DURABILITY PERFORMANCE OF NANO-SILICA BASED HIGH PERFORMANCE CONCRETE

Jashanpreet Singh Narang[1], Aditi Chauhan[2], Umesh Kumar Sharma[2], Rajib Chowdhury [2]

1. Department of Civil Engineering, Punjab Engineering College, Chandigarh, India
2. Department of Civil Engineering, Indian Institute of Technology-Roorkee, Roorkee, India

ABSTRACT. In the present study durability properties of high performance concrete made with nano-silica and micro silica were evaluated using laboratory experiments. Nano-silica (NS) powder was extracted from Rice Husk Ash (RHA) by controlling different process parameters. Durability tests namely accelerated chloride migration test, volume of permeable voids, water permeability test, sorptivity test, acid attack test, accelerated carbonation test, electrical resistivity test, chloride diffusion test were performed. It was concluded that incorporation of NS improves the microstructure of concrete, and hence improves the waterproof ability, decreases the diffusion coefficient of various ions, elevate the ability to resist sulphate erosion, and is helpful to improve concrete's long-term properties.

Keywords: Durability, Nano silica, Micro silica, Permeability, Carbonation, Diffusion.

Jashanpreet Singh Narang is an undergraduate student of Civil Engineering at Punjab Engineering College, Chandigarh, India.

Umesh Kumar Sharma is Associate Professor of Civil Engineering at Indian Institute of Technology-Roorkee, Roorkee, India.

Aditi Chauhan is a Ph.D. scholar at Indian Institute of Technology-Roorkee, Roorkee, India.

INTRODUCTION

Cement is the main binding material in concrete. Over the past three decades, production of cement has grown rapidly all over the world. The cement production in India is expected to grow three-folds by 2050 [1]. However, cement production has major environmental issues that are of concern worldwide [2],[3]. For every one tonne of clinker manufactured, approximately one tonne of CO_2 is released to the atmosphere [4] which contributes almost 5-7% of global anthropogenic carbon dioxide emissions. In the manufacturing process of cement, the main sources of gas emissions are combustion of fuels and decomposition of $CaCO_3$ to CaO and CO_2.

Construction industry is one of the sectors, which recently realized the potential of nanotechnology applications. A wide range of construction materials could possibly be modified in their performance remarkably by nano-engineering. It is expected to fill the shortcomings of the conventional building materials such as cement / concrete, glass, steel, coatings etc. It is expected that civil engineering industry will get tremendous benefit through nanotechnology.

Concrete is normally reinforced by steel bars. Besides compressive strength, durability properties are also of high importance, when dealing with reinforced concrete. While strength of concrete containing NS has received particular attention in the last decade, less consideration has been paid to its durability properties [5]. So, recently, there are increasing number of studies in which several durability related properties of cement composites were investigated such as water sorptivity, resistance to chloride penetration, water permeability, resistance to acid attack, electrical resistivity, and carbonation resistance.

It was found that the water absorption of concrete decreases with the addition of NS [6]. In another study, it was reported that water absorption and water sorptivity of concrete were not influenced by NS [7]. The water absorption of mortar was reduced by the addition of 2.5% NS [8], while a little higher content of NS (around 3%) increased the water absorption of mortar [9]. It had been reported that chloride diffusion coefficient of concrete was reduced by NS addition [10]. According to Madani [11] and Belkowitz [12], the bulk electrical resistivity of concrete samples was increased after the addition of NS.

As far as carbonation resistance is concerned, [9] reported no change in carbonation resistance of mortar containing NS, while [13] found that 5% NS addition to cement paste led to reduction in the degree of carbonation. Although there are some works considering carbonation resistance of cementitious materials, detailed quantitative data on NS impact on the advancement of carbonation in time, especially in concrete, are lacking in the literature [5].

EXPERIMENTAL PROGRAM

Materials

To achieve the objective of the study, following materials were used to prepare the high performance concrete.

