Construction and Building Materials 113 (2016) 794–804

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

The effect of Colloidal Nano-silica on workability, mechanical and durability properties of High Performance Concrete with Copper slag as partial fine aggregate

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HIGHLIGHTS

- Addition of Nanosilica in HPSC improves strength and durability properties.
- Early age strength is enhanced due to the use of nanosilica.
- Good correlation exists between compressive strength with splitting tensile strength and flexural strength.

ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form 10 March 2016
Accepted 21 March 2016
Available online 25 March 2016

Keywords:
High Performance Concrete
Copper slag
Nanosilica
Mechanical properties
Durability properties

ABSTRACT

This study was conducted to investigate the effect of colloidal nanosilica on the properties of High Performance Concrete with copper slag as fine aggregate at a constant replacement level of 40%. Cement mortars and concrete mixes were produced by replacing Portland cement by colloidal nanosilica at 0.5%, 1%, 1.5%, 2%, 2.5% and 3%. Tests on workability, compressive strength, splitting tensile strength, flexural strength, rapid chloride penetration, water absorption, sorptivity and abrasion resistance were conducted on concrete mixes. The results indicate that the water demand increases due to the increase in the percentage of nanosilica owing to its high specific surface area. The amount of super plasticizer was adjusted in each mix to maintain a constant workability. The strength, penetration properties and resistance to abrasion of High Performance Slag Concrete (HPSC) were generally improved with the increment of nanosilica content in the concrete mix. The results denote that the colloidal Nanosilica act as a filler material that improves microstructure as well as an activator to promote Pozzolanic action. The addition of nanosilica enhances the strength characteristics up to 2% replacement level.

1. Introduction

High Performance Concrete (HPC) has been widely used throughout the world for the past three decades. The compressive strength of High Performance Concrete may vary between 20 MPa to 200 MPa. In addition to the strength requirements, workability and durability criteria play a vital role in the production of HPC. Therefore, it becomes necessary to use high quantity and quality materials to meet the above requirements. Also, the properties of the constituents of concrete namely cement, fine aggregate and coarse aggregate influence the properties of HPC. Aggregates constitute about 70%–80% of the volume of the concrete and hence there is a rapid increase in the consumption of natural aggregates throughout the world. This leads to the depletion of natural aggregates which affects the sustainable development.

Industrialization and population growth has led to the production of enormous waste materials and by-products that upon dumping or disposal of these materials causes environmental problems. Therefore, there is an urgent need to find and utilize alternative material for aggregates by utilizing the waste materials and by-products with little or no property modification which leads to a sustainable and greener environment along with the technical advantages.

To make HPC as an economical and ecological material, several mineral admixtures like silica fume, fly ash, metakaolin and rice husk ash are added or replaced with cement. There is an improvement in workability, mechanical and durability properties of HPC

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http://dx.doi.org/10.1016/j.conbuildmat.2016.03.119
0950-0618/

when the mineral admixtures are used as a partial substitute to Portland cement due to strengthening of interfacial transition zone. Nowadays, the use of nano materials in concrete is gaining more importance owing to its better properties in the fresh and hardened states of concrete due to their specific surface area. The materials used in nanosize are nano-SiO_2, nano-TiO_2, nano-Fe_2O_3, nano-Al_2O_3, carbon nanotubes/fibers. Among all the nanomaterials, nanosilica is the most widely used material in the cement and concrete to improve the performance, because of its pozzolanic reactivity besides the pore-filling effect. Due to the rapid development of infrastructure, it is necessary to develop a high strength, durable, sustainable and environment friendly cementitious composites [1]. Nanosilica is available in the form of compacted dry powder or colloidal suspension. Small amount of nanosilica, usually at 0–6% replacement is enough to enhance the properties of HPC. The addition of nanosilica accelerates the hydration process and also reacts with Calcium Hydroxide and produces more amounts of Calcium-Silicate-Hydrates thereby improving the mechanical properties. Concretes incorporated with nanosilica results in denser and compact microstructure with lesser amount of calcium hydroxide crystals [2–5,27]. Pozzolanic reactivity is found to be much higher and quicker in nanosilica added concrete up to 3% [3].

The incorporation of nanosilica in concrete resulted in higher compressive strength [2,6,7,24,35], increase in tensile strength and bending strength [7,8,35] and improvement in abrasive resistance than that of normal concrete to a considerable level. Also, the concrete becomes denser with improved durability properties. Researches on permeability characteristics of nanosilica concrete showed reduction in water absorption, capillary absorption and water permeability than normal concrete [4–6,8,18]. The addition of nanosilica in concrete with ground granulated blast furnace slag increased the rate of hydration and splitting tensile strength [9]. The addition of nanosilica in high volume fly ash and slag concrete reported reduction in the initial and final setting time of the concrete, the length of dormant period during hydration, Chloride ion penetration. Nanosilica addition improved the compressive strength due to acceleration of hydration [22,23]. Nanosilica addition in ceramic waste powder concrete improved the early age strength [10]. Addition of nanosilica improves the early age strength of fly ash cement mortar but rate of later age strength gain is slowed down [39]. High volume replacement of waste glass powder with cement in concrete is made possible by incorporating nanosilica [11]. Use of nanosilica in green-concrete mixtures, which is primarily made with the replacement of cement by waste materials overcomes the problem of low strength and delay in setting. Incorporation of Nanosilica in Recycled aggregate concrete resulted in improvement of compressive strength than conventional aggregate concrete [12]. Addition of nanosilica in oil well cement increases the strength and reduces the setting time [13].

The negative effects associated with sludge incorporation in terms of setting time and initial strength of sludge/fly ash mortars can be compensated by use of Nanosilica [19]. The addition of nanosilica was reported to an increase in strength of cement composites by 15–20% [20]. Also nanosilica particles improve the performance of sludge/clay mixtures in the tile production with reduction in water absorption and increase in abrasion and impact strength [21]. The improvement in mechanical and durability properties of concrete containing nanosilica is achieved due to its ultra fine particle size and its high specific surface area. The nanosilica particles fill the microscopic voids between cement, thus forming a dense structure. The calcium hydroxide produced during hydration reacts with nanosilica to form additional C-S-H gel [26]. Thus nanosilica act as centres of nucleation due to its high surface area, thus accelerating the hydration [26,27]. Also due to its high specific surface and high surface energies, increasing the amount of Nanosilica results in agglomeration thereby preventing uniform distribution of Nanosilica particles within the mortar. Thus the compressive strength improvement is decreased while increasing the amount of nanosilica content. Nano particles adsorb more Ca^{+2} ions and lower the concentration of calcium ions, thus accelerating the rate of dissolution of C_3S which increases the rate of hydration more effectively [32]. The bond between the cement paste and aggregate is also improved. Adding of Colloidal nanosilica is easier and efficient than adding powder nanosilica [41]. Nanotechnology has more potential in the field of construction and building materials which requires research in the field of nanotoxicity and care should be exercised while handling nano particles [25].

