Properties Enhancement of Super Absorbent Polymers (SAPS) Modified Self-Compacting Cement Pastes (SCPs) By Nano Silica (NS) Addition

MS STRUCTURES THESIS DISSERTATION

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This is to certify that

Thesis entitled

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THESIS ACCEPTANCE CERTIFICATE

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Dedication

I dedicate this research to
Dr. Muhamad Usman my supervisor,
And
To my parents

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I am thankful to Allah Almighty, The Most Gracious and The Most Bountiful, who gave me the strength to complete this dissertation. After that, I would like to express sincere gratitude to my mentors and advisors Prof. Dr. Muhammad Usman and Prof. Dr. Syed Ali Rizwan for their continuous support, guidance and valuable discussions on the topic throughout the research phase.

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ABSTRACT

In this exploratory study, the effect of super absorbent polymers (SAPs) on the properties of self-compacting pastes (SCPs) incorporated with nano silica (NS) has been investigated. NS was added to cement pastes containing SAPs in varying amounts of 1 %, 2% and 3%. SAPs were found out to be successful in mitigating shrinkage in all formulations, however they were more effective in formulations without super plasticizers (SPs). SAPs reduced 100% shrinkage in formulations without SPs compared with 75% in SCPs. SAPs particles reduced flow, increased air content and also reduced strength slightly due to formation of macro-pores. NS was beneficial in improving the mechanical properties of the SAP modified cement pastes particularly at early ages. SAPs improved the hydration and microstructure of pastes especially in its vicinity while addition of NS resulted in further dense microstructure. The dense microstructure of the NS modified pastes compensated for the macro pore formation associated with SAP incorporation, leading to strength increase. With NS, there was better bonding of the SAP particles in the matrix, due to the enhanced interface. The reduced Ca(OH)2 content in NS modified samples showed increased pozzolanic activity associated with NS in cement pastes

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LIST OF NOTATIONS\ABBREVIATIONS

ACI	American Concrete Institution
ASTM	American Society of Testing Of Materials
SCP	Self-Compacting Paste
SCM	Self-Compacting Mortar
SCC	Self-Compacting Concrete
HCP	High Performance Concretes
XRD	X-ray diffraction
XRF	X-ray Fluorescence
SP	Super plasticizer
NS	Nano Silica
W/B	Water to Binder Ratio
SCCs	Self-Compacting Cementitious Systems
OPC	Ordinary Portland Cement
SEM	Scanning Electron Microscope
SAPs	Super Absorbent Polymers

CHAPTER 1

INTRODUCTION

1.1 Background

Concrete is a composite material made by mixing cement, sand, aggregate and water. Concrete has become the most versatile and widely used construction material due to its strength, economy, durability and the ability to cast into any shape. An estimated consumption of concrete was 35-50 billion tones in 2014 compared to less than 2 billion tones in 1950[1,2].

Along with usage, the performance of concrete is greatly improved with the passage of time. Many chemical and mineral admixtures are being used to modify and enhance fresh and hardened properties of concrete. One of the challenges we face is efficient placing of concrete as skilled labor is required for compaction and failure to do so reduces strength, durability and aesthetics of concrete. Furthermore, it is difficult to obtain homogeneous mix as there is no particular standard for mechanical vibration and can produce noise pollution. All of these issues can be resolved by using Self Compacting Systems achieved by increasing the dosage of super plasticizers. The use of mineral admixtures at low w/c ratio 0.25-0.35 modifies the hydration kinetics and internal pore structure of concrete causing it to undergo bulk shrinkage [3]. This shrinkage if unrestrained can cause cracking and reduce strength of concrete. Super absorbent polymers (SAPs) act as water reservoir and can mitigate shrinkage in concrete systems by employing the concept of internal curing.

1.2 Research Significance

Although few studies are carried out on SAPs incorporated SCCPs but there is very minimal data on SAPs interaction with constituents other than cement (i-e mineral and chemical admixtures). Similarly, there are no studies undertaken on the use of NS in SAPs incorporated SCCPs. This study tries to bridge these research gaps as it focuses on interaction of covalently crosslinked suspension polymerized SAPs with SPs and various dosages of NS in Self compacting and conventional cement paste systems. The absorption capacity of SAPs was calculated in different liquid environments. The response of paste system including early age shrinkage, Air content, Flow tests, mechanical performance and microstructure was investigated.

1.5 Research Objectives

The primary objectives of this research are as follows:

- To study the effect of super absorbent polymers (SAPs) and nano silica (NS) on properties of self-compacting and conventional cement pastes.
- To offset the strength reduction effect of SAPs using NS

1.4 Research Methodology

The relevant literature review was conducted prior to testing in lab. Having gained a deeper insight into the topic in question, some elementary tests were conducted on the research materials to see how cements, admixtures and SRMs in question behave in moisture and varying temperature conditions. Next characterization tests such as XRD, XRF and PSD were conducted to find out the type of elements/compounds and particle sizes that are present in the research materials. After these tests, the main laboratory tests were carried out. These included tests for flow, setting times, density, total shrinkage, air content and the compressive strengths. Finally, detailed discussions with reference to relevant literature review and the researcher’s own understanding and knowledge about the problem statement are presented.

1.6 Thesis Organization

The first chapter gives an introduction to the thesis topic. The next chapter presents the literature review. The third chapter presents various standard methods and apparatuses employed for conduction of laboratory tests. The fourth chapter presents discussions and reasoning. The fifth chapter gives conclusions and recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 Super Absorbent Polymers

Superabsorbent polymers (SAPs) have this interesting property to absorb significant amount of water from their surroundings, resulting in the formation of hydrogel that is up to 99% water [7].SAPs have been use d worldwide in various application because of this property.

SAP can absorb up to 1500 times their own weight due to osmotic pressure, although this value is remarkably reduced in cementitious systems to about 10-20 g/g or their weight due to high Ca^{+2} ion concentration, in the resulting fluid which is still higher than swelling capacity of any other absorbing material [8]. Absorption capacity depends on properties of SAPs and ionic composition of exposure aqueous solution.

SAPs are classified mainly on the basis of manufacturing process i-e solution polymerized and solution polymerized.

2.1.1 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 2.1.

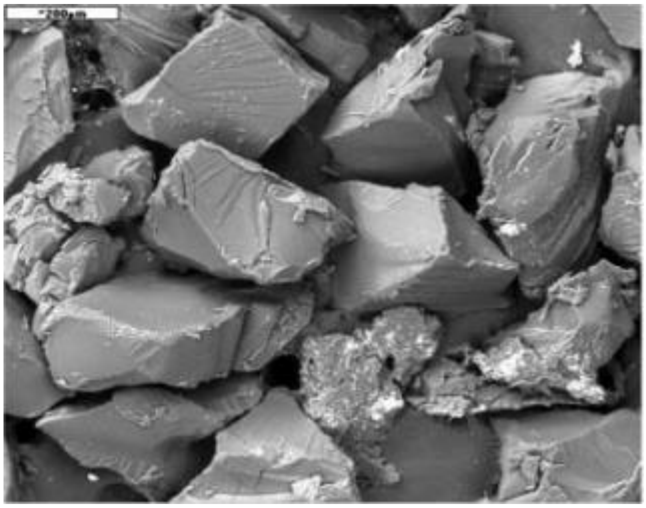

Fig. 2.1 Crushed Particles of Solution Polymerized SAPs [9]

2.1.2 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 2.2.

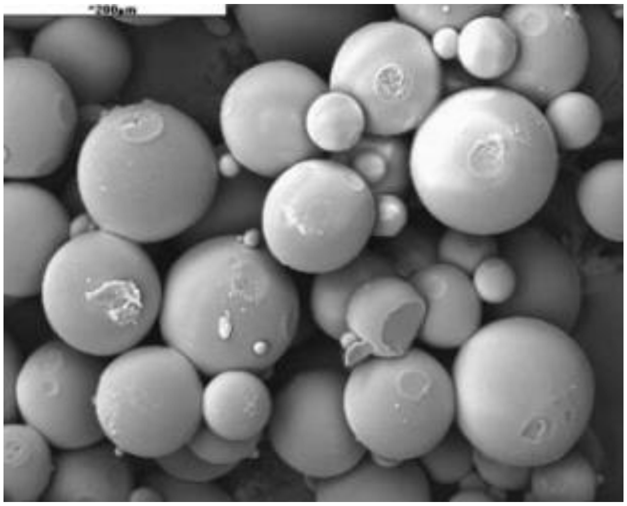

Fig. 2.2 Spherical particles ofSuspension Polymerized SAPs [9]

2.1.3 Dry State of SAPs

SAPs are highly hygroscopic in nature and can absorb moisture quickly if exposed to humid conditions. SAPs can be heated in an oven at 105 C which removes absorbed water from the sap and dry sap can be obtained for further use. This method however is not very efficient as loss of water from SAPs is a slow process because of its high absorption capacity. One possible solution is to increase the heating temperature but as we go above 180 C, the polymeric chains of SAPs particles begin to break. These issues make oven drying inefficient.

To overcome this problem SAPs were kept in desiccators with silica gel for more than 24 hours. Silica Gel acts as desiccant and absorbs water from the dissector causing RH to fall. This potentially leads SAPs to lose absorbed water. These dry SAPs were further used in the research to avoid any error in the experiments.

2.1.4 Application of SAPs

SAPs are nowadays used in many applications because of their unique ability to absorb significant amount of water. They are currently being used in diapers[10], sanitary napkins[11] and biomedical purposes (i-e tissue engineering, wound healing, drug release etc) [12–14]. They are also being used in the field of agriculture as soil nutrient and water reservoir in dry areas [11,15].