Coarse aggregates

Locally available crushed stone coarse aggregate (CA) of maximum size 12.5 mm confirming to IS: 383:1970 [14] were used. The fineness modulus of coarse aggregate used was 6.3.

Fine aggregates

Fine aggregates (FA) confirming to Zone II of IS: 383-1970 [14] were used in this study. The fineness modulus of zone II sand is 2.47.

Cement

All through the experimental study, Ordinary Portland Cement 43 Grade conforming to IS: 8112 - 1989 [15] was used. The Specific Gravity of cement used was 3.15.

Mineral admixtures

Nano-silica (NS) obtained from Rice Husk Ash (RHA) and Micro silica Grade 920 D (MS) were used as supplementary cementitious materials to prepare the mix.

Super plasticizer

A high performance concrete superplasticizer GLENIUM® 51 based on modified polycarboxylic ether was used to improve the workability of given mix.

Mix Design

Trial mixes were prepared to achieve the target strength of 60 MPa of concrete and slump in the range of 100 to 125 mm for pumpable concrete. It has been observed earlier that 0.5% NS dosage results in the optimum compressive strength of concrete. Table 1 shows the mix design for the adopted concrete. NS based mix was compared with micro-silica (MS) based concrete for durability evaluation.

Table 1 Mix Design adopted in the study

MIX	W/C RATIO	WATER (kg/m^3)	CEMENT (kg/m^3)	NS (0.5%) (kg/m^3)	MS (5%) (kg/m^3)	FA (kg/m^3)	CA (kg/m^3)
NS-MS based HPC	0.3	160	521.8	2.67	26.67	686.5	1052.6
MS based HPC	0.34	158	440	-	25	726	1046

Durability Tests

Table 2 lists the durability tests performed to evaluate the performance of developed high performance concrete.

Table 2 Durability Tests to be carried out

S. No.	NAME OF TEST	STANDARD TO BE FOLLOWED	TYPE OF SPECIMEN	NO. OF SPECIMEN
1.	Chloride Migration Test	NT BUILD 492	Cylinder (100mm×50mm)	3
2.	Volume of Permeable Voids	ASTM C642 – 2013	Cube (100mm)	3
3.	Water Permeability Test	IS 3085 – 1965	Cylinder (150mm×150mm)	3
4.	Sorptivity Test	ASTM C1585-2013	Cylinder (100mm×50mm)	3
5.	Acid Attack Test	-	Cube (100mm)	3
6.	Accelerated Carbonation Test	RILEM_CPC-18 - 1988	Prism (100mm×100mm×350mm)	3
7.	Electrical Resistivity Test	-	Prism (100mm×100mm×200mm)	3
8.	Chloride Diffusion Test	ASTM C1556 11a-2016	Cylinder (100mm×200mm)	3

Accelerated chloride migration test

Accelerated chloride migration test was used to determine the chloride migration coefficient in concrete by non-steady-state migration experiment in accordance with NT Build 492[16]. Chloride migration coefficient is a measure of the resistance of concrete to chloride penetration. Three cylindrical specimens of 100 mm diameter and 50 mm height were prepared as per the codal provisions. Figure 1 below shows the setup used for the test.