Most of the research focused on the study of properties of addition of nanosilica in cement pastes and mortars. Only a few researches carried out on determining the mechanical properties and permeability of the concrete with nanosilica. Many researchers reported different and contradictory optimum quantities of nanosilica along with some unusual effects which needs much concentration in the further research [2,7,14–17]. The optimum quantity of nanosilica must be arrived for each material individually.

Utilization of industrial wastes and by products is the major challenges faced today due to the disposal cost and potential pollution problem associated with it. The above problem can be reduced or even eliminated along with the achievement of resource conservation if it is efficiently used in the construction industry. Many slags have cementitious or pozzolanic properties which trigger the researchers to use it in cement or concrete. Copper slag is a by-product obtained during the matte smelting and refining of copper. Copper slag finds its use in abrasive tools for sand blasting, roofing granules, cutting tools, abrasives, tiles, glass, filling material in road base construction, railway ballast, asphalt pavements and cement and concrete industries [52,55]. Recently, many researches were carried out to study the possibilities of using waste materials and industrial by-products as partial/full replacement of cement/aggregates or as admixtures [54]. The use of copper slag as sand substitution in High Strength Concrete (HSC) improves strength and durability characteristics at same workability while super plasticizer is a very important ingredient in HSC made with copper slag in order to provide good workability and better consistency for the concrete matrix. The United Nations (UN) Basel Convention on the Transboundary Movement of Hazardous Wastes and their Disposal stated that copper slag is not a hazardous waste in the recent year after studying various researches conducted using copper slag. The use of copper slag in cement clinker production, and the effects of copper slag on the properties of Portland cement mortar and concrete in the form of cement replacement, coarse and fine aggregate have been investigated by many researchers [42,43–45,53,55]. Several works reported that the compressive and tensile strengths of concrete specimens made with copper slag as fine and coarse aggregates shows improvement than that of normal concrete [44–48].

Longer delay in the setting time is reported due to the decrease in the particle size of copper slag [46]. Bleeding and segregation is noticed in concrete containing more than 40% copper slag as fine aggregate replacement [44]. The above effect is due to glass like smooth surface of copper slag and the low moisture absorption [44,47]. The abrasion resistance of cement mortar containing copper slag as fine aggregate is increased [49]. For every tonne of copper produced, approximately 2.2–3 tonnes of slag were generated as per a scientific estimate. As per the survey in the year 2011, copper slag production was estimated around 33 tonnes all over the world. India is generating 6–6.5 tonnes of copper slag from the three copper industries [50,51]. M/s. Sterlite Industries, Tuticorin is producing 4,00,000 tonnes of copper every year from which approximately 8,00,000 tonnes of copper slag is generated every year [50]. Copper slag is a waste material which when used in cement and concrete provides potential, environmental, technical as well as economic benefits.

2. Research objectives

The development of nanosilica based high performance concrete is expected to reduce the cement consumption for specific grade of concrete thereby protecting the environment to a great extent, lowers the overall cost of the structure, saves time, materials, better durability which leads to sustainable concrete construction, reduces repair and maintenance costs to a great extent [1]. Although, there are few reports on adding nano-particles in cement- based materials, little attention has been focused on the influence of Nanosilica in concrete. Also nanosilica addition marks a novelty in the high performance cements technology and is expected to improve the physical and mechanical properties of the final product. The effect of copper slag as partial substitution of fine aggregate on strength and durability properties of HPC, HSC, normal concrete were studied by various authors [44,46,47,51]. As a preliminary work, optimum content of copper slag to be used in the study was investigated and concluded that 40% replacement as the optimum content for fine aggregate replacement in the concrete. Most of researches concluded that segregation and bleeding of copper slag contained concrete is of great issue [43,44,47]. Here the study is extended to investigate the effect of addition of nanosilica on the mechanical and durability properties of High Performance Slag Concrete (HPSC) at constant workability in which copper slag is incorporated as partial replacement for fine aggregate.

3. Materials

Ordinary Portland Cement of 53 grade (IS 12269:1987) was used. The specific gravity of the cement is 3.15 and the chemical composition is shown in Table 1.

River sand with a specific gravity of 2.66 and fineness modulus of 2.91 was used as the main fine aggregate for this study and copper slag as replacement material. The sand used was well graded and conforms to zone II as per IS: 383-1970 [71] with a bulk density of 1780 kg/m^3. The copper slag used in the study conforms to zone II with a specific gravity of 3.91, fineness modulus of 3.39 and bulk density of 2180 kg/m^3. The chemical composition of copper slag is shown in Table 2. The gradation of sand and copper slag is shown in Fig. 1 and they meet the specification requirements. Crushed granite coarse aggregate of maximum size 12.5 mm with specific gravity of 2.73 and bulk density of 1650 kg/m^3 was used in this study. Ordinary tap water available in the laboratory was used for making mixes.

A polycarboxylic ether based superplasticizer Glenium B233 conform to IS 9103: 1999 with specific gravity of 1.08, Relative Density of 1.08 ± 0.01 at 25 °C, pH greater than 6, Chloride ion content less than 0.2% and solid contents of not less than 30% by weight was used in this study.

Commercial type aqueous colloidal Nanosilica solution with a specific gravity between 1.3 and 1.32, pH value at 20 °C between 9.4 and 10, active nano SiO_2 content (%wt/wt) between 40.0 and 41.5 along with the particle size in the range of 5–40 nm was used for this study. The results of XRD and SEM analysis of nanosilica to evaluate the size and morphology are presented in Figs. 2 and 3. XRD patterns were acquired using Shimadzu XRD 6000 and operating at 40 kV voltages and 30 mA current and using Cu X-ray source. SEM images were obtained from Jeol JSM 6390 Scanning electron microscope. From the XRD analysis of nanosilica, it was observed that a broad peak varied between 16° to 30° was obtained which confirmed the presence of compounds in nano form and amorphous nature. From XRD analysis, presence of silicon oxide in higher content was identified. The size of nanosilica as determined from XRD analysis was 7 nm. From the SEM image of nanosilica, it can be observed that the particles are available in the spherical shape.

4. Experimental study

4.1. Cement with nanosilica

The standard consistency and setting time tests were done for cement with nanosilica at various replacement levels in accordance with IS: 4031 (Part 4) – 1988.

4.2. Mortar study with setting times

Preliminary studies have been done in cement mortar cubes with different proportions of copper slag (i.e. 0, 10%, 20%, 30%, 40% and 50%) as fine aggregate replacement to study the effect of admixture on the properties of mortars incorporating copper slag. Mortar specimens were cast in two sets: (a) without adding super plasticizer and (b) adding super plasticizer. It was found that due to low w/b ratio adopted, mix with super plasticizer yielded better performance than mix without super plasticizer and the optimum replacement of copper slag for fine aggregate replacement is 40%.