It was only a matter of time as SAPs found its way in cementitious systems as an additive[16]. SAPs are being used to mitigate autogenous shrinkage[17], improving freeze thaw resistance [18,19], promoting self-healing[20] and self-sealing of concrete[21] and also for modifying rheology of cementitious system[4]

2.1.5 Absorption Mechanism of SAPs

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[22]. Figure 2.3 shows the schematic on polymer network.

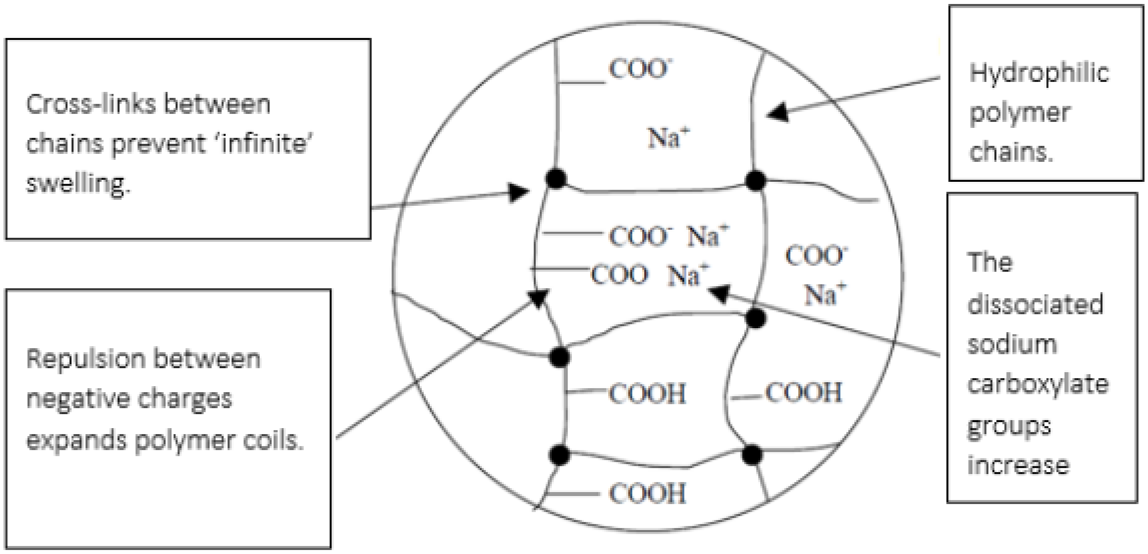

Fig. 2.3 Diagrammatic representation of part of the polymer network[22]

This polymeric network is hydrophilic i-e water loving as it contains water loving COOH groups. When SAPs particle come in contact with water, there is a polymer/solvent interaction. Hydration and Hydrogen bonding are two of these interactions.

2.1.5.1 Hydration

The figure 2.4 shows when the hydration reaction occurs, how the interaction between the solute ions, the COO- and Na+ ions and the polar water molecules occurs.

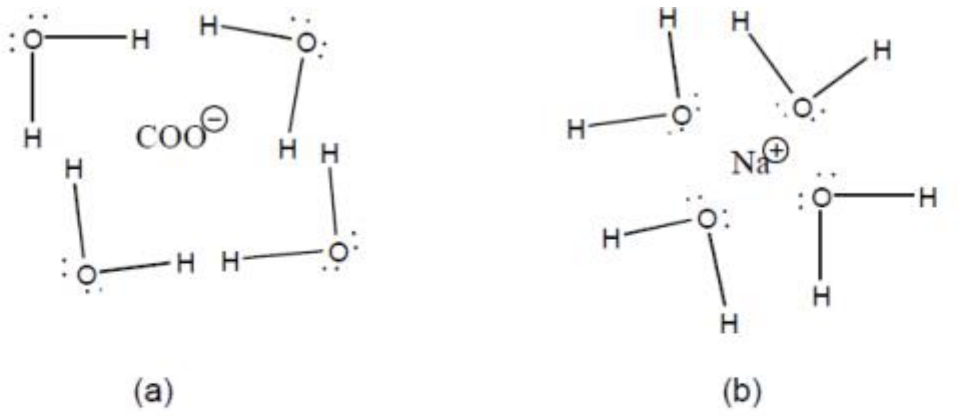

Fig. 2.4 Interaction of ions of a solute with molecules of a solvent[22]

2.1.5.2 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 electro-negative elements like nitrogen, fluorine and oxygen. The attraction between hydrogen and the lone pair of electrons form a strong bond.

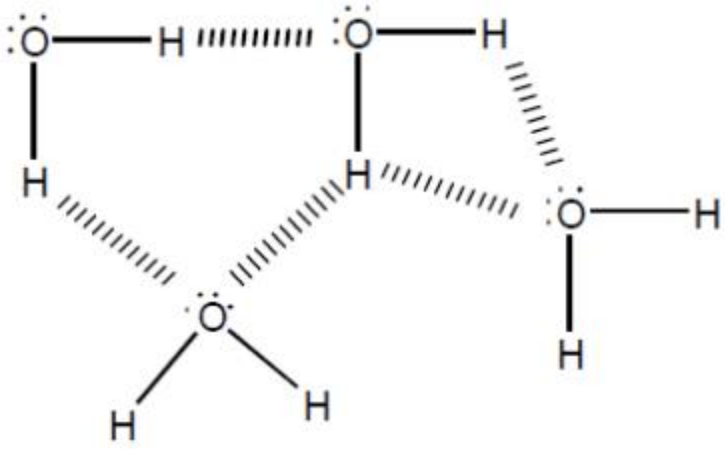

Fig. 2.5 Hydrogen bonding of water molecules[22]

2.2 Silica Nano Particles (NS)

Silica products are manufactured widely for many industrial applications. Amorphous silicas find their usage as thixotropic material in liquids such as paints, thermosetting resigns and printing inks, reinforcement of elastomers products and as fillers in silicone rubber[23]. Demand of special forms of silica such as fumed silica, silica gel, silica sol and precipitated silica was 1.9 m metric tons in 2009 and it rose to 2.7 million metric tons in 2014 worth $5.8 billion[24]. It was just a matter of time that NS found its application in cementitious systems as a highly reactive pozzolanic material. NS as of time being is the most common used nano particle in cementitious systems and have gained importance in their usage in advanced concrete materials. [25,26]. They greatly improve the strength, viscosity, and durability of the system mainly because of their pozzolanic reaction with CH which leads to the production of CSH gel. Several other mechanisms are also studied in literature which describe their mode of action in cementitious systems[27,28].

2.3 Shrinkage of Paste System

2.3.1 Background

Shrinkage refers to reduction of volume in cementitious systems. This behavior is accompanied by several mechanisms operating simultaneously in the concrete matrix. Theses mechanisms can be drying shrinkage, plastic shrinkage, chemical shrinkage or autogenous shrinkage. It is important to recognize and evaluate the respective mechanisms but at the end Structural engineers are more interested in total shrinkage and not the individual mechanisms contributing to it. Certain design codes also have limitations on total shrinkage of the structure.

2.3.2 Chemical Shrinkage and Autogenous Strain

Jensen and Hansen [24] defined chemical shrinkage as “the volume reduction associated with the hydration reactions in a cementitious material” and autogenous strain as “the bulk strain of a closed, isothermal, cementitious material system not subjected to external forces” Chemical shrinkage can be contractive or expansive. The expansive nature is brought by the production of expansive ettringite or calcium hydroxide crystals but either reaction is accompanied by the chemical shrinkage. It has been studied in literature that autogenous shrinkage consists only a small portion of chemical shrinkage and as time goes on their path deviate[29]. The relationship between the two is not proportional and there is no simple relationship that exists between them. When w/c ratio becomes less autogenous shrinkage start to become significant as water is drawn rapidly from the matrix and demand for more water creates fine capillaries. The surface tension within the capillaries increases the autogenous deformation. This phenomenon is also known as self-desiccation.

2.2.3 SAPs in mitigating autogenous shrinkage

In high performance concrete systems, trend is shifting to lower water to cement ratios incorporating mineral admixtures to enhance its properties. With all the benefits in strength and durability, these enhancements have increased the autogenous shrinkage of concrete causing cracking and corrosion problem. In order to mitigate autogenous shrinkage, convention curing is not enough as water has to be drawn into the capillaries to negate autogenous deformation. Several different materials are discussed in the literature[30–33] which can mitigate shrinkage by acting as an internal curing agent but the use of Super Absorbent Polymers and Light weight aggregates (LWA) particles are considered to be most practical in cementitious systems[33]. The usage of LWA reduces shrinkage but also has its major drawbacks such as difficulties in controlling consistency of paste and significant reduction in strength[17].

2.3 Self-Compacting Concrete Systems (SCCs)

In 1980s the Japanese were facing some serious challenges with regard to the durability and serviceability of the concrete structures. Mechanical vibration was problematic as skilled labor was required and even then, it was difficult to place conventional concrete in places with overcrowded reinforcement such as in heavily reinforced piers, foundations, Tunnel linings etc.

Because of these issues with conventional concrete Japanese came up with the idea of Self Compacting Cementitious Systems (SCCS). SCCS has the ability to flow under its own weight so that it is able to fill small interstices of formwork without the need of vibration and can be pumped to long distances and heights. The result is homogenous, durable concrete having almost same properties as conventional concrete without the need of vibration. ACI committee 237R-07[23] defines SCC as

Self-compacting concrete (SCC) is a highly flowable, non-segregating concrete that can spread into place, fill formwork and encapsulate the reinforcement without any mechanical consolidation.

SCCS differs from conventional concrete because of its flowability characteristics. This flowability is achieved by using a chemical admixture known as superplasticizer. SCCS can be categorized in three systems.