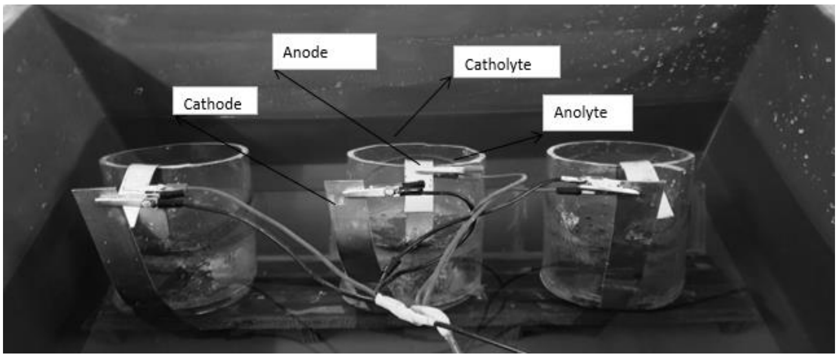


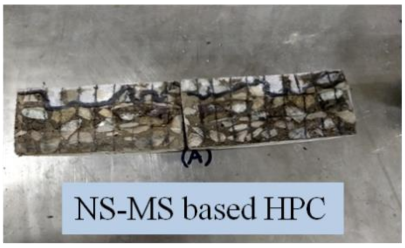
Figure 1: Chloride migration test setup arrangement

The catholyte solution is 10 % NaCl by mass in tap water (100 g NaCl in 900 g water, about 2 N) and the anolyte solution is 0.3 N NaOH in distilled or de-ionised water (approximately 12 g NaOH in 1 litre water).

After performing the experiment, when the white silver chloride precipitation on the split surface was clearly visible (after about 15 minutes), the penetration depths of each specimen were measured with the help of the slide calliper and a suitable ruler, as illustrated in Figure 2 to obtain seven depths.

Figure 3 shows the calculated coefficient values for both the mixes, while Table 3 shows the categorization of concrete based on the coefficient values as per NT Build 492.

From the calculated values both the mixes fall in the category of good quality concrete.



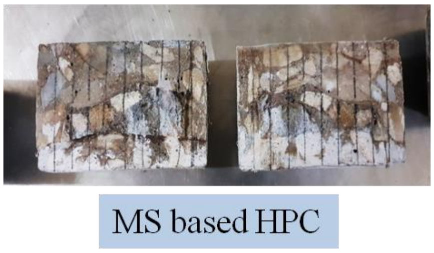


Figure 2: white precipitate formed after spraying $AgNO_3$ solution, representing chloride ion penetration

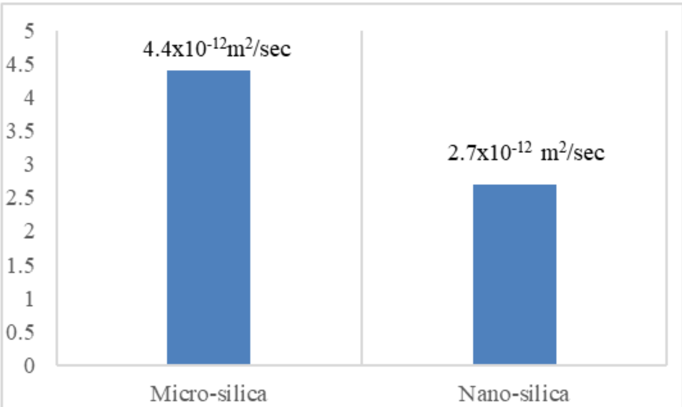


Figure 3 Average chloride migration coefficient values obtained for each mix.

Table 3 Concrete quality based on NT Build 492

Nordtest Method BUILD 492, Migration coefficient (m^2/s)	**Concrete quality**
$< 2 \times 10^{-12}$	Very good
$2 – 8 \times 10^{-12}$	Good
$8 – 16 \times 10^{-12}$	Normal
$> 16 \times 10^{-12}$	Poor

Thus, the average non-steady-state migration coefficient (D_{nssm}) for the nano-silica based and micro-silica based mixes are 2.70×10^{-12} m^2/s and 4.4×10^{-12} m^2/s respectively.

Volume of permeable voids

Permeability is defined as the ease with which fluids can penetrate in the concrete. Permeability can be lowered by reducing the number of connected pores within the paste system of a mixture. The density, percent absorption, and percent voids in hardened concrete are determined in accordance with ASTM C 642- 2013 [17].

The average volume of permeable pore space (voids) in the given concrete mixes was found to be 3.84% for NS based mix and 7.06% for MS based concrete, as mentioned in Table 4.

