

Preparation of Silica Nanoparticles and Its Beneficial Role in Cementitious Materials

Regular Paper

L. P. Singh*, S. K. Agarwal, S. K. Bhattacharyya, U. Sharma and S. Ahalawat

CSIR-Central Building Research Institute (CBRI), India

*Corresponding author E-mail: lp Singh@cbri.in

Received 5 May, 2011; Accepted 21 July, 2011

Abstract Spherical silica nanoparticles ($n\text{-SiO}_2$) with controllable size have been synthesized using tetraethoxysilane as starting material and ethanol as solvent by sol-gel method. Morphology and size of the particles was controlled through surfactants. Sorbitan monolaurate, sorbitan monopalmitate and sorbitan monostearate produced silica nanoparticles of varying sizes (80-150 nm), indicating the effect of chain length of the surfactant. Increase in chain length of non-ionic surfactant resulted in decreasing particle size of silica nanoparticles. Further, the size of silica particles was also controlled using NH_3 as base catalyst. These silica nanoparticles were incorporated into cement paste and their role in accelerating the cementitious reactions was investigated. Addition of silica nanoparticles into cement paste improved the microstructure of the paste and calcium leaching is significantly reduced as $n\text{-SiO}_2$ reacts with calcium hydroxide and form additional calcium-silicate-hydrate (C-S-H) gel. It was found that calcium hydroxide content in silica nanoparticles incorporated cement paste reduced ~89% at 1 day and up to ~60% at 28 days of hydration process. Synthesized silica particles and cement paste samples were characterized using scanning electron microscopy (SEM), powder X-ray diffraction (XRD), infrared spectroscopy (IR) and thermogravimetric analysis (TGA).

Keywords Amorphous materials, Nano-silica, Nanostructures, Sol-gel chemistry

1. Introduction

Various methods for the preparation of nanoparticles are employed such as plasma synthesis, chemical vapour deposition, micro emulsion processing, combustion synthesis, sol-gel processing, hydrothermal techniques etc. Recent efforts for the preparation of nanoparticles are focused to control size, morphology and surface reactivity of nanoparticles. Sol-gel method has been widely used and a method of choice for the preparation of nanoparticles, as it has several advantages such as synthesis may be carried out at low temperature, desired pH to yield high purity and also, the reaction kinetics of the process may be controlled by varying the composition of the reaction mixture.

Silica particles of 1 μm were first prepared using sol-gel method and systematically characterized by Stober and coworkers [1]. Bogush et.al. have done extensive work on the preparation of silica nanoparticles ranging from few hundred nanometers to several micrometers by the control hydrolysis of TEOS in ethanol [2]. The size and shape of silica nanoparticles may be controlled by

additives such as electrolytes, surfactants and organic acids etc. Kim et al. have prepared silica nano particles using electrolyte, sodium iodide, whereas Rehman et. al. used ammonium bromide to control the particle size of silicon dioxide [3,4]. Cubic silica nanoparticles using organic acid such as tartaric acid have been reported by Wang and coworkers [5]. Ikari et. al. used binary surfactants method, to control the particle size of silica on the nanometer scale, in which by inhibiting the particle's growth with a nonionic amphiphilic agent, silica nanoparticles with hexagonally arrayed mesopores were produced [6]. Mollar and coworker synthesized nanometer-sized mesoporous silica particles by addition of triethanolamine as the base and cationic surfactant as the template [7]. Hexagonal shaped mesoporous silica particles have also been reported [8]. Venkatathri synthesized mesoporous silica nanospheres with uniform size and morphology using polyvinyl pyrrolidone and different types of cationic surfactants [9]. Mesoporous silica was synthesized using cetyltrimethyl ammonium bromide (CTAB) and sulphonated aromatic poly (ether ether ketone) (SPEEK) or poly(allylamine hydrochloride) (PAACl), as co- templates under a basic condition by Pang and coworker. The use of CTAB/SPEEK as structure-directing agents results in hierarchical mesoporous silica that contains hexagonally ordered mesopores (2nm) directed by CTAB and larger mesopores (20–50 nm) directed by SPEEK [10]. A convenient and environmentally friendly synthesis of monodispersed and mesoporous silica nanospheres by the addition of sugar molecules like glucose and fructose as templates into the Stober process is reported by Mukherjee [11], wherein silica nanoparticles of 50–1140 nm were produced by simply increasing template concentration in a reaction mixture consisting of TEOS, NH₃, H₂O, ethanol and the nonsurfactant sugar templates. Spherical mesoporous silica particles with tunable pore size and tunable outer particle diameter in the nanometer range were successfully prepared in a water/oil phase using organic templates method by Okuyama [12].

Nano silica is used in variety products ranging from cosmetic to construction materials. Most of the nanoparticles reported in literature exhibit various size, shape and orientation and therefore significantly differ in product development. These nanoparticles are either in colloidal form or agglomerated dry powder. Our efforts are to prepare uniform size, dry powder of silica nanoparticles and to study their beneficial role in cementitious materials. If dry powder of nanoparticles are added, they may behave significantly different than that of commercially available colloidal or agglomerated silica nanoparticles. During the cement hydration process these nanoparticles act as reaction centres. During the hydration of cement paste calcium-silicate-hydrate is formed as a major constituent (60-65%) alongwith calcium hydroxide (20-25%), which leaches out during the hydration process. Our efforts are to

control the calcium leaching in hydration process by the reaction of dry powdered silica nanoparticles with calcium hydroxide and thus imparting higher strength and durability to cementitious materials..

2. Experimental Details

Tetraethoxysilane (TEOS) (99.9% Alfa Aesar, UK), absolute ethanol (99.9% Merck, India), ammonium hydroxide (25% Thomas Baker, India) and orbitan monolaurate (span20), sorbitain monopalmitate (span40), sorbitain monostearate (span60) (Loba Chemie, India) were used without any further purification. Chemical structure of the surfactants used in present studies is shown in Figure 1. Ordinary Portland Cement (OPC), 43 grade, conforming to IS: 8112 was used as such. The chemical and mineralogical characteristics of the OPC are given in Table 1. Other reagents and solvents used were of AR grade.

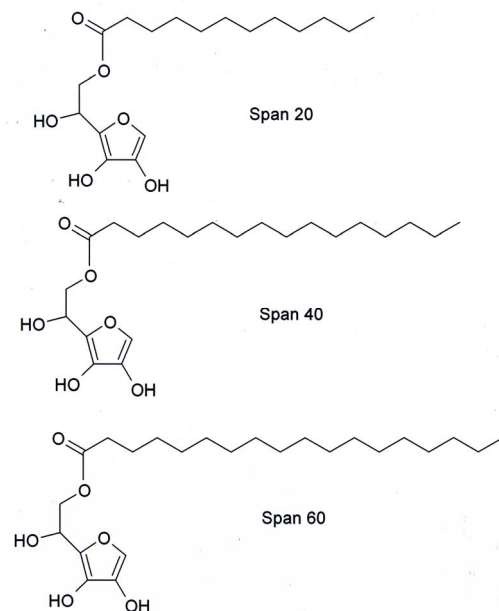


Figure 1. Surfactants used in the preparation of nanosilica powder

Items	Content (%)
SiO ₂	22.3
Al ₂ O ₃	6.1
Fe ₂ O ₃	2.2
CaO	61.1
MgO	3.1
SO ₃	2.1
LOI	2.3
C ₃ S	49.4
C ₂ S	27.2
C ₃ A	10.9
C ₄ AF	11.3

Table 1. Chemical and mineralogical properties of OPC.

Sol-gel method was used for the preparation of silica nanoparticles. These n-SiO₂ particles were synthesized by hydrolyzing TEOS in a mixture of ethanol, water, ammonia and surfactant. TEOS, ethanol and ammonia were used as silica precursor, common solvent and catalyst, respectively. For each experiments, 10 ml ethanol, 3 ml deionised water, 1 ml TEOS and 2.5 gm of non-ionic surfactant were added to the reaction container and stirred for 30 min for homogeneity. Then ammonium hydroxide was added drop wise to the mixture to control the pH of the reaction mixture. Upon addition of ammonia, the reaction mixture remained clear for some time and slowly turned turbid due to the formation of silica. The reaction was completed in 2h. The resulting white powder was dried overnight at 100°C and then calcined in air for a period of 1h at 650°C. The reaction was also performed without surfactants for comparative studies of particle size of silica nanoparticles. Experimental sample containing silica fume in place of n-SiO₂ were also prepared in similar way for comparison purpose.

To study the effect of n-SiO₂ addition in cement paste, 5% (w/w) of dry powdered n-SiO₂ were added to cement paste and comparative morphology and mineralogy were analyzed through SEM, XRD and TGA analysis. For morphological and mineralogical analysis of cement paste with n-SiO₂, 0.2 gm of n-SiO₂ was mixed with 4 gm of cement. Water cement ratio (w/c) 0.5 was fixed for all the experiments. Acetone was used to discontinue the hydration process of cement paste.

Morphological attributes of nanosilica were measured using Scanning Electron Microscope (LEO-438 VP) at an accelerating voltage of 15-20 kV. The samples were analysed under Variable Pressure (VP) mode with gold coating so as to improve the surface conductivity. The samples were deposited on a sample holder with a double stick conducting carbon tape. Powder X-ray diffraction data were recorded at room temperature on a Rigaku D-Max 2200 using Cu-K α radiation at a scanning rate of 1°min⁻¹. Various chemical bonding of silica nanoparticles were studied with Thermo Nicolet NEXUS FTIR. Each IR spectra were collected from 400-4000 cm⁻¹. TGA studies were performed on a Perkin Elmer (TG/DTA) analyser at a heating rate of 25 °C/ min. N₂ adsorption-desorption using Belsorp instrument of samples evacuated at 350°C for 3 h was used to determine BET specific surface area (SSA).

3. Results and Discussion

In the sol-gel method silica precursors are first hydrolysed and combined with the head groups of surfactants. The interaction between the surfactant and silica precursor is either by electrostatic force or hydrogen bond depending upon the nature of surfactants. The hydrophilic-lipophilic balance values of span 20, span 40 and span 60 are 8.6, 6.7,

4.3, respectively. The interaction between surfactants and silica precursor depends on the pH value of the reaction system and affect the morphology of the particles. Under neutral condition the hydrogen bonding between non-ionic surfactants and charged silica precursor takes longer duration whereas under basic condition the charged precursor and surfactant of opposite charge form the strong interaction yielding to ordered silica particles. The specific surface area (SSA) of these silica nanoparticles was obtained by BET method. Data presented in Table 2 indicates that at silica nanoparticles prepared using span 60 as surfactant exhibit higher surface area (~11,500 m²/Kg) and particle size is approximately 80nm. SEM micrographs of the synthesized n-SiO₂ as shown in Figure 2 indicate that as the chain length of the surfactants is increases, the particle size decreases. Silica particles in the range from 150-80 nm could be prepared using span 20, span 40 and span 60 series of non-ionic surfactants. Shi et.al. have reported that non-ionic surfactant (Brij 65) results in the improved particle and tunable particle size however, the ordering of the structure is decreased [13]. Whereas using span series of non-ionic surfactant, we could not only control the size of nano silica but the ordering could also be maintained.

Nanosilica	SSA (m ² Kg ⁻¹)
n-SiO ₂	5,500
n-SiO ₂ (span 20)	6,200
n-SiO ₂ (span 40)	9,100
n-SiO ₂ (span 60)	11,500
n-SiO ₂ (pH<10)	10,400
n-SiO ₂ (pH 10)	6,500
n-SiO ₂ (pH 11)	5,300
n-SiO ₂ (pH 12)	4,900

Table 2. Specific surface area (SSA) of silica nanoparticles synthesized using different surfactants and pH.

The particle size of nano-silica also depends on the pH of reaction system i.e. the concentration of ammonia. Particle size increases with the increase in the concentration of ammonia i.e. high pH. SEM micrographs of the synthesied n-SiO₂ as shown in Figure 3 indicate that as the pH of the system is increased, the particle size is also increased. The rate of polymerization and monomer addition reactions depends upon the pH of the reaction system. Above pH 7, condensed species are ionized and therefore, become mutually repulsive. Due to greater solubility of silica above pH 7, particles grow in size by particle aggregation and decrease in number as highly soluble small particles dissolve and reprecipitate on longer, less soluble particles. This process is referred to as Ostwald ripening [14-15].

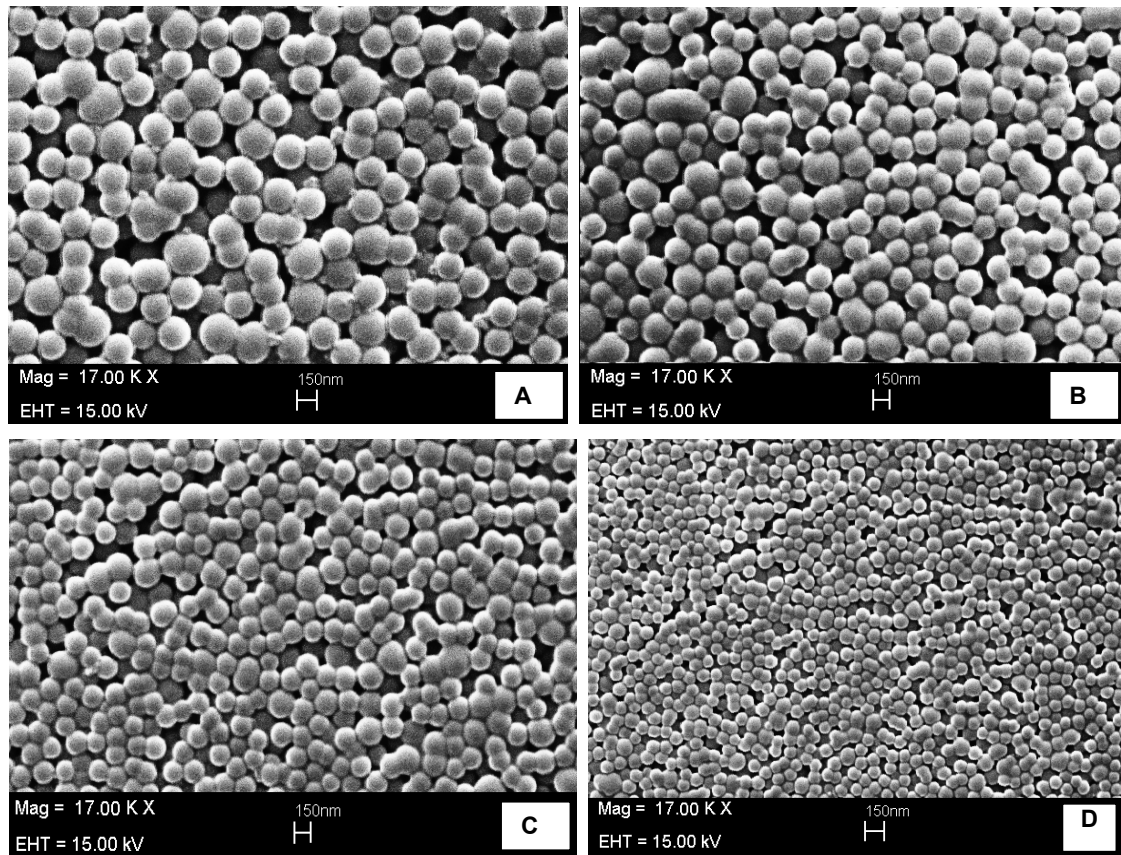


Figure 2. SEM micrographs of n-SiO₂ particles (80-200nm) prepared without surfactant (A), span 20 (B), span 40(C) and span 60 (D), respectively.

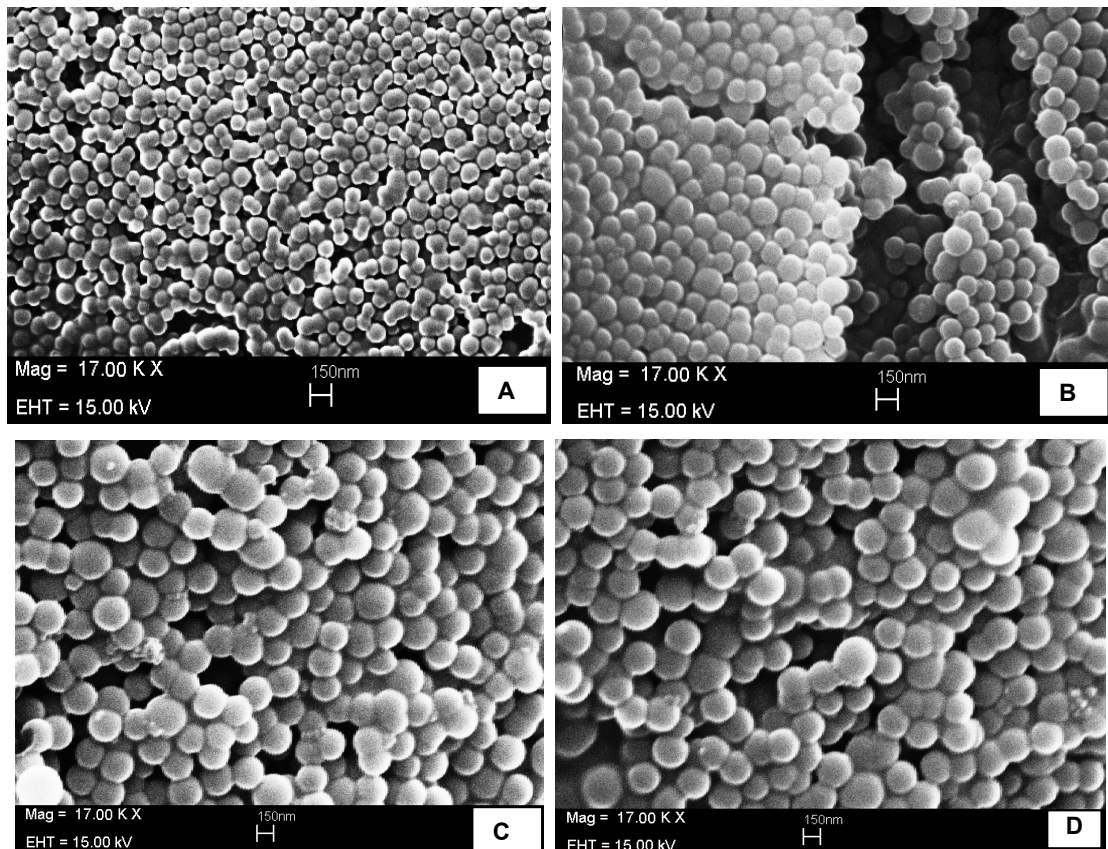


Figure 3. SEM micrographs of n-SiO₂ particles (100-250nm) prepared at pH <10 (A), pH 10 (B), pH 11(C) and pH 12 (D), respectively.

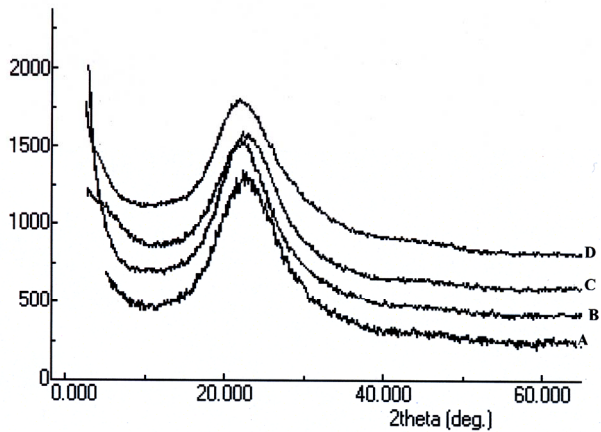


Figure 4. XRD of silica nano particles synthesised by sol-gel method, without surfactant (A), with span 20(B), span 40(C) and span 60(D).

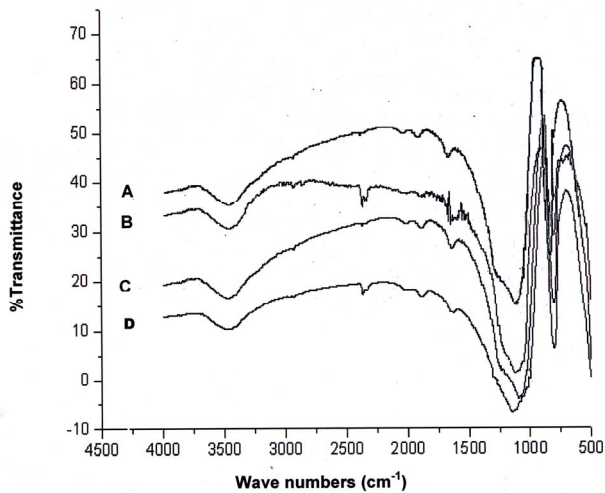


Figure 5. IR spectra of nano silica particles synthesized using, without surfactant (A), span 20 (B), span 40 (C) and span 60 (D).

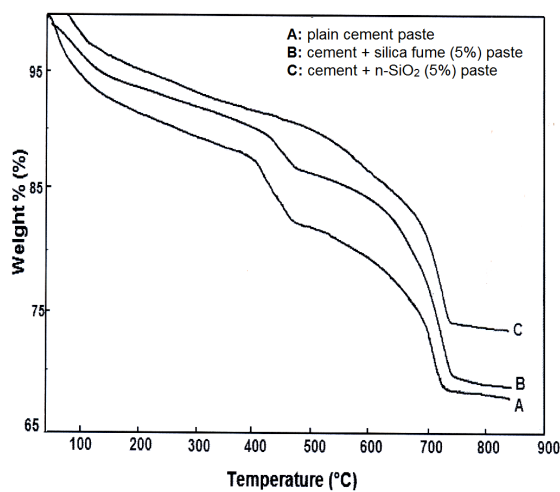


Figure 6. TGA of cement pastes at 28 days of hydration.

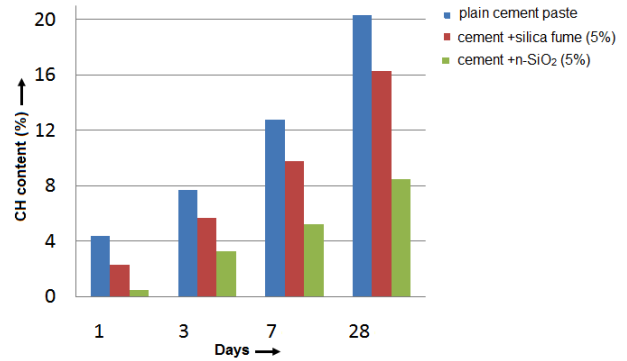


Figure 7. Calcium hydroxide content (%) in cement paste at 1,3,7 & 28 days of hydration.

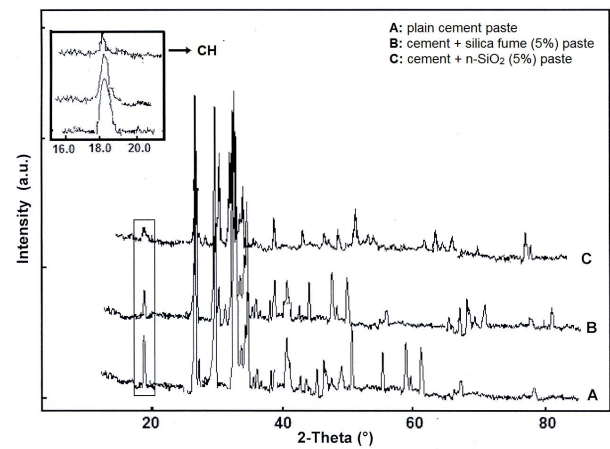


Figure 8. XRD patterns of cement pastes at 28 days of hydration.

XRD patterns of silica nanoparticles shown in Figure 4 reveal that the n-SiO₂ synthesized by sol-gel method is amorphous, which is advantageous for cementitious reaction. A representative IR spectrum of n-SiO₂ synthesized using span 20, span 40 and span 60 is shown in Figure 5. The two strongest IR absorption bands at ~1100 and 480 cm⁻¹ initiate from the extension and flexural vibrations of Si-O-Si bonds. The IR absorption band at ~800 cm⁻¹ originated from the vibration of (SiO₄) tetrahedrons. The ~3453 and 1630 cm⁻¹ absorption bands come from O-H bonding vibration of adsorbed molecular water. IR analysis also showed that the band at 1076 cm⁻¹ was slightly shifted towards lower wave number as the particle size is reduced. This observation suggests a change in the local bonding structures of Si and O atoms at smaller particle size [16, 17].

Further, these nanoparticles were incorporated in cement paste for calcium leaching resistant. The two silicate phases of cement, tricalcium silicate and dicalcium silicate, give calcium-silicate-hydrate (C-S-H) and calcium hydroxide (CH) as hydration products. The C-S-H gel being the main component of cement hydration is responsible for the strength and microstructure of the

cement paste. The amount of CH formation in cement paste was evaluated by thermogravimetric analysis (TGA) during hydration process. This was characterized by CH residue determination in cement paste admixture. Further, silica fume was also added to cement paste for comparison. Hydrated cement shows a reduction in weight up to 200°C due to surface water desorption as well as loss of water from C-S-H gel layer and from the dehydration of ettringite. Further, weight loss ~450-500°C is due to the thermal decomposition of CH followed by the decomposition of carbonated phases and calcite. The

amount of CH in the specimen is calculated directly from the TG curves using the following equation:

$$CH(\%) = WL_{CH}(\%) \times \frac{MW_{CH}}{MW_H}$$

where WL_{CH} corresponds to the weight loss attributable to CH dehydration and MW_{CH} and MW_H are the molecular weights of CH (74.01 g/mol) and water (18 g/mol), respectively [18].

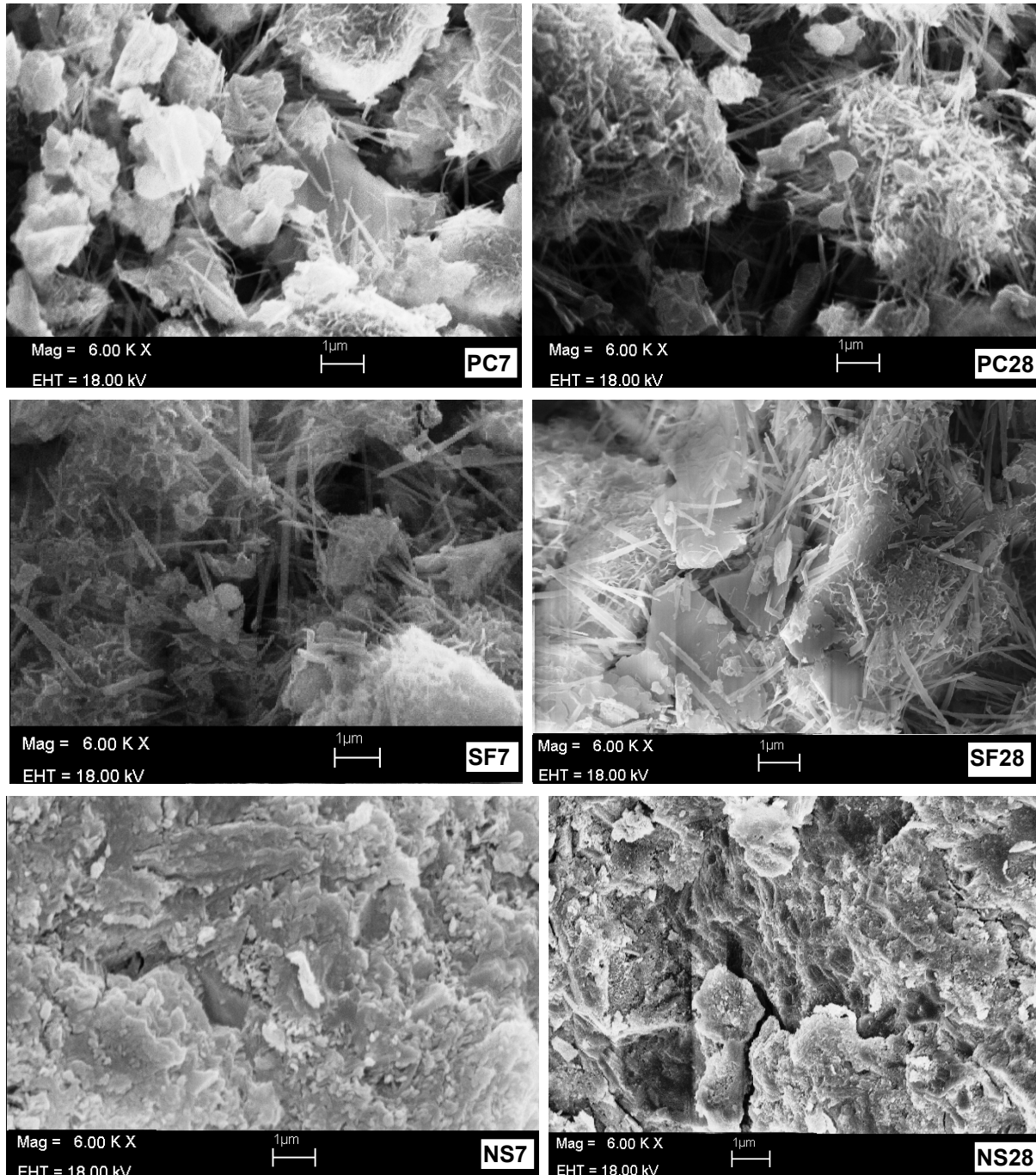


Figure 9. SEM micrographs of plain cement paste (PC7 & PC28), silica fume incorporated cement paste (SF7 & SF28) and nano silica incorporated cement pastes (NS7 & NS28) at 7 & 28 days of hydration.

TGA curves of pure, n-SiO₂ and silica fume incorporated cement pastes are shown in Figure 6 at 28 days of hydration. CH content in various cement paste during the hydration process is shown in Figure 7. At early stage of hydration plain cement paste has 4.4% of CH whereas silica fume incorporated cement paste has 2.3% and n-SiO₂ incorporated paste has only 0.5% CH content. During the hydration, CH is continuously formed and at 3, 7 and 28 days it amounts to 7.7%, 12.8% and 20.3%, respectively in plain cement paste. Whereas the CH content, in silica fume incorporated cement paste is upto 16.3% at 28 days. n-SiO₂ has much significant effect as compared to plain and silica fume incorporated cement paste and at 28 days of hydration only 8.5% CH content was observed. XRD profiles of plain cement, n-SiO₂ and silica fume incorporated pastes at 28 days of hydration are shown in Figure 8. It is evident from XRD profiles that the CH peak is almost disappeared with the addition of n-SiO₂; while the same is significantly present in plain and silica fume incorporated cement paste. It is therefore inferred from Figure 8 that n-SiO₂, reacts with CH produced during the hydration process. Therefore, the pozzolanic reactivity of n-SiO₂ at early stage of hydration is significantly high and improves the microstructure of cementitious system, thereby enhancing the durability and mechanical properties of the cementitious materials. SEM micrographs of plain cement paste, silica fume and with n-SiO₂ (5%) at 7 and 28 days are shown in Figure 9. It was observed that in the microstructure of the plain cement paste and silica fume incorporated cement paste, the C-S-H gel existed along with needle and plate shaped hydrates of CH. The deposited CH around the C-S-H gel is uniformly distributed among the entire cement phase (Figure 9). The microstructure of the cement paste with the addition of n-SiO₂ revealed that the formation of hydration products was denser, becomes significantly different and showing absence of the needle shaped crystals of CH.

4. Conclusions

Spherical and amorphous silica nanoparticles can be prepared by the hydrolysis reaction of TEOS in ethanol using water and ammonia using sol-gel method. The particle size of nano silica can be controlled by adding span 20, span 40 and span 60 surfactants. The particle size of nano silica powder also depends on the pH value of reaction system. Particle size increases with the increase of the pH of the reaction system. It was observed from SEM, XRD and TGA studies that addition of n-SiO₂ to cement reduced CH leaching by reacting at early stage of hydration and forming additional C-S-H gel. It was found that, CH content in n-SiO₂ incorporated cement paste reduced approximately ~89% at 1 day and upto approx. 60% at 28 days. Therefore, addition of small quantity of n-SiO₂ significantly improves the morphology and mineralogy of the cementitious materials.

5. Acknowledgements

Authors are thankful to Uttarakhand State Council for Science and Technology (UCOST), Dehradun, India for financial support. One of the authors (S. Ahalawat) is grateful to UCOST, Dehradun for fellowship assistance.

6. References

- [1] W. Stober, A. Fink, J. Bohn, "Controlled growth of monodisperse silica spheres in the micron size range" *J. Coll. Int. Sci.* vol 26, pp 62, 1968.
- [2] G.H. Bogush, C. F. Zukoski, "Preparation of monodisperse silica particles: Control of size and mass fraction" *J. Non-Cryst. Sol.* vol 104, pp 95, 1988.
- [3] S.S. Kim, H.S. Kim, S.G. Kim, W.S. Kim, "Effect of electrolyte additives on sol precipitated nano silica particles" *Ceramics International* vol 30, pp171, 2004.
- [4] I.A. Rahman, P. Vejayakumaran, C.K. Chee, "Effect of anion electrolytes on the formation of silica nanoparticles via the sol-gel process" *Ceramics International* vol 32, pp 691, 2006.
- [5] Z. Wang, J. Zhao, X. Ding, K. Yu, "Synthesis of silica nanocubes by sol-gel method" *Materials letters* vol 59, pp 4013, 2005.
- [6] K. Ikari, K. Suzuki, H. Imai, "Structural Control of Mesoporous Silica Nanoparticles in a Binary Surfactant System" *Langmuir* vol 22, pp 802, 2006.
- [7] K. Möller, J. Kobler, T. Bein, "Colloidal Suspensions of Nanometer-Sized Mesoporous Silica" *Advanced Functional. Materials* vol 17, pp 605, 2007.
- [8] Q. Cai, Z. Luo, W. Pang, Y. Fan, X. Chen, F. Cui, "Dilute Solution Routes to Various Controllable Morphologies of MCM-41 Silica with a Basic Medium" *Chemistry of Materials* vol 13, pp 258, 2001.
- [9] N. Venkatathri, "Synthesis of mesoporous silica nanosphere using different templates" *Solid state communications* vol 143, pp 493, 2007.
- [10] J. Pang, H. Na, Y. Lu, "Effect of ionic polymer on cetyltrimethylammonium bromide templated synthesis of mesoporous silica" *Microporous and Mesoporous Materials* vol 86, pp 89, 2005.
- [11] I. Mukherjee, A. Mylonakis, Y. Guo, S. P. Samuel, S. Li, R. Y. Wei, A. Kojtari, Y. Wei, "Effect of nonsurfactant template content on the particle size and surface area of monodisperse mesoporous silica nanospheres" *Microporous and Mesoporous Materials* vol 122, pp 168, 2009.
- [12] A. Bayu D. Nandiyanto, S. G. Kim, F. Iskandar, K. Okuyama, "Solvent-free infiltration method for mesoporous SnO₂ using mesoporous silica templates" *Microporous and Mesoporous Materials* vol 120, pp 447, 2009.

- [13] J. Shi, L. Guo, F. Cui, X. Cui, "Size-controlled synthesis of monodispersed mesoporous silica nano-spheres under a neutral condition" *Microporous and Mesoporous Materials* vol 117, pp 609, 2009.
- [14] G.H. Bogush, C.F. Zukoski, "Studies of the kinetics of the precipitation of uniform silica particles through the hydrolysis and condensation of silicon alkoxides" *J. Coll. Int. Sci.* vol 142, pp 1, 1991.
- [15] G.H. Bogush, C.F. Zukoski. "Uniform silica particle precipitation: An aggregative growth model" *J. Coll. Int. Sci.* vol 142, pp 19, 1991.
- [16] I.A. Rahman, P. Vejayakumaran, C.S. Sipaut, J. Ismail, C.K. Chee, "Size-dependent physicochemical and optical properties of silica nanoparticles" *Materials Chemistry and Physics* vol 114, pp 328, 2009.
- [17] X. Li, Z. Cao, Z. Zhang, H. Dang, "Surface-modification in situ of nano-SiO₂ and its structure and tribological properties" *Applied Surface Science*, vol 252, pp 7856, 2006.
- [18] J. Jain, N. Neithalath, " analysis of calcium leaching behaviour of plain and modified cement pastes in pure water" *Cement Concrete Research*, vol 31, pp 176, 2009.