- Self-compacting paste systems
- Self-compacting mortar systems
- Self-compacting concrete systems

2.3.1 Self-Compacting Paste System

SCPs act as medium of carrying aggregate phase and proves to be important in determining the overall attributes of the system[34]. Majority of studies are performed on paste system as introduction of aggregate phase can interfere with some test results. Because of these reasons research was performed on SCPs as optimization of SCPs would eventually improve the quality of overall system.

2.3.3 Super plasticizer (SP)

ASTM C 494-92 refers to superplasticizers as “water-reducing, high range admixtures”, classifying them as Type F admixtures or when retarding effect is also induced, as Type G admixtures[35]. SP consist of long molecule chains having negative charge. When SP is added in cementitious system negative charge is induced on cement phases causing repulsion between cement particles. This results in deflocculating and dispersion of cement particles. It can be stated therefore that the presence of SPs not only increase the fluidity of the mix it also makes it more durable as cement particles are more dispersed in the matrix.

CHAPTER 3

EXPERIMENTAL PROGRAM

The overview of research has been established in Chapter 1 and 2. In this chapter, the experimental program conducted at NUST Institute of Civil Engineering has been explained in detail.

3.1 Materials

3.1.1 Cement

Best Way Grade 53 cement is used during the course of study. Fresh OPC 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 in Table 3.1.

Table 1 XRF results of OPC

Major Oxides	Percentage (%)
SiO_2	20.51
Al_2O_3	5.25
Fe_2O_3	3.39
CaO	61.53
MgO	2.33
K_2O	0.77
Na_2O	0.32
SO_3	2.8

3.1.2 Super Absorbent Polymers

Suspension-polymerized covalently cross-linked acrylamide/acrylic acid copolymer 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.

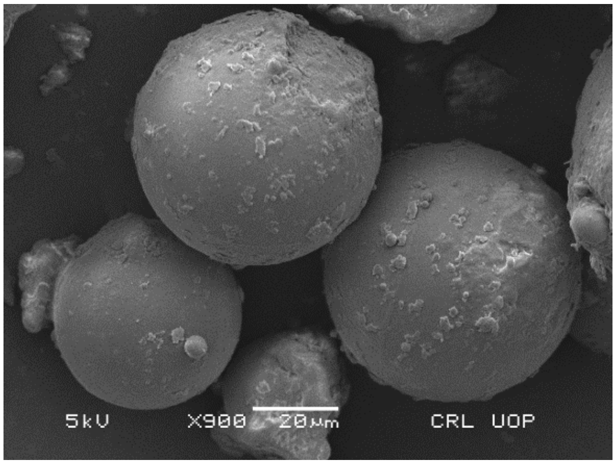

Fig. 3.1(a) SEM image of used SAP

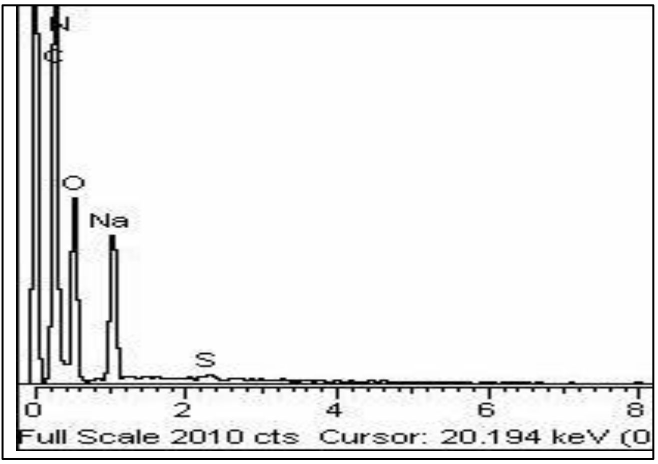

Fig. 3.1(b) EDX analysis results of used SAP

Scanning electron microscopy with EDX tests were performed on SAP to get an idea of the shape, size and chemical composition of SAPs particles. SEM images shows that SAPs used are suspension polymerized. 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.

3.1.3 Super Plasticizer

Meflux is a third-generation high-performance super-plasticizer used in cement based mixes. Meflux 2651F manufactured by BASF Germany is used in this study. It is poly-carboxylate ether (PCE) powder optimized for use as a plasticizer and water reducing agent and ensures development of high early strength. When used in right proportions, it reduces bleeding and segregation.

3.1.4 Nano Silica

Nano fumed silica was acquired from Bestway Pakistan and was kept in sealed containers to avoid lumps formation. In order to study morphology of Nano silica, TEM and X-Ray Diffraction (XRD) tests were performed. NS sample was scanned from 10° to 70° at scanning speed of 10°/min. The result pattern in Figure 3.2 shows that it is poorly crystalline and possesses high pozzolanic activity.

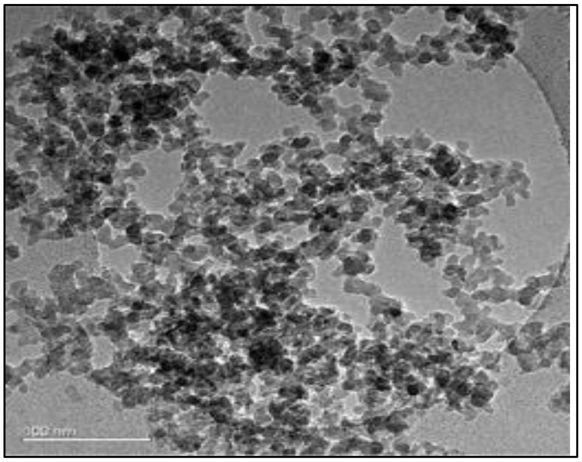

Fig. 3.2 TEM image of NS particles

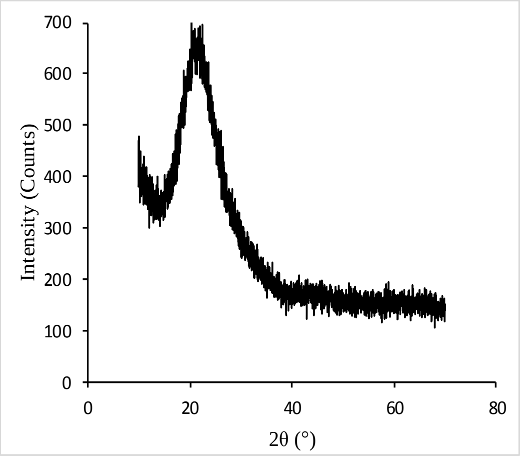

Fig.3.3 XRD pattern of NS

3.2 Formulations and Mixing Regime

3.2.1 Formulations

A total of ten formulations were studied having W/C ratio of 0.3. An additional 0.054 entrained water/ratio ($(W/B)_e = 0.054$) was incorporated in formulations containing SAP. This value was calculated using powers model [4] and is basically 0.18 times the basic w/c ratio of 0.3. This extra water added is referred to as entrained water in rest of the paper. First five formulations mentioned are conventional formulations followed by five SCP formulations in the next section. SAPs were kept in desiccators for more than one day to ensure its dry state before usage.

Table 2. Formulations Studied

Formulations	**$(W/C)_t$**	**SP**	**SAP**	**NS**
CC	0.3	0	0	0
CNS0	0.35	0	0.49	0
CNS1	0.35	0	0.49	1
CNS2	0.35	0	0.49	2
CNS3	0.35	0	0.49	3
SC	0.3	0.14	0	0
SNS0	0.35	0.41	0.49	0
SNS1	0.35	0.69	0.49	1
SNS2	0.35	0.93	0.49	2
SNS3	0.35	1.16	0.49	3

3.2.2 Mixing Regime

The ingredients were mixed in the Hobart mixer. Five minutes of wet mixing time was decided as it was observed that almost 50% of the swelling of SAPs occur in first five minutes [38]. All dry constituents were first mixed together for 30 seconds followed by 5-minute mixing of the pastes. Water was added in two steps to ensure homogeneity of mix and dispersion of NS. The breakdown of mixing recipe is as follows

- Manual dry mixing of all ingredients.
- Addition of ¾ water followed by slow mixing (145 rpm) for 90 sec.
- Addition of ¼ water followed by fast mixing (285 rpm) for 210 sec.

3.3 Absorption Capacity of SAPs

Absorption capacity is 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[8]

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. Tea-Bag method has shortcomings when measuring absorption capacity of SAPs in cementitious environment. Graduated cylinder method was used to determine absorption capacity in this study as it is most appropriate method for SAPs having particle size less than 100.

In order to simulate cementitious environment, cement slurry was made by adding 20g of cement in 200 g of water. This solution was stirred and subsequently filtered to get the pore fluid. Three different liquid environments (tap water, deionized water and cement slurry) were used to study the effect of PH and ionic composition on absorption capacity of SAPs.

3.3.1 Method of Graduated Cylinders

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 (V1) is completely filled and mass m1 of SAP is noted. Then a known mass m2 of SAP is filled into the cylinder (in our case, a beaker). Three types of fluids have been used tap water, De-ionized water and cement slurry. Each fluid is poured into the beaker containing mass m2 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 v2 of gel was noted[8]. 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.