Table 4 Results of permeable voids test

Specimen		Absorption after immersion (%)	Absorption after immersion and boiling (%)	Bulk density dry (g/cm^3)	Bulk density after immersion (g/cm^3)	Bulk density after immersion and boiling (g/cm^3)	Apparent density (g/cm^3)	Volume of permeable voids (%)	Avg. Permeable Voids (%)
NS-MS based HPC	a.	1.60	1.60	2.43	2.47	2.47	2.53	3.88	3.84
	b.	1.57	1.57	2.43	2.47	2.47	2.52	3.81	
	c.	1.38	1.58	2.42	2.45	2.46	2.52	3.83	
MS based HPC	a.	2.98	2.98	2.35	2.42	2.42	2.53	7.01	7.06
	b.	2.83	3.04	2.35	2.42	2.42	2.53	7.14	
	c.	2.98	2.98	2.36	2.43	2.43	2.53	7.01	

Water permeability test

Permeability is defined as the property that governs the rate of flow of a fluid into a porous solid. Water permeability test procedures were carried out as per the standard IS: 3085-1965 [19]. High permeability, due to porosity or cracking, provides ingress for water, chlorides and other corrosive agents. If such agents reach reinforcing bars within the structure, the bars get corroded. Hence the study of water permeability of concrete is very important. To conduct the permeability test cylinders of 150 mm diameter and 150 mm height were casted and cured for 28 days. At the age of 56 days specimens were placed in permeability cells and water was supplied to the cell with a pressure of 10 kg/cm^2.

During the test no outflow was obtained so the test was continued till 100-hour duration and hence penetration depth was measured by splitting the specimens and then coefficient of permeability was calculated by the following equation:

$$K = \frac{D^2P}{2TH}$$

Where,
K = Co-efficient of permeability in m/s
D = Depth of penetration in m
P = Porosity of concrete in fraction in accordance with ASTM C 642-2013[17]
T = Time in sec
H = Pressure head in m

Coefficient of water permeability was found to be 1.54×10^{-13}m/s for NS based HPC and 3.17×10^{-13}m/s for MS based HPC, as shown in Table 5.

Table 5 Coefficient of water permeability for different specimens

SPECIMEN		DEPTH OF PENETRATION (mm)	POROSITY	COEFFICIENT OF PERMEABILITY (m/s)	AVERAGE COEFFICIENT OF PERMEABILITY (m/s)
NS-MS based HPC	A	18	0.0384	1.728×10^{-13}	1.54×10^{-13}
	B	17	0.0384	1.541×10^{-13}	
	C	16	0.0384	1.365×10^{-13}	
MS based HPC	A	19	0.0701	3.51×10^{-13}	$3.17 \text{ x } 10^{-13}$
	B	17	0.0714	2.87×10^{-13}	
	C	18	0.0701	3.15×10^{-13}	

Sorptivity test

Sorptivity is the rate of absorption of water by concrete which is measured by the increase in the mass of a specimen resulting from absorption of water as a function of time when only one surface of the specimen is exposed to water. Test was conducted in accordance with ASTM C1585-2013.As per the codal guidelines exposed surface of the specimen was immersed in water and gain in mass of the specimen is determined at intervals specified in the code.

The absorption, I, is the change in mass divided by the product of the cross-sectional area of the test specimen and the density of water.

$$I = \frac{m_t}{a * d}$$

where,
I = the absorption,
m_t = the change in specimen mass in grams, at the time t,
a = the exposed area of the specimen, in mm^2, and
d = the density of the water in g/mm^3 i.e. 0.001 g/mm^3

The initial rate of water absorption is the slope of the best fit line to the Absorption v/s $Time^{1/2}$ plot, which was determined by linear regression analysis of this plot for all points from 1 minute to 6 hours. The secondary rate of water absorption is the slope of the best fit line to the Absorption v/s $Time^{1/2}$ plot, which was determined by linear regression analysis of this plot for all points from day 1 to day 8. For any of the absorption rate if correlation coefficient is less than 0.98 i.e. it does not follow a linear relationship, in such case the rate cannot be determined.