To study the effect of nanosilica substitution as a replacement for cement on the strength of copper slag cement mortars, cubes (70.7 mm × 70.7 mm × 70.7 mm) were prepared with different percentages of nanosilica (by weight) with cement fine aggregate ratio of 1:3 with a constant w/b ratio of 0.31. Mortar cubes were cast by replacing cement with 0.5%, 1%, 1.5%, 2%, 2.5% and 3% of colloidal nanosilica and the copper slag replacement for fine aggregate was kept at a constant value of 40% for all mixes. The super plasticizer was added at a constant rate of 0.5%. Fifteen mortar cubes were cast for each mix to determine the compressive strength and tested at 3, 7, 28, 56 and 90 days.

4.3. Concrete

4.3.1. Mix proportions

ACI [75] method of mix proportioning was adopted to arrive at the reference mix proportion for M60 grade concrete. Seven concrete mixes at different dosages of colloidal Nanosilica (i.e. 0, 0.5%, 1%, 1.5%, 2%, 2.5% and 3% by weight of cement) were prepared for workability between 25 mm to 50 mm with 40% copper slag as fine aggregate replacement. The water-binder ratio for all concrete mixes was kept as 0.31. The super plasticizer content was adjusted in each mix so that the slump was maintained at the desirable range. The mix proportion chosen for the study is shown in Table 3.

Table 1
Chemical composition of OPC.

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO_3	Na_2O	K_2O	Cl	LOI	IR
	21.8	4.8	3.8	63.3	2.2	0.9	0.21	0.46	0.04	2	0.4

LOI-Loss on Ignition IR-Insoluble Residue.

Table 2
Chemical composition of copper slag.

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Na_2O	K_2O	Cl	Mn_2O_3	CuO	TiO_2	LOI	IR
	25.84	0.22	68.29	0.15	0.11	0.58	0.28	0.018	0.22	1.2	0.41	6.59	14.88

LOI-Loss on Ignition IR-Insoluble Residue.

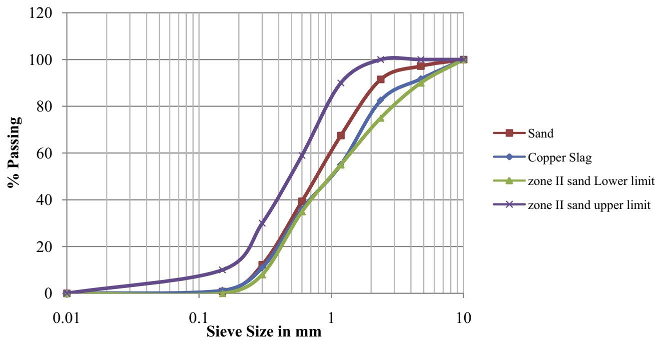

Fig. 1. Sieve analysis of Sand and copper slag.

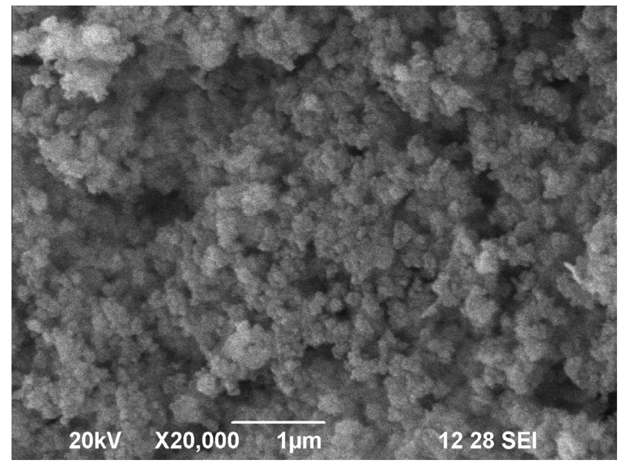

Fig. 3. SEM image of nanosilica.

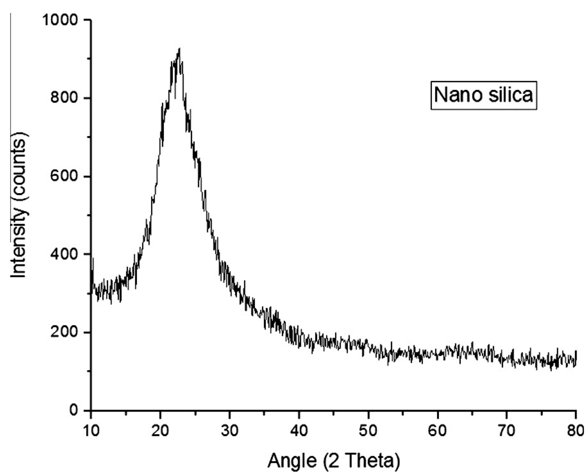

Fig. 2. XRD spectra of nanosilica.

4.3.2. Casting and testing of specimens

The materials were stocked at room temperature 27 ± 2 °C for at least 24 h before mixing in order to maintain a constant mixing temperature. The materials were mixed using pan mixer (IS 12119:1987) at room temperature. Several trials were done to obtain the mix proportion [57,58,68–70], mixing sequence [58] and optimum content of super plasticizer [59]. The overall mixing time was about 7 min. The coarse aggregate, fine aggregate, copper slag and cement was fed one by one to the pan mixer and mixed in the dry state for 2 min. Colloidal nanosilica was premixed with water and stirred properly to obtain uniform dispersion of nano particles. The colloidal nanosilica mixed with 60% of the mixing water was added and mixing of concrete was continued for 1 min. The super plasticizer mixed with the remaining mixing water was added last and mixed for another 1 min. The mix was kept at rest for 1 min in order to allow the super plasticizer to react for achieving better workability. Finally, the mixing is again done for 2 min for avoiding loss of slump and achieving the homogeneous mix. The concrete mixes were placed in four layers and compacted using vibrating table to ensure appropriate compaction. The slump of the fresh concrete was determined for each mix to ensure the achievement of desired workability and to study the effect of nanosilica replacement on the workability of slag concrete. Several trial batches were mixed in order to adjust the amounts of super plasticizer for each added quantity of nanosilica to maintain the slump value within the desirable range. The specimens were covered to prevent water loss and were kept in room temperature till the de-moulding time. The specimens were then demoulded after 24 h, cured in water and tested at room temperature at the required age.

Eighteen cubes (100 mm × 100 mm × 100 mm), were cast for each mix to determine the compressive strength, three samples were tested for compressive strengths of concretes at 1, 3, 7, 28, 56 and 90 days. Twelve cylinders (150 mm × 300 mm) were prepared for each mix to determine splitting tensile strength of concrete at 3, 7, 28 and 90 days. Twelve prisms (100 mm × 100 mm × 500 mm) were cast for each mix in order to determine the modulus of rupture of concrete at 3, 7, 28 and 90 days.