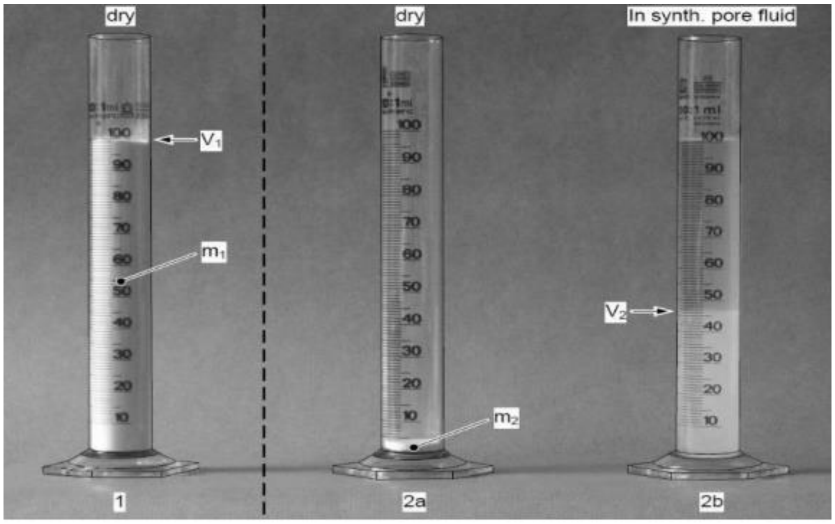

Fig. 3.3 Graduated Cylinder method steps [31]

Fig. 3.4 Saturated SAPs after mixing

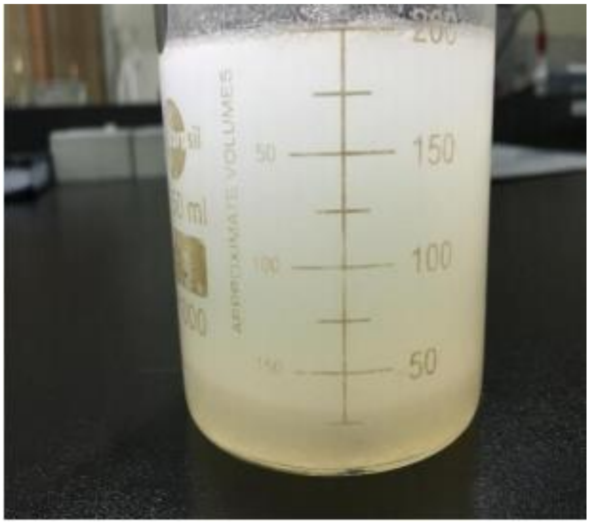

Fig. 3.5 Precipitation of saturated SAPs

Absorption capacity was calculated using equation (1)

$$K = \frac{\rho_{water}}{\rho_{SAP}}\left[\frac{V_2}{V_1} . \frac{m_1}{m_2} - 1\right] \tag{1}$$

Where K = Absorption capacity in (g/g).

ρ_{water} = Density of water 1g/cm3

ρ_{SAP} = Dry density of SAP

V_1 = Volume of dry SAP completely filling the cylinder.

m_1 = Mass of dry SAP completely filling the cylinder.

m_2 = Known mass of dry SAP placed in the cylinder.

V_1 = Volume of swollen SAP

3.3.2 Dry Density of SAPs

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.

3.4 Setting Times of paste systems

The water demands and se determined using the Vicat Apparatus as per EN-196-1. The zero error is eliminated by setting the bottom-top scale to zero over the base plate. The plunger for finding the normal consistency was used for initial setting times, the initial set needle is penetrated after every 15 mins. When the needle penetration reaches 5 ± 1 mm from the bottom, initial set is assumed to have occurred. For the final set, the ring impression is observed until it vanishes on the paste surface.

Fig. 3.7(a) Vicat Needle for Initial Set

Fig. 3.7(b) Vicat Needle For Final Set

Fig. 3.7(c) Setting time test in progress

3.5 Flow Measurements:

The Super Plasticizer demand was determined using Hagerman’s cone measuring 6x7x10 cm3 for SCP formulations. SP dosage was adjusted by trial and error until the target flow of (30 ± 1) cm was achieved as this value helps in better self-consolidation. To further asses the flow characteristics of the cement pastes T30 cm was recorded using a stopwatch

Fig. 3.8 (a) Hagerman’s Flow Apparatus

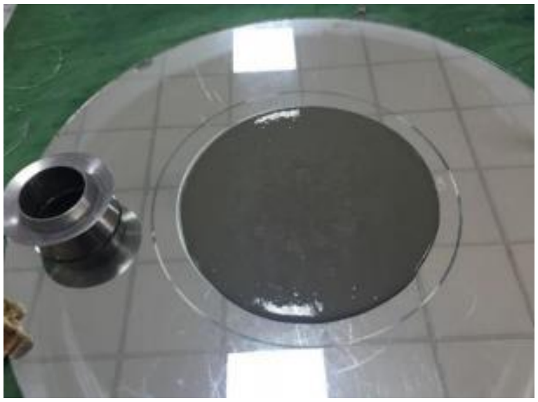

Fig. 3.8 (b) Target flow of a typical formulation at 30 ± 1 cm

3.6 Casting And Curing

Prism moulds of 40x40x160 mm^3 were used to cast paste samples as per DIN 196. In order to study both internal curing and strength degradation effect of SAPs, both air curing and water curing was employed. Samples were taken out of the moulds after 24hrs and then were put in air or water curing tank

Fig. 3.9 (a) 160x40x40 mm moulds (Empty)

Fig. 3.9 (b) Fresh paste filled in the moulds

3.7 Strength Testing

Compression strength were measured using a dual chamber strength testing machine. Results of strength at ages seven, fourteen and twenty-eight days were recorded. For compression, a uniform loading rate of 0.25 kN/sec and for flexure a uniform loading rate of 0.025 kN/sec was adopted. First of all, flexure testing was done on two samples leaving 4 samples for compression. 3 samples were than selected for compression to ensure that results are reliable.

Fig. 3.10(a) Assembly for Compression in UTM

3.8 Shrinkage

Engineers are interested in total shrinkage of the system and not the individual mechanisms contributing to it. In order to measure total shrinkage of the formulations a modified version of German classical “Schwindrinne” channel apparatus was used. Fresh paste after mixing were placed in the apparatus and data was recorded for 48 hours. The resulting response of the formulations were then plotted. Vicat final setting times of the respective formulations were also plotted to give a starting mark of hardening process

Fig. 3.11(a) Shrinkage channles

Fig. 3.11(b) Shrinkage channels with samples

3.9 X-Ray Diffraction Analysis

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[37].

In our case XRD was used to analyze the composition of hydration products of selected samples. Water cured samples at 28 days were dried at 50 C for 12 hrs and then crushed in powdered form. XRD was performed using machine having Copper as target. The scan range was 10-70 at 0.02/step

3.10 Thermogravimetric Analysis

Thermo-Gravimetric Analysis (TGA/DTG) was carried out to investigate the pozzolanic activity of NS in hardened paste samples. (TGA/DTG) of powdered samples were performed from 25°C to 1100°C at 10°C min^{-1}.

3.11 Scanning Electron Microscopy

In order to study microstructure and macro pores of cement paste system, SEM studies were carried out using scanning electron microscope (SEM, JMS-5900, JEOL, Tokyo, Japan). Small fractured sample were taken and hydration was stopped using ethanol before testing. Samples were coated with 20nm of gold to make them conductive.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 SAP Properties

4.1.1 Dry Density of SAPs

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 equal to the one mentioned by Professor O.M.Jensen. The results are shown in Table-4.2

Table. 3 Dry Density of SAPs

Trials	Mass Of SAPs (g)	Volume (cm3)	Density (g/cm3)
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	1.5
			P_{SAP} (dry) =1.5 g/cm3

4.1.2 Absorption Capacity of SAPs

Considering the results of dry density, absorption capacity was calculated using graduated cylinder method as described in chapter 3. Three different liquid environments were considered for which results are shown in graph below.

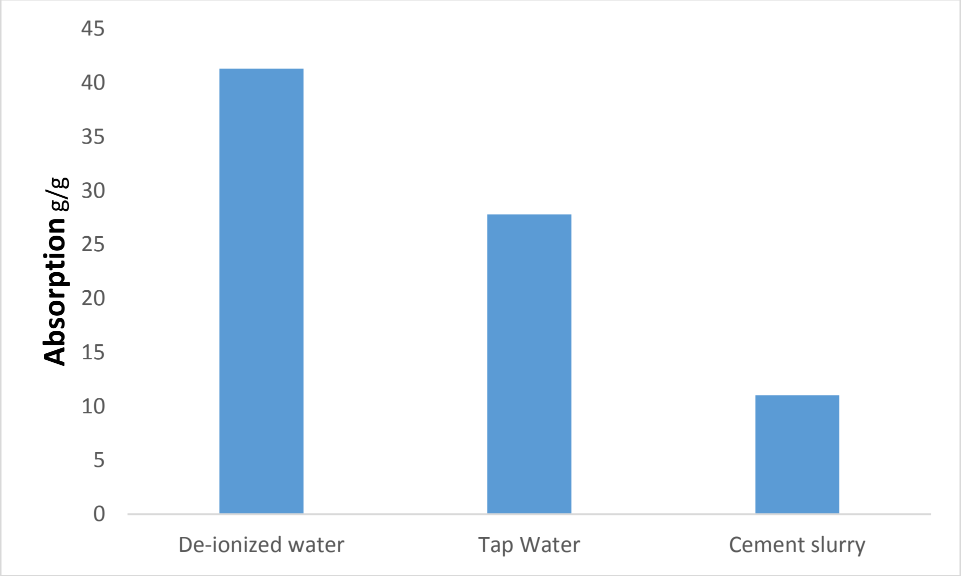

Fig. 4.1 Absorption capacity of SAPs in different environment

It can be seen that SAPs absorption capacity considerably reduced in cement slurry. This is due to the presence of ionic species Ca+ in cement slurry. 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[8]. As cement slurry was assumed to represent cementitious environment, absorption capacity of 11 g/g was used in further study.