The average initial rate of absorption was found to be $3.33\times10^{-4}mm/sec^{1/2}$ for nano-silica based mix. However, the average secondary rate of absorption was found approximately 10 times lesser i.e. $3.00\times10^{-5}mm/sec^{1/2}$. Similarly for the second mix, average initial rate of absorption was found to be $5.33\times10^{-4}mm/sec^{1/2}$ and $6.00\times10^{-5}mm/sec^{1/2}$ as secondary rate of absorption.

The data collected for each specimen is presented in Figure 4 and Table 6. The initial and secondary rate of absorption was determined since correlation coefficient was found to be more than 0.98 in each case.

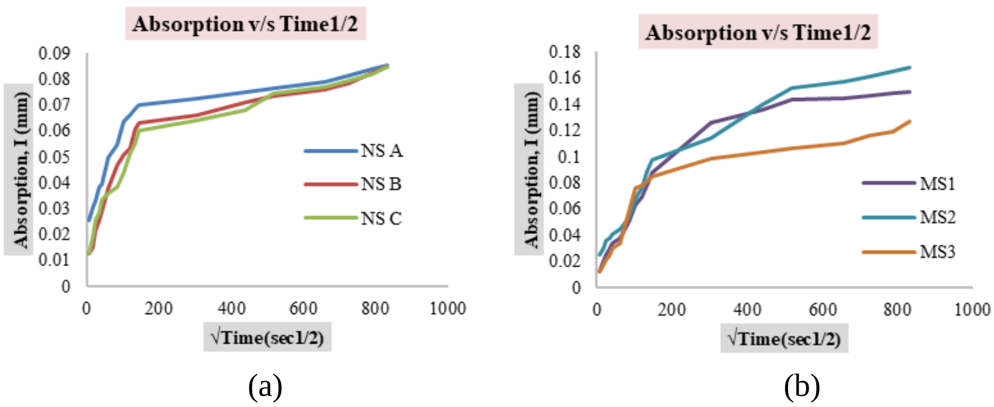


Figure 4 Plot for Absorption, *I* (mm) v/s square root of Time ($sec^{1/2}$) for (a) NS-MS based HPC and (b) MS based HPC

Table 6 Average Initial and Secondary rate of water absorption

SPECIMEN	INITIAL RATE OF ABSORPTION (mm/s$^{1/2}$)	SECONDARY RATE OF ABSORPTION (mm/s$^{1/2}$)	SPECIMEN	INITIAL RATE OF ABSORPTION (mm/s$^{1/2}$)	SECONDARY RATE OF ABSORPTION (mm/s$^{1/2}$)
NS-MS A	3×10^{-4}	2×10^{-5}	MS 1	5×10^{-4}	4×10^{-5}
NS-MS B	4×10^{-4}	3×10^{-5}	MS 2	5×10^{-4}	9×10^{-5}
NS-MS C	3×10^{-4}	4×10^{-5}	MS 3	6×10^{-4}	5×10^{-5}
Average	3.33×10^{-4}	3×10^{-5}	Average	5.33×10^{-4}	6×10^{-5}

Acid attack test

Concrete is susceptible to attack by sulphuric acid produced from either sewage or sulphur dioxide present in the atmosphere of industrial cities. This attack is due to the high alkalinity of Portland cement concrete, which can be attacked by other acids as well. Sulphuric acid is particularly corrosive due to the sulphate ion participating in sulphate attack, in addition to the dissolution caused by the hydrogen ion. 100 mm cube specimens were weighed in surface dry condition and then were immersed in the H_2SO_4 acid solution with a concentration of 2.5% by volume after 28 days of curing. All specimens were kept under the same deteriorating environment until the date of testing (for 28 days). To determine the extent up to which the damage is caused by acid attack to immersed specimen, the specimens were taken out from the acidic solution and were rinsed with tap water as shown in Figure 5. The specimens were then weighed in surface dry condition to determine the weight loss.
Table 7 presents the mass loss determined after exposure to sulphate attack.