One cylinder (100 mm × 200 mm) was cast and prepared after 28 days for each mix to assess the durability of High Performance Slag Concrete by performing Rapid chloride penetration test. The specimens were cut into three discs (100 mm × 51 ± 3 mm) after 28 days of casting using water-cooled silicon carbide saw. The specimens were positioned in the cell with a fluid reservoir at each face of the specimen. One reservoir was filled with Sodium Chloride (3% NaCl) solution and the other with Sodium Hydroxide (0.3 M NaOH) solution. A potential difference of 60V DC was maintained across the ends and the amount of electrical current passed through the concrete slices was monitored for a period of 6 h. The total charges passed (in Coulomb) are considered to be directly related to the Chloride ion penetration of the specimen.

Water absorption is used to determine the quantity of water absorbed by concrete under specified conditions and also indicates the open porosity of the concrete specimen. Water absorption test was conducted in accordance with ASTM C 642-97 [78].

Sorptivity is the tendency of a material to absorb and transmit water by capillary action. 100 mm dried cube specimens were placed above the steel mesh in a water tub and the lower side of the sample was immersed in water to a depth of 5 mm. The side

Table 3
Mix proportion.

Mix designation	Quantity (kg/m^3)								
	OPC	S	CS	CA	CNS	SP (%)	W	w/b	Slump (mm)
CN0	516	360.6	240.4	1174	–	0.4	160	0.31	43
CN0.5	513.42	360.6	240.4	1174	2.58	0.4	160	0.31	39
CN1	510.84	360.6	240.4	1174	5.16	0.4	160	0.31	32
CN1.5	508.26	360.6	240.4	1174	7.74	0.45	160	0.31	38
CN2	505. 68	360.6	240.4	1174	10.32	0.5	160	0.31	42
CN2.5	503.1	360.6	240.4	1174	12.9	0.55	160	0.31	45
CN3	500.52	360.6	240.4	1174	15.48	0.6	160	0.31	47

OPC-Ordinary Portland Cement, S-Sand, CS-Copper slag, CA-Coarse Aggregate, CNS-Colloidal Nanosilica, SP-Super plasticizer, W-Water, w/b-Water/binder ratio.

faces of the cubes were sealed with an adhesive tape up to a height of 40 mm from the bottom of the cube specimen in order to maintain unidirectional flow of water from the bottom surface alone. The specimens were periodically removed and increase in weight was measured. A graph between water absorbed against square root of time was plotted and the slope of the graph denotes the sorptivity. Six cubes (100 mm × 100 mm × 100 mm) were cast for each mix to determine sorptivity at 28 and 90 days.

Abrasion resistance test at 28 and 90 days was done in accordance with IS 1237-1980 [74] which is specifically for the determination of abrasion resistance of concrete tiles. Specimens of size 70.6 mm × 70.6 mm × 70.6 mm was used for abrasion test. The dried specimen was weighed and the thickness of the specimens were measured at five point i.e., one at the centre and four corners. The abrasive (Aluminium) powder of 20 g was spread on the disc and the specimen was fixed in the abrasion testing machine and a load of 300 N was applied. The grinding disc was rotated at a speed of 30 rpm and the abrasive powder was continuously fed into the grinding path. After every 22 revolutions, the disc was stopped, the abraded tile powder and the reminder of the abrasive powder was removed. Fresh abrasive powder in quantities of 20 g was applied each time. After every 22 revolutions, the specimen was turned about the vertical axis through an angle of 90° in the clockwise direction and it was repeated 9 times thereby the total number of revolutions was 220. The disc, the abrasive powder and the specimen was kept dry throughout the duration of the test. At the end of the test, the weight and thickness of the specimen was measured. The difference in thickness before and after the abrasion test is the extent of abrasion. The abrasion thickness can be confirmed from

$$T = \frac{W_1 - W_2}{W_1} \times \frac{V_1}{A}$$

T is the average loss in thickness in mm, W_1 is the initial weight of the specimen in grams, W_2 is the weight of the specimen after abrasion in grams, V_1 is the initial volume of the specimen in mm^3, A is the surface area in mm^2.

After mixing the concrete, the slump test was conducted for each mix in accordance with IS: 1199-1959.

After curing, the following tests were conducted on the concrete specimen:

- Cube compressive strength test was conducted at 1, 3, 7, 28, 56 and 90 days in accordance with IS: 516-1959 [72] using a loading rate of 140 kg/sq cm/min, Total: 126 specimens.
- Cylinder splitting tensile strength test was conducted at 3, 7, 28 and 90 days in accordance with IS: 5816-1999 [73] using a loading rate of 1.2 N/(mm^2/min) to 2.4 N/(mm^2/min), Total: 84 specimens.
- Flexural strength test was done at 3, 7, 28 and 90 days in accordance with IS: 516-1959 using a simple beam two point loading at a loading rate of 180 kg/min, Total: 84 specimens.
- Rapid Chloride Penetration test was conducted on three samples after the age of 28 and 90 days in accordance with ASTM C – 1202 [77].
- Water absorption test, Sorptivity test and Abrasion resistance test was conducted on three samples after the age of 28 and 90 days, Total: 42 specimens for each test.
- Mortar cube compressive strength test was conducted at 3, 7, 28, 56 and 90 days in accordance with IS: 4031 (Part 6) – 1988 using a loading rate of 140 kg/sq cm/min, Total: 105 specimens

5. Results and discussions

5.1. Consistency and setting time of nanosilica cement paste

The consistency and setting time values of cement partially replaced with nanosilica are presented in Table 4. The consistency of nanosilica cement paste increased with an increase in the content of nanosilica. Also, the setting time of concrete decreased with increase in the nanosilica content. The addition of nanosilica accelerates the cement hydration which in turn reduces the setting time. The above finding is indirectly detected by an increase in the torque values of rheological tests due to increase in plastic viscosity and yield stress [30]. The length of dormant period was reduced and the rate of hydration was accelerated due to the incorporation of nanosilica. Thus, addition of nanosilica shortened the setting times and increased the early age strength of high volume fly ash or slag concrete [22,23].

5.2. Effect of Nanosilica on strength of cement mortars

The compressive strength of nanosilica cement mortar cubes with constant 40% of copper slag replacement for fine aggregate is shown in Table 5. The strength of all nanosilica mixes was higher than the control mix. The strength of cement mortar cubes increased with the percentage of nanosilica addition up to 2% and then reduced. The enhancement in 3 days compressive strength of mortar cubes was 25.87%, 52.8%, 80.4%, 100.6%, 95% and 86.5% for MCN0.5, MCN1, MCN1.5, MCN2, MCN2.5 and

Table 4
Standard consistency and setting time of cement with nanosilica.

Nanosilica replacement (%)	Standard consistency (%)	Setting time (min)	
		Initial setting time	Final setting time
0	28	145	324
0.5	28	141	300
1	29	138	281
1.5	29	138	262
2	30	132	240
2.5	30	129	218
3	31	123	209

Table 5
Average compressive strength of cement mortars at different curing ages.