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4.1.3 Required SAP demand

SAP demand was calculated using the following equations.

$$(W/B)_e = K(SAP/B)$$

Where

- (W/B)e is the entrained water/binder ratio
- K is the absorption capacity of SAPs in g/g
- SAPs/B is the ratio of required SAPs to binder

Now according to power for complete hydration at W/B < 0.36

$$(W/B)e = 0.18(SAP/B)$$

Using this equation, we get the value of 0.054 which is entrained W/B ratio. This value is then divided by absorption capacity i-e 11 g/g to get 0.49 % SAP weight of cement.

Table 4 Required SAP demand

(W/C)b	(W/C)e	(W/C)t	SAP Demand
0/3	0.054	0.354	0.49%

4.2 Super Plasticizer Demand

The amount of SP required to achieve the target flow and T30 were according to the protocol discussed in chapter 3. Results are shown in Fig. 4.2.

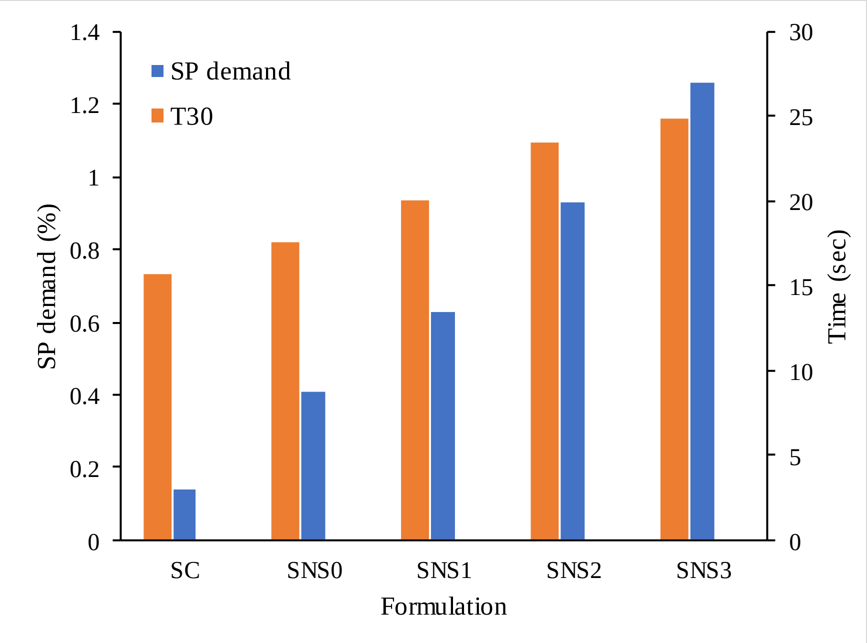


Fig. 4.2 SP demand and T30 of SCP formulations

Incorporation of both SAPs and NS lead to significant increase in the SP demand of the system. Even though additional water was added for SAPs it caused a reduction in workability. This may be caused by the presence of SAPs as a hydrogel in the matrix. Because of this property SAPs are used for modifying rheology of concrete systems [12]. NS increased the SP demand and flow time comparatively more than SAPs because of its high surface area and polar interactions of with positively charged cement particles. It is important to note that both SP demand and T30 increase non-linearly with increase in NS content which should be considered before using NS in cementitious systems.

4.3 Setting Times of Paste System

Initial and Final Setting times of all formulations were determined using Vicat Apparatus. Results of all formulations are displayed in Fig. 4.3 and Fig. 4.4.

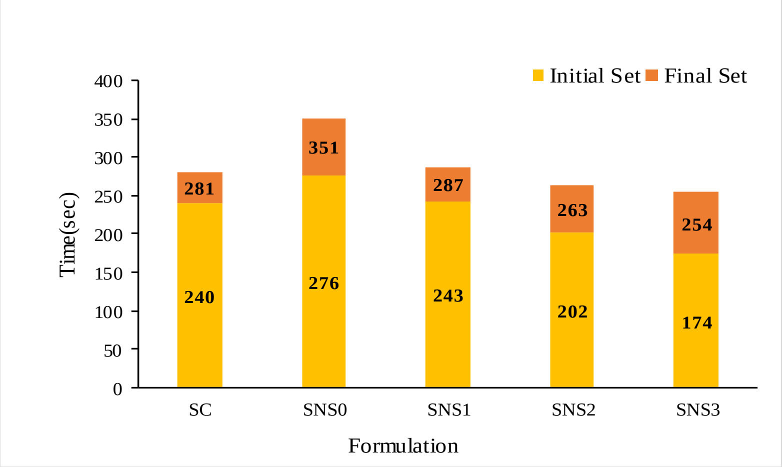


Fig. 4.3 Initial and Final Set of SCP Formulations

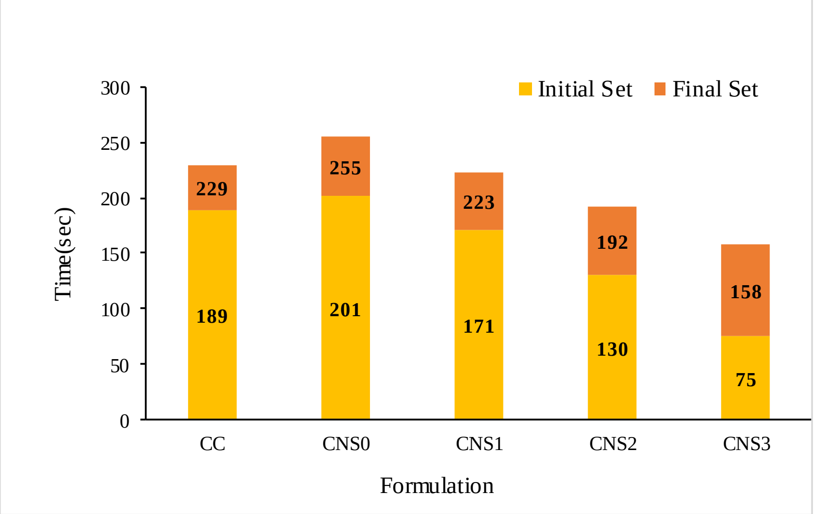


Fig. 4.4 Initial and Final Set of Conventional Formulations

It can be clearly seen that introduction of SP has a retardation effect on cement paste. This observation is supported by previous studies as SP 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 [8] resulting in slow building up of their concentration, thus delaying the hydration process.

However, with the addition of NS, acceleration was observed in all formulations. It was noted that addition of NS shortened Initial set time comparatively more than the final set. NS modifies the hydration kinetics by increasing the surface energy, as a result speeding the hydration reaction. Both C-S-H and $Ca(OH)_2$ are produced at a faster rate contributing to initial early set. This reduction in setting times becomes more apparent when amount of NS is increased.

4.4 Early Age Shrinkage of Paste System

The shrinkage responses of both SCP and Conventional formulations were plotted against time. Results are shown in Fig 4.5 and Fig 4.6

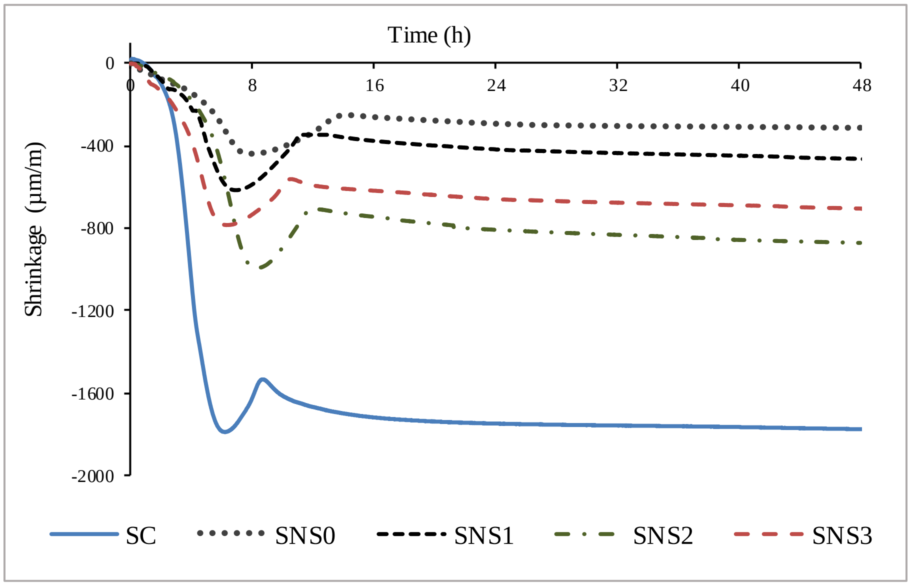


Fig. 4.5 Early age shrinkage of SCP formulations

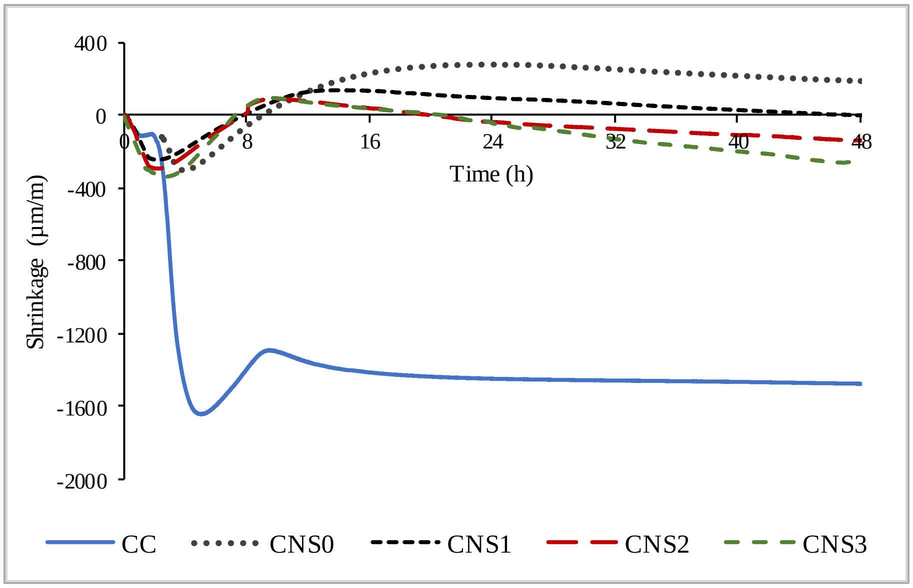


Fig. 4.6 Early age shrinkage of Conventional formulations

It can be seen that introduction of SP increased the shrinkage in control formulations. This can be attributed to increased heat of hydration caused by de-flocculation of cement particles. It can be seen in the results that SAPs were efficient in reducing total early shrinkage in all formulations by acting as an internal curing agent. SAPs were more efficient in the conventional formulations which suggest that they have some kind of interaction with the SPs particles present in SCP formulations. SAPs reduced 100% shrinkage in the control formulation without SP compared to 75% in SCP control formulation.