(a) (b)

Figure 5 Deteriorated surface of (a) NS based concrete and (b) MS based concrete after immersion in H_2SO_4 solution

Table 7 Test data of acid attack on concrete specimens

SPECIMEN		INITIAL MASS (gm)	FINAL MASS (gm)	CHANGE IN MASS (gm)	MASS LOSS (%)	AVERAGE MASS LOSS (%)
NS-MS based HPC	A	2580	2440	140	5.4	5.03
	B	2620	2495	125	4.8	
	C	2630	2500	130	4.9	
MS based HPC	A	2585	2450	135	5.2	5.26
	B	2605	2465	140	5.4	
	C	2580	2445	135	5.2	

Thus, the average mass loss in Nano silica based high performance concrete was found to be 5.03% after 28 days of exposure in acidic solution, while that for micro-silica based concrete was 5.26%.

Accelerated carbonation test

Carbonation occurs in concrete because the calcium bearing phases present are attacked by carbon dioxide of the air and converted to calcium carbonate.

$$Ca(OH)_2 + CO_2 \quad \rightarrow \quad CaCO_3 + H_2O$$

Carbonation induced corrosion is a major concern related to the deterioration of the structures in semi-arid exposure. Hence, it is required to determine the carbonation resistance of concrete. The process of carbonation is actually a long-term reaction. So, an accelerated carbonation testing system has to be used to simulate natural carbonation process in short duration. The test was carried out on concrete prism specimen (100 mm x 100 mm x 350 mm) as per recommendations of RILEM CPC-18 -1988. The concentration of CO_2 in the chamber was maintained at 4.7%, relative humidity at 65 ± 5% and temperature at 20^0C.
After exposing the specimens for duration of 28 days, 50 mm slices were obtained from specimens and when 0.1 % phenolphthalein solution was sprayed over freshly sawn surface. It was observed that no carbonation occurred as shown in Figure 5.

Electrical resistivity test

Electrical resistivity of concrete is used to determine the resistance of concrete against the flow of ions. Four-point Wenner probe technique was used to measure the surface resistivity of the concrete prisms (100mm x 100mm x 200mm) at the age of 28 days and 56 days. The results are shown in Figure 6. The outer two electrodes induce the measuring current and the inner electrodes measure the resulting potential drop into the voltage. The resistance R calculated from the four-point measurement could be converted to resistivity ρ using a cell constant based on theoretical considerations by:

$$\rho = 2 * \pi * a * R,$$

where a is the electrode spacing.