Mix ID	Cement (%)	Nanosilica (%)	Compressive Strength (MPa)				
			3 days	7 days	28 days	56 days	90 days
MCN0	100%	0	16.3	34.9	56.5	60.6	62.7
MCN0.5	99.5%	0.5%	20.5	40.9	60.1	62.3	65.4
MCN1	99%	1%	24.9	42.4	63.6	64.5	66.9
MCN1.5	98.5%	1.5%	29.4	45.5	65.7	66.9	68.4
MCN2	98%	2%	32.7	48.9	68.3	69.7	70.9
MCN2.5	97.5%	2.5%	31.8	46.6	66.6	67.2	68.1
MCN3	97%	3%	30.4	43.8	64.7	65.2	66.4

MCN3 mixes respectively than the reference mix MCN0. Many results have been focused on the excellent performance in the early age strength gain. With more benefits reported on the effects of nanosilica in cement based materials, it is worthwhile that there are some contradicting results on the optimum percentage of nanosilica replacement. Also, the strength gain is directly attributed to the method of production of nanosilica and the dispersion of nano particles in cement based materials. The main role of Pozzolanic reaction is strength development and reduction of pore size distribution. The increase in compressive strength of cement paste was observed to increase up to 2% nanosilica beyond which the strength reduced [31].

The strength gain for MCN2 mix is 20.9% and 13% at the age of 28 and 90 days respectively whereas strength gain for MCN3 mix decreased to 14.5% and 5.9% at 28 and 90 days. Specimens with higher content of nanosilica suffer excessive self desiccation and cracking and this can be overcome to a certain extent by adjusting water and HRWRA dosages in the mixture [10,16,28]. The strong tendency to form agglomerates by the nano particles when added to water affects the fresh and hardened properties of cement based materials. Thus, formation of agglomeration due to lack of effective dispersion of nano sized particles during mixing limits the optimum quantity of nanosilica. Improvement in compressive strength of cementitious systems with nanosilica resulted due to both densification and filler effect of ITZ [34].

5.3. Effect of Nanosilica on workability of HPSC

Slump test values are indicated in Table 3 and the results indicate that the samples had a plastic consistency. The results from our previous study indicated that the workability of concrete mixes made with copper slag increased substantially as the copper slag content increased due to its low water absorption and the glassy surface in comparison with sand and it was also observed by other authors [42–44].

Addition of copper slag improves the workability of the mortars and concrete due to its glassy surface and less water absorption. But, higher percentage of copper slag addition results in segregation and bleeding. Addition of nanosilica in concrete decreases the workability and this is attributed to the fact that some portion of the mixing water is absorbed by nanosilica particles. Water molecules are readily attracted towards the nanosilica particles due to high specific surface area and high reactivity. Thus, a reduction in the amount of free water which is required for improving the fluidity of the mix was observed. Therefore the viscosity of the mix was increased resulting in decrease in workability upon addition of nanosilica. To overcome this water demand, the quantity of super plasticizer was adjusted to achieve proper workability during production of concrete mixes. A study conducted on the effect of nanosilica on Portland cement paste concludes that the addition of nanosilica to cementitious mixes produces a remarkable reduction of the mix workability, due to instantaneous interactions between the Nanosilica sol and the liquid phase of the cementitious mixes with the formation of gel characterized by high water retention capacities [38]. Many authors confirm the fact that additions of high surface area mineral particles to cement mixes require higher amounts of water or admixtures to maintain the workability of the mix [68,70].

It was observed that for CN0, CN0.5, CN1 mixes, the super plasticizer content was constant and for mixes CN1.5, CN2, CN2.5, CN3 the super plasticizer content was gradually increased to achieve the required workability. Workability increased with copper slag replacement and decreased with nanosilica replacement. Thus, the above two materials are added to the concrete in order to achieve the benefit of each material thus counteracting the short coming of the other. Nanosilica addition reduces segregation and bleeding and improves cohesiveness of the mixture. Water demand increased with addition of nanosilica in order to retain its workability [33,40].

5.4. Effect of nanosilica on strength properties of HPSC

To properly evaluate the effect of addition of nanosilica on the mechanical properties of High Performance Slag Concrete (HPSC), all the mixes were made with same water/binder ratio and workability although it was quite difficult to satisfy the above two conditions simultaneously. Fig. 4 shows the variation of compressive strength due to the addition of nanosilica in slag concrete at 1, 3, 7, 28, 56 and 90 days of curing. The strength of all concrete mixes increased with age. From the result, it was observed that the concrete mixes made with nanosilica exhibited higher compressive strength than control mix.

The percentage increase of compressive strength in comparison to the control mix at various ages is presented in Table 6. The mixes CN0.5, CN1, CN1.5, CN2, CN2.5 and CN3 showed an improvement in compressive strength of 40.1%, 56.4%, 75.6%, 89%, 78.5% and 71.5% respectively with respect to the control mix CN0 at 1 day. The same trend was noticed on all other days of curing. It was observed that the compressive strength enhanced up to 2% nanosilica replacement and then declined slightly. The greater consumption of $Ca(OH)_2$ is noticed in the early ages (1–7 days of curing) due to the enhanced hydration by nanosilica. This result is

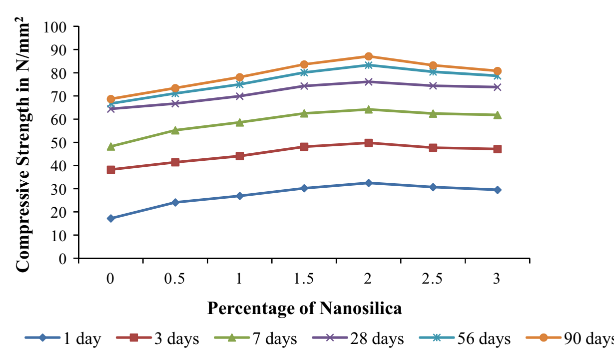

Fig. 4. Effect of nanosilica on Compressive strength.

Table 6
Increase in compressive strength at various ages in comparison with the control mix (CN0).

Mix Id	1 day (%)	3 days (%)	7 days (%)	28 days (%)	56 days (%)	90 days (%)
CN0.5	40.1	8.4	14.5	3.6	6.6	6.8
CN1	56.4	15.4	21.6	8.5	12.4	13.7
CN1.5	75.6	25.9	29.7	15.4	20.1	21.7
CN2	89	30.4	33.2	18.2	24.9	26.8
CN2.5	78.5	24.9	29.5	15.5	20.5	21.1
CN3	71.5	23.3	28.2	14.6	18	17.6

advantageous up to Nanosilica replacement of 2% by weight of cement. The well compacted hydration products formed by Pozzolanic reaction of nanosilica and calcium hydroxide coats the unhydrated cement thus lowering the rate of hydration. Also hydration products fills the pores between the cement thus shortcutting the entry of water to the unhydrated cement particles thus lowering the strength gain beyond 2% replacement of nanosilica.

Fig. 4 shows the variation of compressive strength due to the addition of nanosilica at all ages. It was observed that the development in 90 days compressive strength was 6.8%, 13.7%, 21.7%, 26.8%, 21.1% and 17.6% for CN0.5, CN1, CN1.5, CN2, CN2.5 and CN3 mixes respectively than control mix CN0. The increase in strength is attributed to the fact that the $Ca(OH)_2$ liberated during the hydration of cement is utilized by nanosilica resulting in higher strength at early ages. Further, the products of hydration fill the pores in the concrete thus making it denser.

The 1 day compressive strength of CN0 mix was observed to be 0.267 times the 28 day compressive strength. The increase in compressive strength at 1 day was observed to be 0.361–0.427 times the 28 day compressive strength for nanosilica mixes. Similarly, the 3 days, 7 days, 56 days and 90 days compressive strength was observed to be 0.593, 0.748, 1.036 and 1.067 times the 28 day compressive strength of CN0 mixes respectively. The improvement in compressive strength at 3 days, 7 days, 56 days and 90 days was observed to be 0.621–0.654, 0.828–0.844, 1.066–1.095 and 1.095–1.145 times the 28 day compressive strength respectively for CN0.5 to CN3 mixes. The mix CN2 shows maximum strength gain at all days of curing and the ratio of increase in compressive strength with respect to 28 days was higher at 1 day for all nanosilica mixes. The enhancement of mechanical properties of recycled aggregate concrete mixes at early days was observed due to high Pozzolanic activity of nanosilica at initial periods [29]. The decrease in the calcium hydroxide content at 1 day was reported higher than at 28 day by another author [37] and this supports the result of present study. The ratios of 7–28 day compressive strength for all the HPSC mixes with nanosilica varied from 0.826 to 0.844 and it is comparable with the 0.8–0.9 range reported by ACI 363 R-92 [76] based on the studies carried by Parrrott [67].

From the above results, it was observed that the strength gain is higher during the 1 day of curing when compared with other ages of curing. But the less significant effect on the1 day strength of nanosilica incorporated slag mortar than at 3 and 7 days when compared with nanosilica incorporated fly ash mortar were attributed to the retarding effect of higher dosages of super plasticizer was reported by an author [22]. In this study, proper care was exercised in fixing the dosage of super plasticizer and hence the above adverse effect has been overcome to some extent.

The splitting tensile strength and flexural strength development is similar to the compressive strength development at all ages of curing. All the specimens show higher strength than control mix. Fig. 5 shows the variation of splitting tensile strength due to the addition of nanosilica at all ages. The mixes CN0.5, CN1, CN1.5, CN2, CN2.5 and CN3 showed an increase in splitting tensile strength of 3.7%, 8.9%, 14.6%, 18.6%, 15.4% and 11.1% respectively with reference to the control mixture CN0 at 3 days. At 7 days, the splitting tensile strength developed was 5%, 10.4%, 16.2%, 21.4%, 18% and 14.6% for CN0.5, CN1, CN1.5, CN2, CN2.5 and CN3 mixes respectively than control mix CN0. The improvement in splitting tensile strength was 7.7%–25.4% and 7.5%–26.5% for nanosilica mixes respectively than control mix CN0 at 28 and 90 days. The splitting tensile strengths of HPSC admixed with nanosilica is substantially higher than the control mix due to the stronger bonding between the cement paste and aggregate.

Fig. 6 shows the variation of flexural strength due to the addition of nanosilica at all ages. At 3 days, the mixes CN0.5, CN1, CN1.5, CN2, CN2.5 and CN3 showed an improvement in flexural strength of 16%, 24.3%, 32.5%, 41%, 33% and 25.3% respectively than control mix CN0. It was observed that the 7 days flexural strength was 6.25 MPa for the control mix CN0 and the flexural strength enhancement was 11.7%, 20.1%, 29.3%, 37.7%, 33.2% and 27.6% for CN0.5, CN1, CN1.5, CN2, CN2.5 and CN3 mixes respectively with respect to the control mix CN0. The increase in 28 days flexural strength was 10.7%, 21.1%, 28.8%, 36.5%, 29.2% and 22% for CN0.5, CN1, CN1.5, CN2, CN2.5 and CN3 mixes respectively than control mix CN0. At 90 days, gain in flexural strength was 10.7%, 18.3%, 25.1%, 32%, 28% and 20.9% for CN0.5, CN1, CN1.5, CN2, CN2.5 and CN3 mixes respectively with reference to the control mix CN0. The mechanical properties of copper slag concrete were improved with the increase in percentage of nanosilica in comparison to the reference concrete particularly at early ages. The maximum compressive strength, splitting tensile strength and flexural strength was obtained in the sample containing 2% of nanosilica. However the compressive strength, splitting tensile strength and flexural strength for all the samples were closer to each other.

Another finding is that the use of nanosilica with reduced water-binder ratio improves the interfacial transition zone and mortar matrix. This is confirmed by the cracks passing through coarse aggregate particles in HPSC with 2% nanosilica as the weakest link in passes through the coarse aggregate. The above finding is confirmed by other authors [22,23].

The decrease in mechanical properties with greater than 2% nanosilica particles replacement is attributed to the reason that the quantity of nanosilica particles is higher than the quantity of liberated lime in the hydration process which results in leaching out of excess silica. Thus, at this stage, nanosilica acts as a cement replacement material used for filling the pores but does not involve in the hydration process.

5.5. Relationship between splitting strength and flexural strength to compressive strength

Compressive strength is considered as an index for all types of strength and since evaluations of strength with different tests are unaffordable, a direct relationship between the compressive

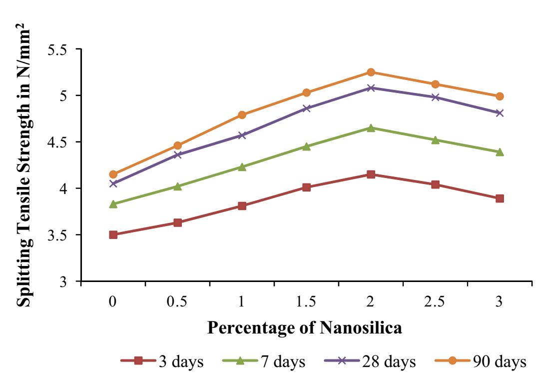

Fig. 5. Effect of nanosilica on Splitting tensile strength.

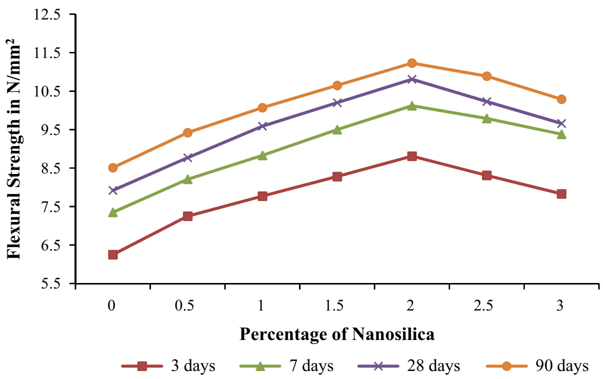

Fig. 6. Effect of nanosilica on Flexural strength.

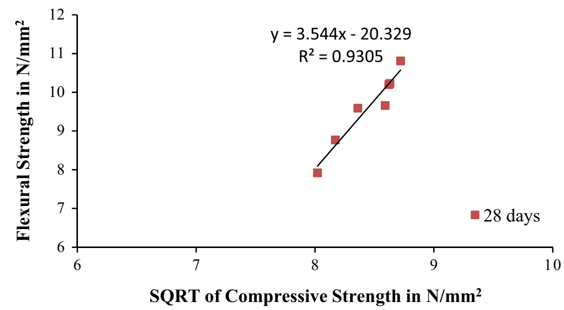

Fig. 8. Relation between SQRT of Compressive strength and Flexural strength.

strength and splitting tensile strength and the relationship between compressive and flexural strength is presented. Fig. 7 shows the relationship between the square root of compressive strength and splitting tensile strength for all mixes at 28 days of curing. Fig. 8 shows the relationship between the square root of compressive strength and flexural strength for all mixes at 28 days of curing. From the R^2 value of the linear plot in the Figs. 7 and 8 shows a good correlation between the two specified strength. From the equations, it is possible to predict a specified strength by knowing at least one of the specimen's strength.

Table 7
Effect of nanosilica on the chloride ion penetration of HPC made with copper slag.

Mix	Charge passed in coulombs (28 days)	Chloride ion penetrability	Charge passed in coulombs (90 days)	Chloride ion penetrability
CN0	1338	Low	1160	Low
CN0.5	1134	Low	991	Very Low
CN1	1054	Low	917	Very Low
CN1.5	985	Very Low	849	Very Low
CN2	821	Very Low	709	Very Low
CN2.5	909	Very Low	787	Very Low
CN3	962	Very Low	817	Very Low

5.6. Effect of nanosilica on chloride ion penetration of HPSC

The ability of concrete to resist the penetration of chloride ions is a critical parameter in determining the service life of steel-reinforced concrete structures exposed to deicing salts or marine environments [56]. It is also quite important to investigate the behavior of concrete containing industrial byproducts like copper slag with respect to resistance to chloride ion penetration.

The RCPT values of nanosilica mixes with a constant 40% fine aggregate replacement by copper slag at the age of 28 days and 90 days are presented in Table 7. From the results, it was observed that all the mixes have low penetrability to chloride. Coulomb value decreased with the increase in nanosilica content up to 2% indicating that the concrete became denser. Beyond 2% nanosilica, a slight increase in the coulomb value was noted. The above aspect has been reflected in the compressive strength result also. Maximum reduction in the coulomb value was observed at 2% nanosilica addition from which it can be concluded that the concrete exhibit more resistance to chloride ion penetrability than other mixes.

In this study, it was observed that HPSC containing nanosilica showed low and very low chloride ion penetrability as compared with the above concretes. The significant reduction in chloride ion penetration may be due to the incorporation of spherical particles like nanosilica and copper slag which resulted in the improvement of the particle packing density of the matrix. Coulomb charges passed at 90 days are less than those of 28 days due to the dense microstructure of concrete. This is in good agreement with the compressive strength values. Addition of nanosilica significantly reduced the Chloride iron penetration in Self Compacting Concrete due to densified microstructure and refined pore structure [33]. Reduction of RCPT values were observed in fly ash based geo polymer mortar with nanosilica additions due to the presence of more crystalline compounds [36].

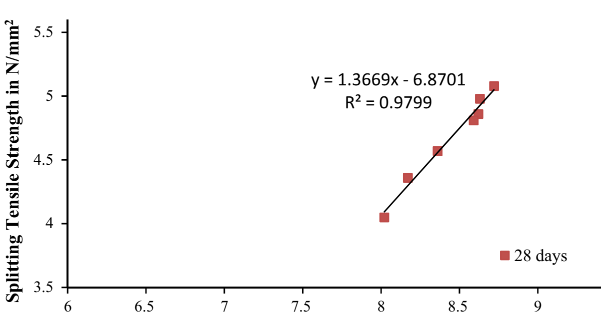

Fig. 7. Relation between SQRT of Compressive strength and Splitting tensile strength.

5.7. Effect of nanosilica on water absorption and sorptivity of HPSC

The impact of nanosilica on the water absorption of HPSC mixes at the age of 28 and 90 days are shown in Fig. 9. It was observed that the water absorption decreased from 2.99% to 1.95% for nanosilica replacement from 0% to 2% and then slightly increased to 2.17% for 3% weight replacement at the age of 28 days. The incorporation of 2% nanosilica resulted in water absorption of 1.95% and 1.52% at 28 and 90 days respectively.

All the mixes showed low water absorption than the control mix at both 28 and 90 days. The water absorption characteristics followed the same trend at 90 days. The low water absorption values in nanosilica mixes was attributed due to the higher pozzolanic effect of nanosilica which made the concrete more compact and dense. Also the effect of pore filling of very fine nanosilica improved the pore structure of the concrete which in turn reduces the water absorption of concrete.

Fig. 10 illustrates the influence of nanosilica on the sorptivity of HPSC mixes. Nowadays sorptivity has been considered as an important index of concrete durability as it is a measure of moisture transport into unsaturated specimens [60]. In the sorptivity test, the driving force for the entry of water into the concrete is capillary suction within the pore spaces of concrete and not the pressure head [61]. Sorptivity coefficient is an important parameter to predict the service life of a concrete structure [62]. Increasing

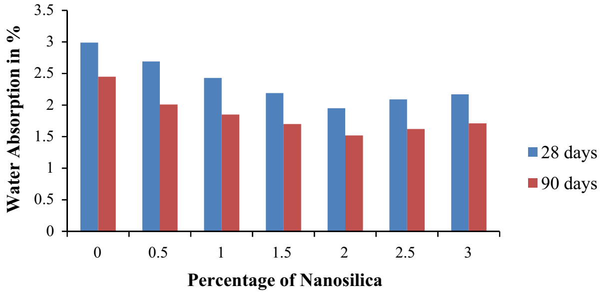

Fig. 9. Effect of nanosilica on water absorption.

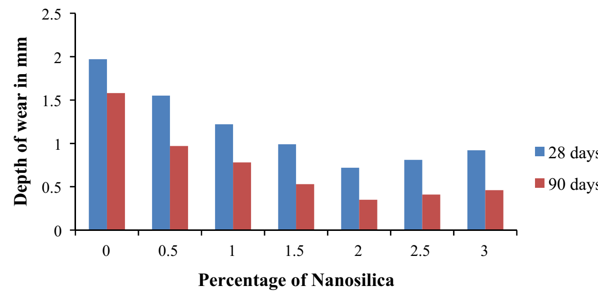

Fig. 11. Effect of nanosilica on depth of wear.

the nanosilica content from 0% to 2%, causes decrease in the sorptivity value by 43.2% and 56.9% at 28 and 90 days respectively. Being very fine particles, the nanosilica fill the pores in the bulk cement paste thus reducing the capillary pores. So the addition of nanosilica can be beneficial to gain in the strength and reduction in the capillary sorption of concrete. The above performance was attributed due to the packed and refined microstructure and pore structure achieved by addition of nanosilica. Decrease in the sorptivity coefficient of concrete with increase in the compressive strength of concrete was reported by other author [63] and the above result is in good agreement with the present study.

5.8. Effect of nanosilica on abrasion resistance of HPSC

The abrasion resistance of nanosilica incorporated HPSC was measured in terms of depth of wear at the age of 28 and 90 days. The variation of depth of wear at 60 min of testing is shown in Fig. 11 for all mixes at 28 and 90 days.

It was observed that the depth of wear decreased with increase in age of concrete for all mixes. It is evident from the Fig. 11 that, with increase in the content of nanosilica, depth of wear decreased which indicated the increase in amounts of nanosilica enhanced the abrasion resistance. At the end of abrasion test, depth of wear for mixes containing 0.5%, 1%, 1.5%, 2%, 2.5% and 3% nanosilica was 1.55 mm, 1.39 mm, 0.99 mm, 0.72 mm, 0.81 mm and 0.92 mm respectively whereas the depth of wear for the control mix was 1.97 mm at 28 days. Similar trend was observed for abrasion resistance at 90 days. The abrasion resistance of concrete mixes containing nanosilica was remarkably improved. The above effect is due to the accelerated Pozzolanic action of nanosilica and improvement in the strength of the concrete particularly the ITZ. The depth of wear decreased up to 2% weight replacement of nanosilica and then slightly increased. Abrasion resistances of HPSC mixes improved by about 63.5% and 77.8% over control mix with 2% nanosilica replacement of cement at ages of 28 and 90 days respectively. The improvement in abrasion resistance of concrete was reported due to the thin mortar layer on the surface of the concrete containing low water and cement content [24]. A slight decline in the abrasion resistance of CN2.5 and CN3 mixes were noticed. Beyond 2% nanosilica replacement, the distance between nanosilica particles decreases which resists the growth of Calcium Hydroxide crystals. Thus the ratio of $Ca(OH)_2$ crystals to C-S-H gel is reduced and the micro structure of cement matrix is loosened. Hence the abrasion resistance of concrete decreased relatively beyond 2% nanosilica replacement. The concrete contains 40% copper slag as fine aggregate replacement which is also a main factor in improving the abrasion resistance due to its better bond with the binder material paste. Similar trend was noticed by other authors when the sand was partially replaced by Metakaolin [64], bottom ash [65] and Flyash [66]. This shows that the abrasion resistance enhanced with inclusion of industrial by products due to their filling effect and making the concrete denser.

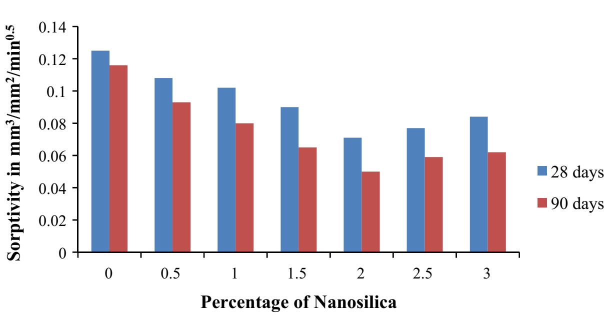

Fig. 10. Effect of nanosilica on sorptivity.

6. Conclusions

Based on the experimental results, the following conclusions can be drawn using nanosilica in cement pastes, mortars and concrete with 40% of copper slag as fine aggregate replacement at a constant w/b of 0.31.

1. As the content of colloidal nanosilica was increased up to 3%, the consistency was increased where as setting time was reduced due to acceleration of hydration.
2. The incorporation of nanosilica in cement mortars with 40% copper slag as fine aggregate replacement increased the compressive strength compared to the reference mortar mix at all ages. The strength was increased up to nanosilica addition of 2% and then reduced but higher than the reference mix. This is due to the formation of hydrated products in the presence of colloidal nanosilica.
3. The results of slump test done on HPSC indicated reduction in slump values with increase in the colloidal nanosilica content. The nanosilica particles have high surface area resulting in higher demand of water. The dosage of super plasticizer was adjusted to maintain a constant workability as that of the control mix.
4. Addition of nanosilica resulted in the enhancement of Compressive strength of HPSC mixes at all ages. The greatest impact in strength development was observed at early curing ages owing to the high Pozzolanic activity of nanosilica at initial periods. The 1 day compressive strength was 0.36–0.43 times 28 day compressive strength of nanosilica mixes as compared with 0.27 times for the control mix. The development in strength at later ages is mainly due to filling effect rather than Pozzolanic action.
5. The maximum compressive strength, splitting tensile strength and flexural strength of High Performance slag concrete (HPSC) was obtained in the sample containing 2% of nanosilica. Incorporation of nanosilica in mortars and concrete increases the

strength gain at early ages due to its high specific surface area and high Pozzolanic activity. The above reaction results in higher production of C-S-H gel and compact structure. Beyond 2% addition, quantity of nanosilica is higher than the quantity of liberated lime thus reducing the Pozzolanic action. It can be concluded that the optimum content of nanosilica in HPSC is 2%.

6. From the R^2 value of the linear plot of strength properties at 28 days, a good correlation between any two specified strength (compressive strength, splitting tensile strength and flexural strength) can be observed.
7. RCPT values of HPSC with 2% nanosilica were very low at both 28 and 90 days. The charges passed in the nanosilica mixes were observed to be less than the control mix. The significant reduction in chloride ion penetration may be due to the incorporation of spherical particles like nanosilica and copper slag which resulted in the improvement of the particle packing density of the matrix.
8. Water absorption and sorptivity values of HPSC reduces with increase in nanosilica content due to the combined action of pore filling effect and acceleration of hydration of nanosilica making the concrete more dense and compact. The maximum reduction in water absorption and sorptivity values was observed in the HPSC mixes containing 2% of nanosilica.
9. Appreciable improvement in abrasion resistance of HPSC containing nanosilica was noticed due to the use of low cement and water content. The depth of wear was 0.52 mm and 0.35 mm at 28 and 90 days respectively for nanosilica replacement of 2%. Decrease in depth of wear was observed up to 2% nanosilica replacement and then increased slightly.

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