Total shrinkage increased with the increase of NS content because of the start of the pozzolanic reaction. NS reacts with $Ca(OH)_2$ to produce more compact and dense C-S-H gel which promotes high early age shrinkage. It is important to note even after the addition of NS up to 3%, Shrinkage is not affected too much compared with control formulations.

Expansion is observed in all samples and is more prominent in the conventional formulations. Similar sort of expansion behavior was observed by Lura et al[39] and was related to the size and higher absorption capacity of SAPs used. Furthermore expansion can also be due to the growth of expansive CH crystals and reabsorption of bleed water as mentioned in the literature [40]

4.5 Air Content of SCP System

Air content of fresh SCPs was determined using Luftgehaltspruefer testing apparatus having 1-liter capacity using the pressure method. The results are shown in Figure 4.7.

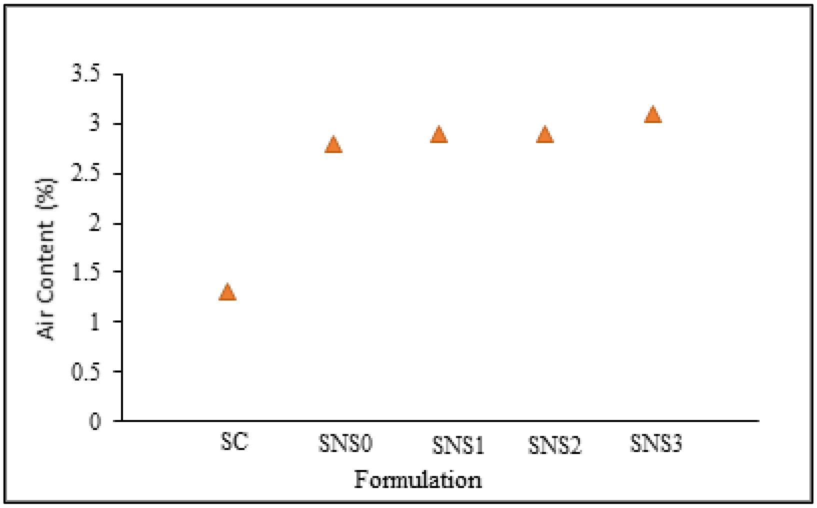


Figure 4.7 Air content of SCP formulations

Introduction of SAPs increased the air content of the SCP system as they induce pores in the system. NS addition has no significant effect on the air content of fresh SCP sample. A slight increase in the air content is noted which can be attributed to the increased amount of SP when NS percentage is increased.

4.4 Compressive Strength of paste system

Results of strength at ages seven, fourteen and twenty-eight days are shown in Figures 4.8.

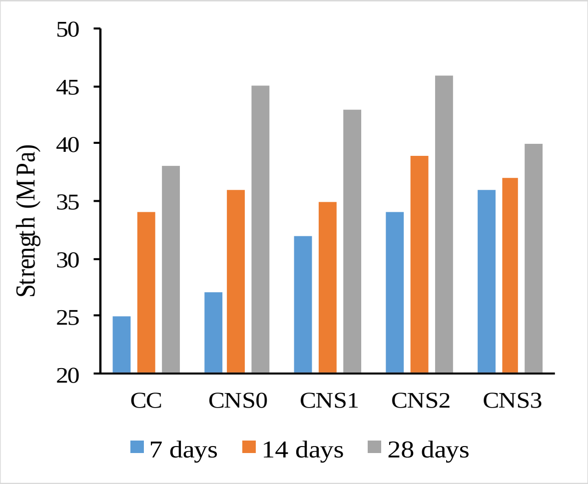


Fig. 4.8 (a) Compressive strength of Air cured Conventional formulations

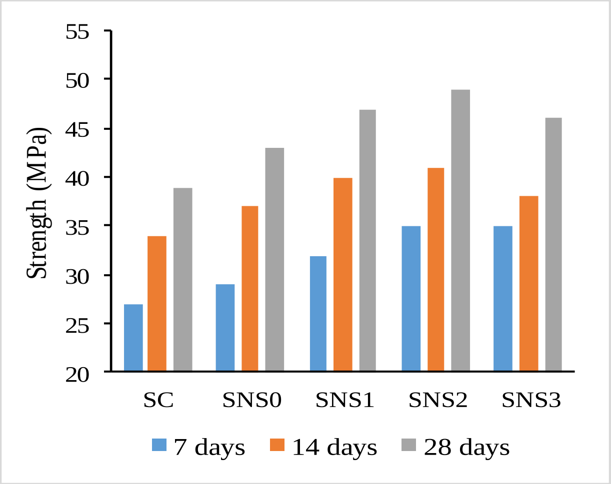


Fig. 4.8 (b) Compressive strength of Air cured SCP formulations

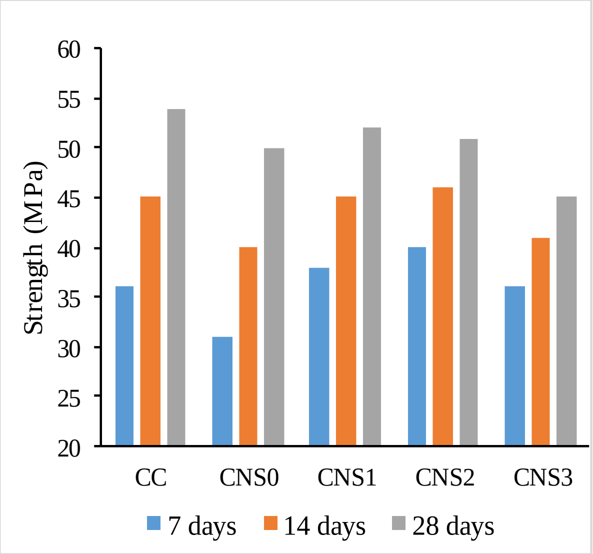


Fig. 4.8 (c) Compressive strength of Water cured Conventional formulations

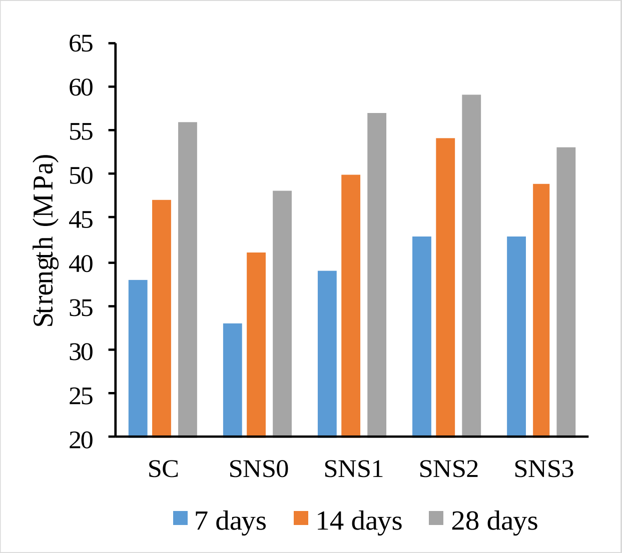


Fig. 4.8 (d) Compressive strength of Water cured SCP formulations

Introduction of SAPs reduced compressive strength of the paste by almost 17% in water curing environment, however, the results were contradictory in air cured samples as almost 30% increase in strength is noted. SAPs have two major effects on microstructure as it improves the hydration reaction of the system by acting as an internal curing agent which affects the strength positively. SAPs also induce voids in the matrix and increase the total porosity causing a strength degradation effect [4,38].

Internal curing is inefficient in water curing environment as ample water is available for hydration in all formulations with and without SAPs. The only criteria which define strength in water cured samples are the induction of pores in the matrix because of SAPs as shown in the SEM images of samples containing SAP. This is the reason why reduction in strength is reported in water cured samples. In the Air cured samples improvement in strength can be attributed to the internal curing ability of SAPs, which improved the microstructure and surpassed the negative effects of pore formation.

Introduction of NS improved the strength in all formulations by acting as a pozzolanic material and also by physical filling effect. This effect was more prominent in SCP formulations because of the presence of SP which causes dispersion of cement particles. NS was also more effective in water curing environment compared with air curing as ample water is available for complete hydration when samples are water cured.

4.5 XRD of Hardened Paste

XRD was used to qualitatively analyze the effect of NS on mineral composition of cement paste. Figure 4.9 shows the XRD results of SCP formulations. It can be seen clearly that addition of NS did not change the hydration products of the SCPs, however intensity peaks of the products changed significantly. The main intensity peak of $Ca(OH)_2$ at about 18° 2θ angle was tested and showed a decrease of 59.9%, 63.1% and 57.9% with the replacement of 1%,2% and 3% of NS at 28 days respectively. This shows that more $Ca(OH)_2$ was consumed by NS during hydration reaction.

The magnitude of not hydrates such as C_2S and C_3S also were tested at the angle of 34° 2θ. The value decreased by 19.8%, 15% and 15.2% with the replacement of 1%, 2% and 3% of NS at 28 days respectively. These results showed that NS reacted with $Ca(OH)_2$ and produced solid C-S-H gel, involved in hydration of C_3S which also resulted in acceleration of hydration reaction. These results are consistent with the literature [41,42].

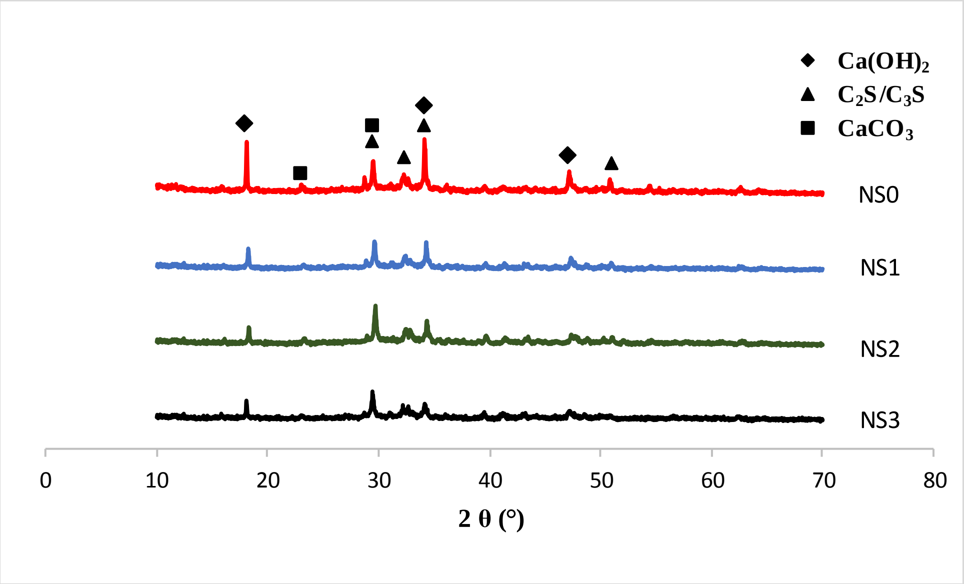
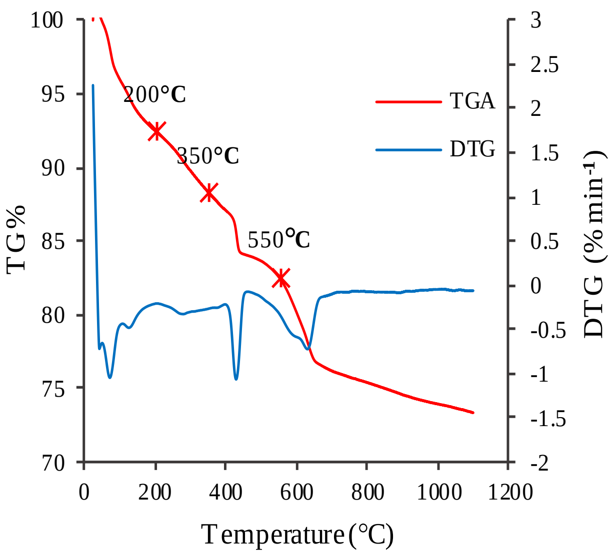


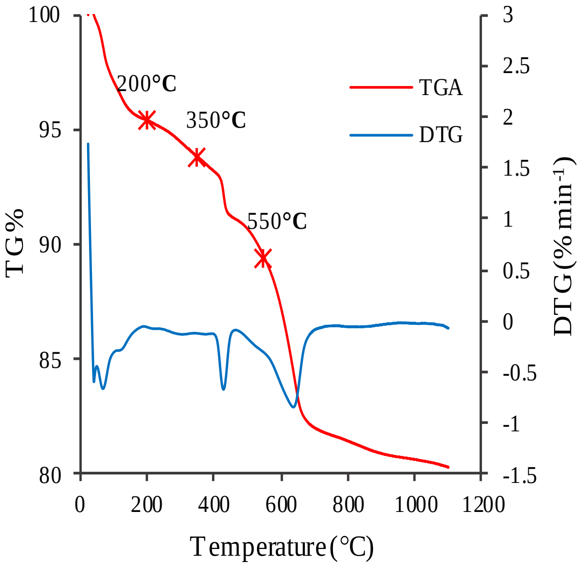
Fig. 4.9 XRD Pattern of SCP Formulations

4.6 Thermo-Gravimetric Analysis of Hardened Paste

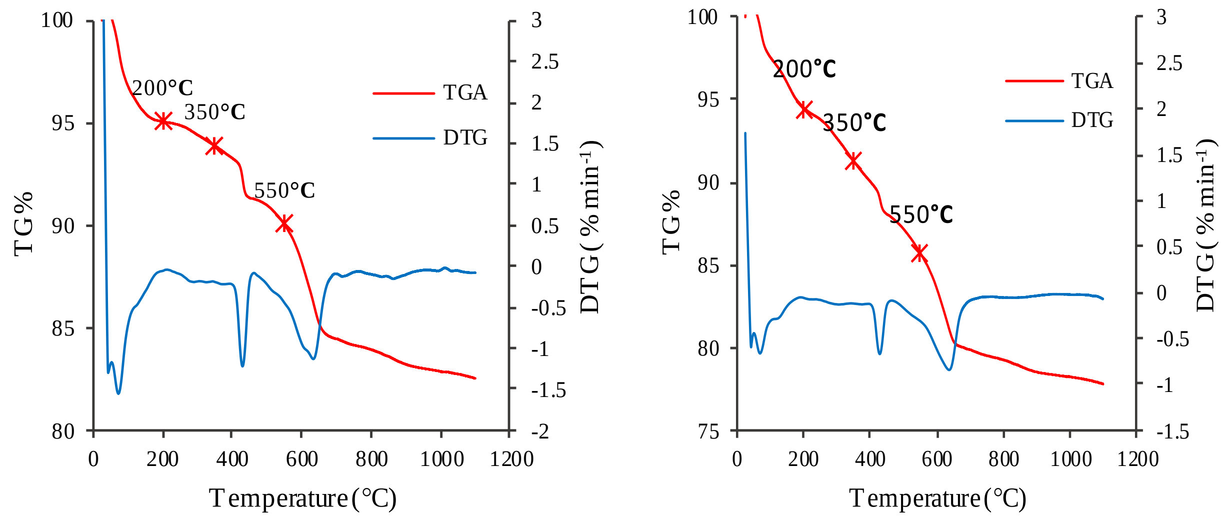
TGA/DTG curves of SCP samples containing SAP with 0%, 1%, 2% and 3% NS content are shown in Figure 4.12. Samples were water cured and tests were conducted at 28 days. TG/DTG curves show typical trend when paste samples were heated from 25 C to 1100 C. Three major reactions took place as identified by the peaks in DTG curve. The dehydration of moisture in the hydrates such as C-S-H and ettringite first took place from room temperature to about 200 C [28,43–46]. The second step of mass loss occurred between 200C and 350C and was associated with the dehydroxylation of free $Ca(OH)_2$ produced during curing [28,43–46].. Mass loss in third step occurred between 550C to about 750C and was due to decarbonation of $Ca(CO)_3$ in cement paste [28,43–46].. Calcium carbonate was not present in the original mixture and should have formed during curing. when the pastes samples were cured, calcium hydroxide reacted carbon dioxide from the atmosphere to form calcium carbonate [47].



a



b



c **d**

Fig. 4.10 TGA/DTG of SCP pastes (a) mix SNS0 (b) mix SNS1 (c) mix SNS2 (d) mix SNS3

Figure 4.11 presents the free CH mass percentage which was calculated simply by multiplying mass loss in second step of TG curve with the stochiometric molar mass ratio of $Ca(OH)_2$ / H_2O as mentioned in the literature [48,49].

$$CH = \frac{74.09}{18.01} \cdot \frac{m_{350} - m_{550}}{m_s} \qquad (2)$$

Where (74.09/18.01) is the stochiometric molar mass ratio between CH and H_2O, m_{350} and m_{550} are mass of samples at 350 C and 550 C recorded during the TGA test and m_s is the anhydrous mass of the sample.

It can be seen that 0% replacement of NS has the maximum concentration of free CH. CH value is lowest in the sample containing 2% replaced NS and then increased in the 3% NS replaced sample. This shows that the pozzolanic reaction is strongest with 2% replacement which is consistent with the strength results as most improvements were seen in SCP samples containing 2% NS.

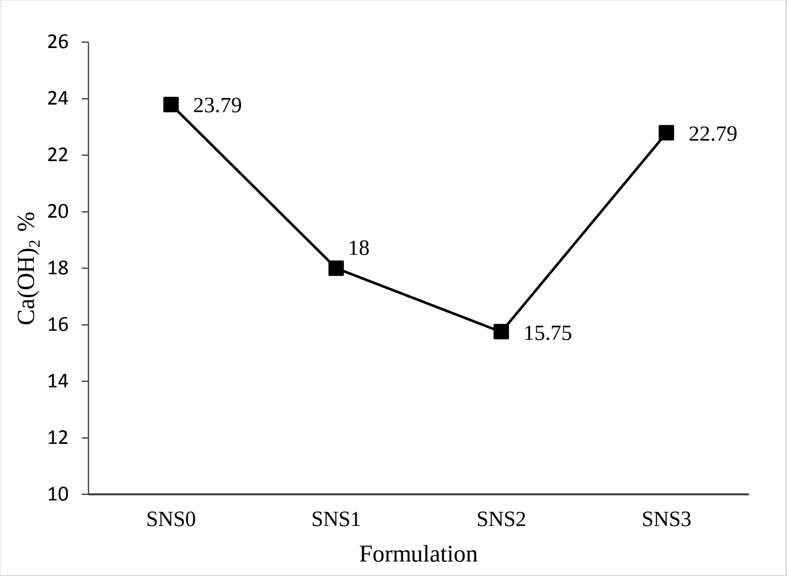


Fig. 4.11 CH % in SCP formulations

4.7 SEM of Hardened Paste

In order to study the effect of SAP and NS on microstructural properties of Cement paste, SEM studies were carried out of pure SCP sample, Cement and SAP and sample containing SAP and 2% NS as best results were obtained with 2% NS in SCP system. The structure of control mix was non-compact having interconnected capillary system. Abundant needle like hydrates and well-formed crystals of Portlandite were also visible in vacant spaces. The addition of 0.49% SAP induced the macro spherical pores which are clearly visible in SEM images. The hydration was improved specially in the vicinity of SAP particles because of internal curing effect of SAPs. Portlandite crystals were again well formed which can be seen in the pores formed by SAPs and CSH formed was comparatively condensed when compared with the control mix. The sample containing both 0.49% SAP and 2% NS shows further improved and compact microstructure having lesser pores. The quantity of both ettringite and Portlandite was reduced due to the pozzolanic effect of NS.

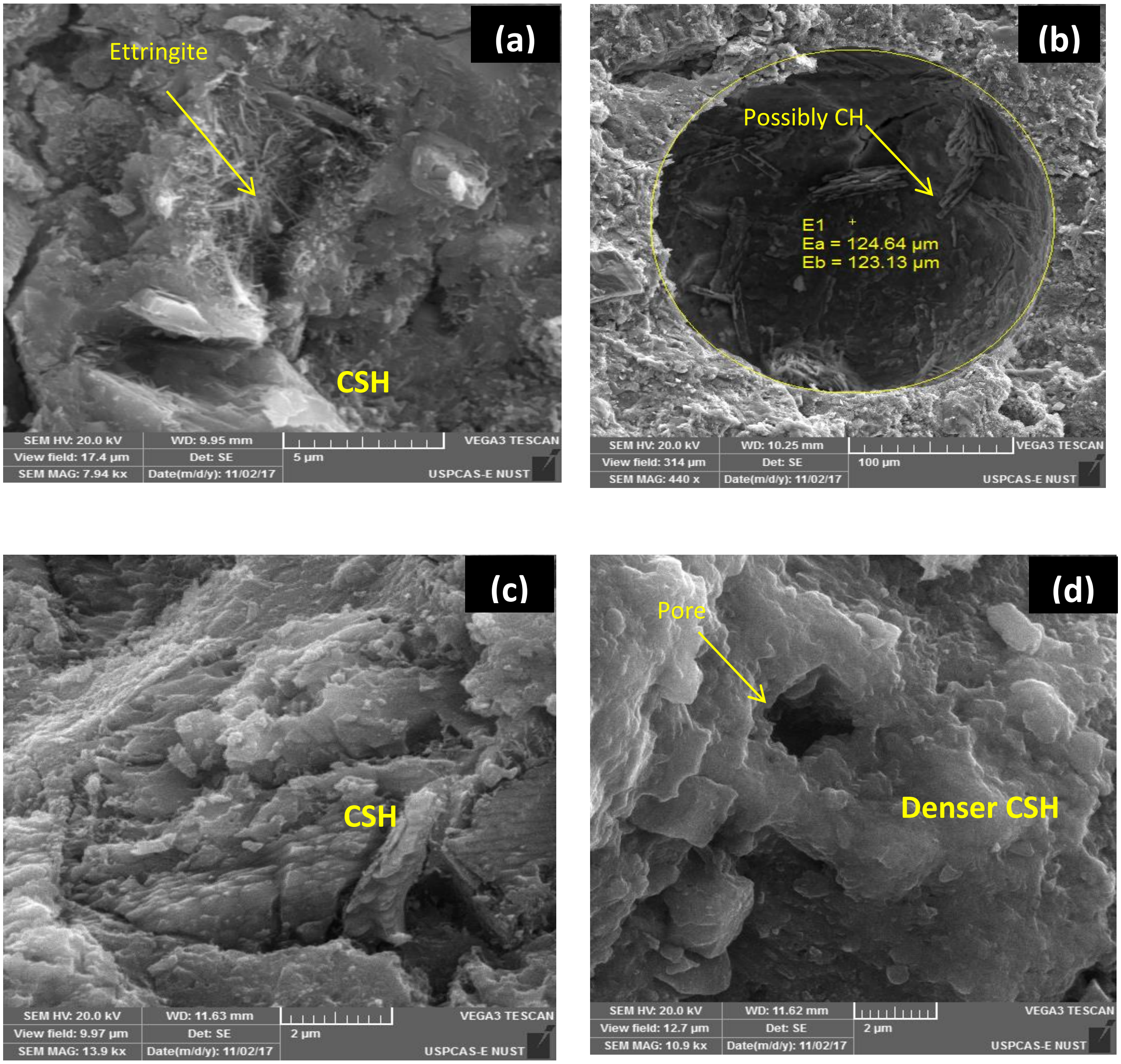


Fig. 4.12 SEM of SCP paste (a) mix SC (control) (b) and (c) mix SNS0 (0.49% SAP) (d) mix SNS2 (0.49% SAP + 2%NS)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- SAPs increased the SP demand of SCP system even with the additional entrained water. The presence of SAP itself as a hydrogel can be responsible for decreased flow. The effect of NS was more pronounced on Flow as compared to SAPs as they increased SP demand considerably

- SAPs are more efficient in conventional paste system compared with SCPs in mitigating shrinkage. There seems to be a possible interaction of SAPs with SP which reduced the effectiveness of SAPs in SCPs. This effect should be studied further and taken into account before using SAPs in conjunction with SPs.
.
- Internal curing effect can be seen dominantly in air cured samples as increase in strength is noted even with formation of macro pores. This is largely due to the significant improved hydration compared with air cured control samples.

- Addition of NS improved the mechanical properties of both SAPs modified conventional and SCP formulations. These improvements are mainly attributed to physical packing effect and high pozzolanic activity of NS particles. Consumption of $Ca(OH)_2$ and increased production of CSH contributed improved properties

- An optimum content of 2% NS for SCPs and 1% for conventional formulations corresponds to best mechanical properties.

- SAPs were able to successfully mitigate shrinkage as an internal curing agent in both SCPs and conventional paste formulations with or without the addition of NS particles at w/b ratio of 0.3

5.2 Recommendations

- Cement slurry is not true representative of concrete environment. There should be a more regressive approach to calculate absorption capacity as it is the most important property of SAPs and can vary depending on the environment**.**
- The incorporation of SAPs and NS should be extended to both self-compacting and conventional mortar and concrete systems.
- Agglomeration of NS particles can be an issue when using high dosages of NS >2%. It could be possible to get even better results with 5+% of NS if some sort of sonication mechanism is present which disperse the highly active particles of NS.
- SAPs should be used carefully alongside SPs as apparently SPs cause reduction in internal curing ability of SAPs. Absorption capacity of SAPs should be adjusted accordingly.

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APPENDIX

1. Absorption Capacity of SAPs

Liquid Solution	Temperature	pH	Absorption Capacity
De-Ionized Water	20.51	7.45	41.3
Tap Water	21.1	7.89	27.8
Cement Slurry	22.3	12.36	11.0

2. Formulations Detail

Formulation	Formulation Type
CC	C1-SP0-SAP0-NS0
CNS0	C1-SP0-SAP0.49-NS0
CNS1	C1-SP0-SAP0.49-NS1
CNS2	C1-SP0-SAP0.49-NS2
CNS3	C1-SP0-SAP0.49-NS3
SC	C1-SP0.14-SAP0-NS0
SNS0	C1-SP0.41-SAP0.49-NS0
SNS1	C1-SP0.69-SAP0.49-NS1
SNS2	C1-SP0.93-SAP0.49-NS2
SNS3	C1-SP1.16-SAP0.49-NS3

3. Vicat Setting Times

Formulation	Initial Set (min)	Final Set (min)

CC	189	229
CNS0	201	255
CNS1	171	223
CNS2	192	130
CNS3	158	75
SC	240	281
SNS0	276	351
SNS1	243	287
SNS2	202	263
SNS3	174	254

4. Compressive Test Results (Water Cured)

Formulation	Day 7	Day 14	Day 28
CC	36	45	54
CNS0	31	40	48
CNS1	35	44	52
CNS2	37	44	51
CNS3	34	41	45
SC	38	47	59
SNS0	33	41	49
SNS1	40	48	56
SNS2	43	50	61
SNS3	38	45	53

5. Compressive Test Results (Air Cured)

Formulation	Day 7	Day 14	Day 28

CC	25	30	36
CNS0	27	36	42
CNS1	32	35	43
CNS2	34	39	39
CNS3	36	37	38
SC	27	31	35
SNS0	29	37	43
SNS1	32	42	46
SNS2	35	41	48
SNS3	31	48	43

6. Flow Test Results

Formulation	SP demand (%)	T30 (s)
SNS	0.14	15.74
SNS0	0.41	18.59
SNS1	0.69	20.10
SNS2	0.93	23.45
SNS3	1.16	24.91