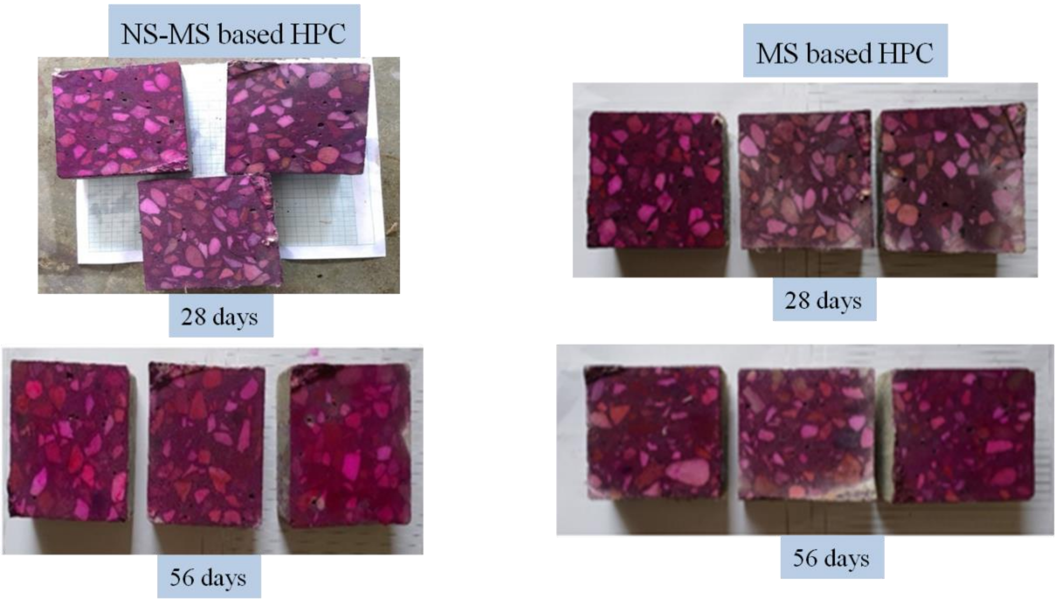


Figure 5: Pink surfaces of specimens of concrete indicating no carbonation has occurred

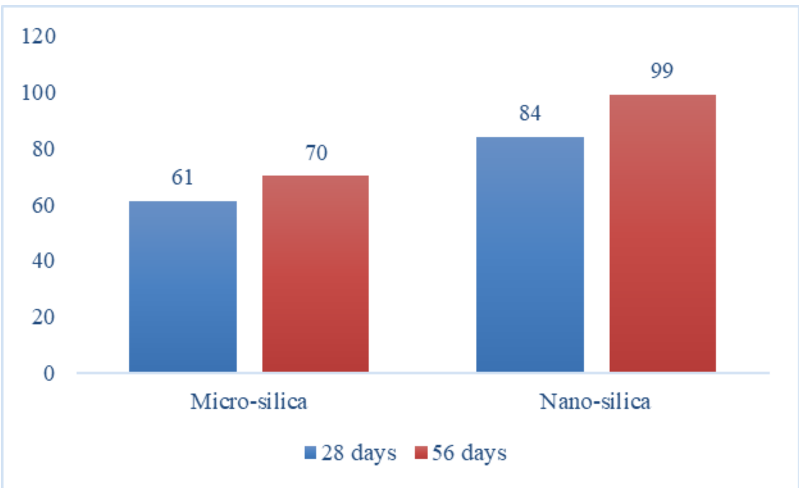


Figure 6 Electrical resistivity of concrete at 28 days and 56 days.

It was observed that the average surface electrical resistivity of given nano-silica based and micro-silica based concrete mixes were 84 kΩ cm and 61 kΩ cm at the end of 28 days. While at the end of 56 days the resistivity as high as 99 kΩ cm was obtained for the former mix and 70 kΩ cm for the latter one.

CONCLUDING REMARKS

Replacement of cement with Nano-silica leads to the optimum strength and proves to be very cost effective for preparing high performance concrete. Within the scope of this experimental study, following conclusions can be drawn:

- 0.5% replacement of cement with nano-silica leads to the optimum strength. Thus, nano-silica can be very cost effective for preparing high performance concrete.

- Mix made with nano-silica shows better durability performance than mix containing micro-silica, under chloride penetration.

- It is appropriate to use nano-silica based concrete in places susceptible to water ingress, as inferred from the water permeability and sorptivity test results.

- Nano-silica based concrete has high electrical resisitivity which increase with time, hence can be used in reinforced concrete structures prone to corrosion activity.

- Use of nano-silica in structure exposed to industrial waste, or biogenic acid attack in concrete sewer lines is justified from the acid attack results

- Nano-silica prepared in the laboratory is very cost effective in comparison to the available nano-silica in the market, and shows better performance from durability and strength point of view.

ACKNOWLEDGMENTS

The data reported in this study is based on experiments performed in the laboratory. The authors would like to acknowledge the contribution made by the laboratory staff of Structural Engineering laboratory at IIT Roorkee.

