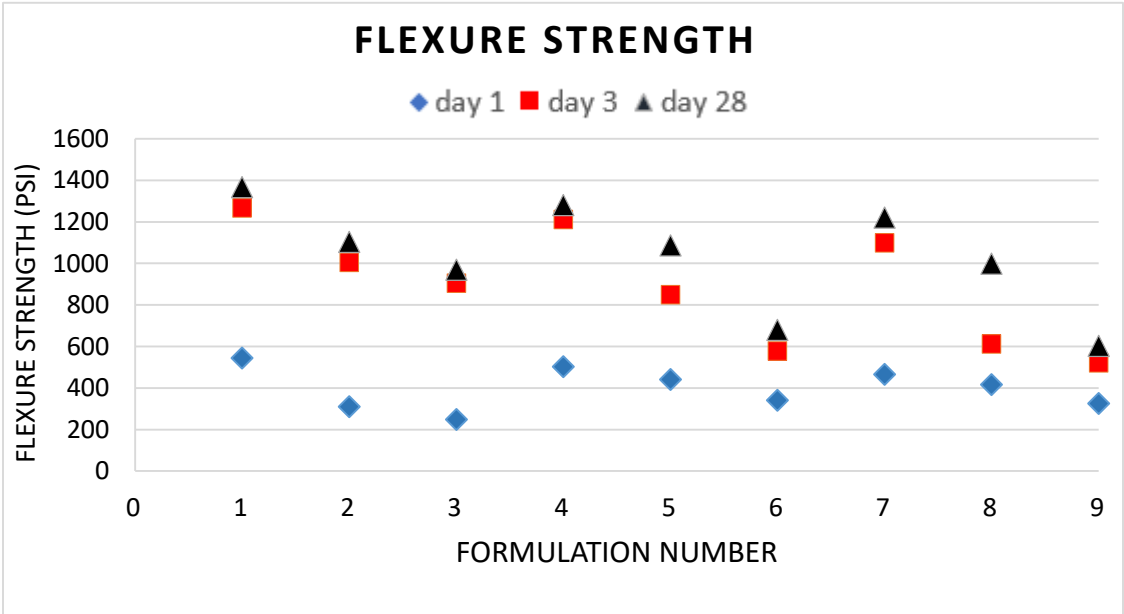


Figure-4.9 Scatter plot of flexure strength of SCM formulations for 1, 3 and 28 days

The graph shows that with the addition of SAP, the compressive and flexural strength of the mortar reduced. This reduction in strength is due to the formation of large voids by SAP particles when they expand. During desorption stage, the SAP particle shrinks but till that time the mortar has hardened enough to retain the void. Thus there is an increase in size of the largest defect in the matrix [13]. SAP's also shift the porosity from micro to macro-porosity which is also a reason behind a decreased strength. It is suggested that the use of SAP of dry particle size less than 100 microns must avoid this loss of strength [14]. Although, this might make the dispersion of SAPs difficult [15].

The measured lower strength of water entrained mortar compared to the reference mortar may also be caused by moisture conditions. Due to low permeability of the samples, ingress of curing water into the samples will be limited. As a result, the samples will have different moisture conditions when tested for compressive strength. The samples with entrained water will have a greater RH as compared to the reference mortar that suffers self-desiccation [16]. Barlett and MacGregor [17] reported the effect of moisture condition on the compressive strength of a well-hardened HPC. The average strength after drying in laboratory air with $RH < 60\%$ was 98MPa whereas it was 76MPa after soaking in water, i.e., a reduction of 22% as compared to the dry condition

CONCLUSIONS

- Shrinkage in mortars have been successfully mitigated by internal curing using SAP. Shrinkage values have been reduced by approximately 770 μm , 600 μm and 305 μm at w/c ratios of 0.38, 0.4 and 0.42 respectively. This shows that internal curing is more effective at lower w/c because shrinkage is more dominant in such mixes
- Maximum Expansion of 80 μm , 190 μm , and 280 μm was observed in SCM formulations with w/c ratio 0.38, 0.4, 0.42 respectively. This may be due to crystallization pressure of expansive species like calcium hydroxide crystals or the absorption of water by the CSH gel as explained by Powers.
- Although extra water was added to cater for the absorption of SAP particles, the SP demand of each SAP containing formulation was increased to achieve the desired target flow. Further study is required to understand the rheological behavior of SAP containing formulations.
- The compressive and flexural strength of the SCM formulations decreased by approximately 44% and 42% respectively. This is because of overall increase in porosity and the size of largest defect in matrix.

RECOMMENDATIONS

- The use of SAPs to mitigate early age shrinkage should be extended to SCC systems.
- The amount of SAP in the cementitious system should be such that the total W/C ratio (i-e $W/C_{\text{BASIC}} + W/C_{\text{ENTRAINED}}$) should be at least 0.42, for complete mitigation of early age shrinkage.
- The effect of SAPs with secondary raw materials should also be studied.
- Smaller size of SAP particles should be used which will form smaller pore sizes by the swollen SAP particles, this will minimize the maximum pore sizes in the system thus the strength reduction will be minimized.
- SAP should tested for their effect on freeze thaw resistance. When water filled SAP particles lose their water they form air voids which can be useful in cold regions where we have problem of freeze thaw effect.
- SAPs should be studied for their carrier ability of concrete healing bacteria in self-healing cementitious systems.

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