REFERENCES

1. WBCSD-IEA. “Cement roadmap targets.” World Business Council for Sustainable Development, 2006.
2. BARCELO, L., KLINE, J., WALENTA, G., AND GARTNER, E. “Cement and carbon emissions.” Materials and Structures, 47, 1055–1065, 2014.
3. DAVIDOVITS, J. “Global Warming Impact on the Cement and Aggregates Industries.” World Resource Review, 6(2), 263–278, 1994.
4. BENHELAL, E., ZAHEDI, G., SHAMSAEI, E., AND BAHADORI, A. “Global strategies and potentials to curb CO_2 emissions in cement industry.” Journal of Cleaner Production, 51, 142–161, 2013.
5. FOROOD TORABIAN ISFAHANI, ELENA REDAELLI, FEDERICA LOLLINI, WEIWEN LI, AND LUCA BERTOLINI, “Effects of Nanosilica on Compressive Strength and Durability Properties of Concrete with Different Water to Binder Ratios,” Advances in Materials Science and Engineering, vol. 2016, Article ID 8453567, 16 pages.

6. M. JALAL, E. MANSOURI, M. SHARIFIPOUR, AND A. R. POULADKHAN, "Mechanical, rheological, durability and microstructural properties of high performance self-compacting concrete containing SiO2 micro and nanoparticles," Materials and Design, 2012, vol. 34, pp. 389–400.

7. H. DU, S. DU, AND X. LIU, "Durability performances of concrete with nano-silica," Construction and Building Materials, 2014, vol. 73, pp. 705–712.

8. M. ZAHEDI, A. A. RAMEZANIANPOUR, AND A. M. RAMEZANIANPOUR, "Evaluation of the mechanical properties and durability of cement mortars containing nanosilica and rice husk ash under chloride ion penetration," Construction and Building Materials, 2015, vol. 78, pp. 354–361.

9. S. RAO, P. SILVA, AND J. DE BRITO ,"Experimental study of the mechanical properties and durability of self-compacting mortars with nano materials (SiO_2 and TiO_2)," Construction and Building Materials, 2015, vol. 96, pp. 508–517.

10. G. QUERCIA, P. SPIESZ, G. HÜSKEN, AND H. J. H. BROUWERS, "SCC modification by use of amorphous nano-silica," Cement and Concrete Composites, 2014, vol. 45, pp. 69–81.

11. H. MADANI, A. BAGHERI, T. PARHIZKAR, AND A. RAISGHASEMI, "Chloride penetration and electrical resistivity of concretes containing nanosilica hydrosols with different specific surface areas," Cement and Concrete Composites, 2014, vol. 53, pp. 18–24.

12. J. S. BELKOWITZ, W. L. B. BELKOWITZ, K. NAWROCKI, AND F. T. FISHER, "Impact of nanosilica size and surface area on concrete properties," ACI Materials Journal, 2015, vol. 112, no. 3, pp. 419–427.

13. S. LIM AND P. MONDAL, "Effects of nanosilica addition on increased thermal stability of cement-based composite," ACI Materials Journal, 2015, vol. 112, no. 2, pp. 305–316.

14. IS 383: "Specification of Course and Fine Aggregates from Natural Sources for Concrete". Bureau of Indian Standards, India,1970.

15. IS 8112: "Specification for 43-Grade Ordinary Portland Cement," Bureau of Indian Standard New Delhi, India, 1989.

16. NT BUILD 492 "Chloride migration coefficient from non-steady-state migration experiments".

17. ASTM C642-2013 "Standard Test Method for Density, Absorption, and Voids in Hardened Concrete".

18. ASTM C1585-2013 "Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic- Cement Concretes".

19. IS 3085-1965 "Method of test for permeability of cement mortar and concrete".

20. ASTM C1556—11a (Reapproved 2016) "Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion".

21. ASTM C1202 - 18 "Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration".