Advances in Nano Research, *Vol. 5, No. 2 (2017) 99-111*
DOI: https://doi.org/10.12989/anr.2017.5.2.099

Strength and durability study on cement mortar containing nano materials

M. Ashok [*1], A.K. Parande [2a] and P. Jayabalan [1b]

[1] *Department of Civil Engineering, National Institute of Technology, Tiruchirappalli, Tamilnadu, India*
[2] *Food Engineering Department, cftri, Mysore, Karnataka, India*

(*Received September 15, 2016, Revised February 02, 2017, Accepted February 07, 2017*)

Abstract. Nano particles have been gaining increasing attention and applied in many fields to fabricate new materials with novel functions due to their unique physical and chemical properties. In the present study two nano materials, namely nano silica (NS) and nano clay metakaolin (NMK) were partially replaced with ordinary Portland cement (OPC). The replacement level was varied from 0.5 to 2.0% in OPC and blended in cement mortar with a water cement ratio of 0.40. Mechanical property studies and durability experiments such as compressive strength, tensile strength, water absorption, depth of chloride penetration test. Nano silica was synthesized from rice husk ash and analyze the size using particle size analyzer. The results indicate that the compressive and tensile strength of the cement mortars containing nano materials were higher strength compared to the plain mortar with the same water cement ratio.

Keywords: nano silica; nano metakaolin; rice husk ash; compressive strength; durability

1. Introduction

Cement and concrete production consume enormous amounts of natural resources and aggregates, thereby causing substantial energy and environmental losses. This production also contributes significantly to the emission of carbon dioxide, a naturally occurring greenhouse gas. Adjustments and improvements to the present concrete making methods are essential in order to address these environmental and economic issues. This has encouraged researchers in the niche area of concrete engineering and technology to investigate and identify supplementary by-product materials that can be used as substitutes for the constituent materials in concrete production. The beneficial effects of some of these materials on the properties of concrete have further enhanced these efforts. Jo (Jo *et al*. 2008) reported that nano-SiO_2 behaves not only as a filler to improve microstructure, but also as an activator to promote the pozzolanic reaction. The study confirmed that strength increases with increasing nano-SiO_2. Increasing the NS content, the rate of bond strength increased results more in compressive strength. Qing (Qing *et al*. 2007) has expressed the Pozzolanic activity of nano-SiO_2 is much greater than that of silica fume. The amount of water

∗Corresponding author, Ph.D. Research Scholar, E-mail: ashok.citizen@gmail.com
[a] Principal Scientist, E-mail: corrparande@yahoo.co.in
[b] Professor, E-mail: pjeya@nitt.edu

http://www.techno-press.org/?journal=anr&subpage=5 ISSN: 2287-237X (Print), 2287-2388 (Online)

needed at standard consistency increased as more nano-SiO_2 added. Addition of nano-SiO_2 can shorten the setting time. Morsy (Morsy *et al.* 2010) studied the replacement of nano clay resulted in improvement in concrete durability, including the resistance to chloride penetration, freezing and thawing reaction. The enhancement of compressive strength was 7% at 8% NMK replacement. NMK was not only acting as filler, but also as an activator to promote hydration process. In another study by the same author Morsy (Morsy *et al.* 2011), expressed that, the reduction period in construction can be derived to lesser time as nano materials can produces high strength concrete with less curing time. Nano Metakaolin also contains alumina that reacts with CH to produce additional alumina containing phases. Metakaolin increases resistance to alkali silica reaction of concrete (ASR) and its effect on sulphate resistance increases systematically with increased level of replacement ratio of cement by metakaolin. Askarinejad (Askarinejad *et al.* 2012) found that, pozzolanic reaction occurs between $Ca(OH)_2$ and pozzolan. The pozzolanic reaction progresses like an acid-base reaction of lime and alkalies with oxides (SiO_2+Al_2O_3+Fe_2O_3) of the pozzolan. Nano-SiO_2 decreased the setting time of mortar when compared with silica fume and reduced bleeding water and segregation. The performance of these cementitious based materials is strongly dependent on nano-sized particles Lin (Lin *et al.* 2008) and Ltifi (Ltifi *et al.* 2002). Sadrmomtazi (Sadrmomtazi *et al.* 2009) has shown that nano-SiO_2 particles were more effective in the reduction of permeability than that of silica fume. Nano-SiO_2 particles block the passages connecting capillary pores and water channels in cement paste. Irassar (2000) has expressed that, the most important factor to prevent external sulphate attack is to reduce the permeability of the mortar (Low *w*/*c* ratio, well compacted and cured).

Thus, this study focuses on improving strength and durability by using these two nano materials. The influence of the nano-silica and nano metakaolin on the cement mortar was investigated with respect to the properties of cement mortar in the hardened state (mechanical properties and durability).

2. Materials and methodology

2.1 Materials

Ordinary Portland Cement of Grade 43 conforming to IS 8112. The chemical compositions are shown in Table 1.

Table 1 Chemical composition of ordinary portland cement

Properties	Values
(1) Lime saturation factor	0.9
(2) Alumina Modulus	1.23
(3) Insoluble residue (%)	0.25
(4) Magnesia (%)	1.1
(5) Sulphuric anhydride SO_3 (%)	1.5
(6) Loss on ignition (%)	0.8
(7) Chloride (%)	0.002
(8) C_3A Content	7
(9) Humidity (%)	65±5

Table 2 Properties of ennore sand

Properties	Ennore sand
Physical properties	
Colour	Grayish white
Specific Gravity	2.64
Absorption in 24 hours	0.80 %
Shape of grains	Subangular
Chemical properties	
SiO_2	99.30 %
Al_2O_3	-
Fe_2O_3	0.10 %
CaO	-
Petrographic analysis	
Quartz	97.40%
Feldspar	2.50%

Fine aggregate used for this study is ennore sand obtained from Ennore, Tamilnadu. Ennore sand, composed of three grades (Grade I, Grade II and Grade III having the sizes 1 mm to 2 mm, 0.5 mm to 1 mm and 0.09 mm to 0.5 mm respectively), each one corresponding to 33.33% weight, was used as fine aggregate in the mortar. Table 2, shows the physical and chemical properties of the ennore sand.

Nano silica was synthesized from rice husk ash. The particle size analyses for synthesized Nano silica are shown in Fig. 1. The synthesized NS has a density of 3.2 g/cc with spherical shape and having particle refractive index 2.55. From the graph, the percentile varied from 110 nm to 249 nm. Nano metakaolin was obtained from ASTRRA chemicals, Chennai. The particle size analyses for nano metakaolin are shown in Fig. 2. Nano metakaolin have on average size of 223 nm at 10% and gradually increase up to 551 nm at 95%.

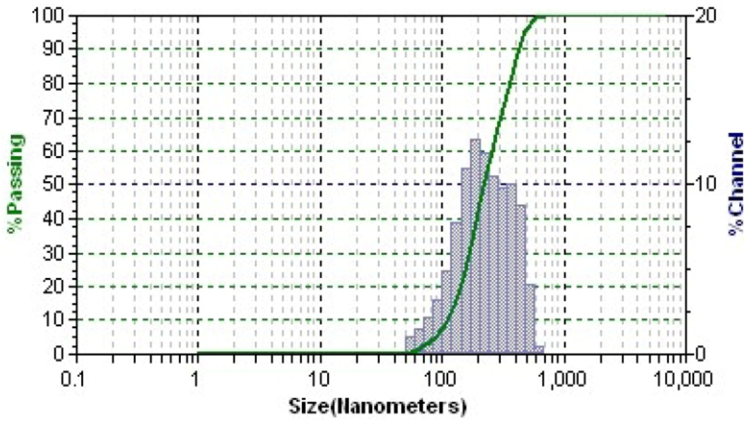

Fig. 1 Particle size analysis for nano silica

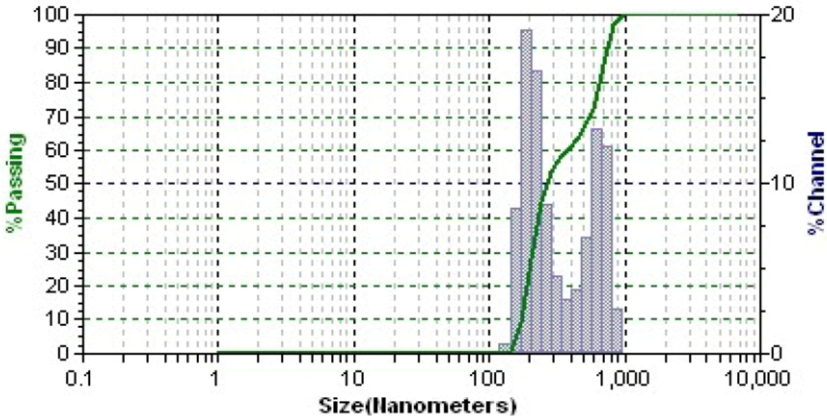

Fig. 2 Particle size analysis for nano metakaolin

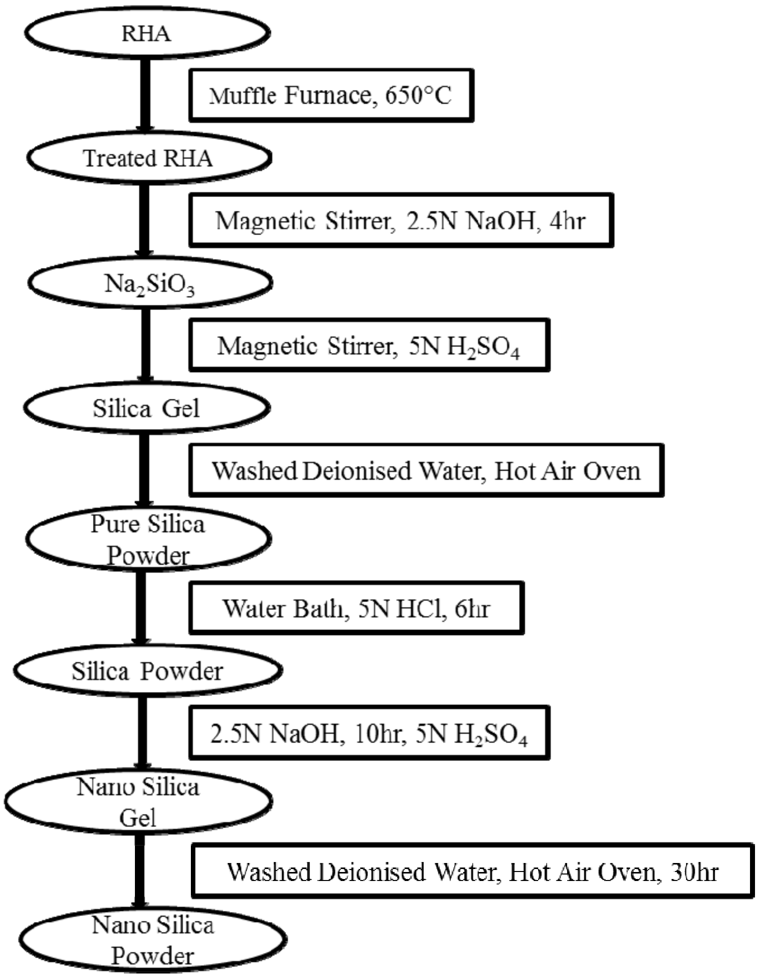

Fig. 3 Synthesis of nano silica from rice husk ash

2.2 Synthesis of nano silica from rice husk ash (RHA)

RHA contains more than 90% silica content and this is the cheapest material. So the synthesis of Nano silica from RHA was achieved. RHA was received from N.K. Enterprises, Orissa. Rice husk ash is produced by burning rice husk which contains a large proportion of silica. The flow diagram of the above procedure is shown in Fig. 3. Amutha (Amutha *et al*. 2010).

2.3 Experimental procedure

Mortar cube specimens of 50 mm^3 in size were cast using partial replacement of the OPC with the various levels of NS and NMK varied from 0.5%-2.0% by the weight of cement. Mortar specimens were prepared using mix ratio 1:3 and water cement ratio as 0.40. The ASTM standard method was used to test compressive strength as per ASTM C39 (2001). The specimens were mechanically vibrated. After 24 hours of setting the specimens were demoulded and were cured for 7 days, 28 days, 56 days and 90 days in normal water. After the curing period, the specimens were tested for compressive strength. Similarly split tensile strength specimens were cast as per the ASTM standards. For durability study the specimens were cast in disk of size 85 mm × 50 mm and were used for rapid chloride penetration test (RCPT) as per ASTM C1202 (1997).

3. Results and discussion

3.1 Strength aspects

3.1.1 Compressive strength

Figs. 4-5 show the compressive strength measurements of NS and NMK. From Figs. 4-5, it's inferred that the compressive strength of mortar increased from 7 days to 90 days. The compressive strength of the mortar increased with the addition of NS rendered of larger specific area and

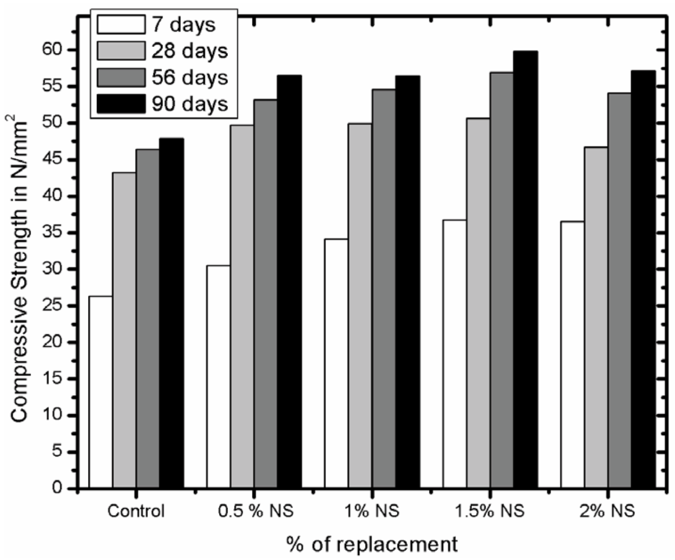

Fig. 4 Compressive strength for nano silica

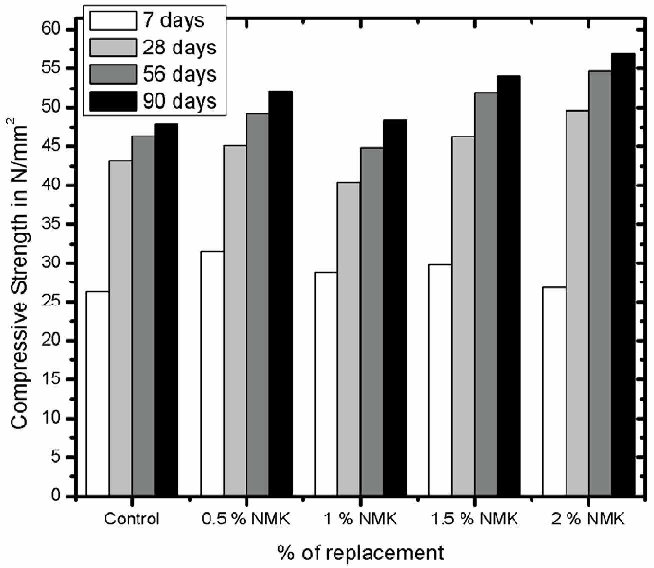

Fig. 5 Compressive strength for nano metakaolin

larger reaction area and higher pozzolanic activity were produced. At the end of 7 days the compressive strength of control mix was found to be 26.32 MPa and at the end of 90 days the compressive strength of the control mix was lesser than the NS and NMK mixes. All the binder assessed show compressive strength high as compared to the control mix.

As NMK belongs to mineral admixture it can improve the micro structural properties and mechanical properties of blended cement. It fills the voids in cement and makes the microstructure of cement mortar with lesser porosity. The pozzolanic reaction of NMK with free lime released during hydration process produces excess of C-S-H gel that deposited in the pore system. The result obtained from the study showed an improvement of mechanical properties.

The cement mortar with NS exhibits superior mechanical properties than that of control mix. During the process of hydration the specific surface area and the number of the surface atoms of the silica nanoparticles are more than that appear in micro silica particles. This higher number of the surface atoms in the nanoparticles translates into a larger number of free and unsaturated atomic bonds on the surface of the nanoparticles, which makes them thermodynamically unstable, as compared with the micro size silica particles Lin (Lin *et al*. 2011).

Furthermore, by reducing the size, the number of the surface atoms on a particle increases which leads to an increase in the appropriate surface area for chemical reactions Zhang (Zhang and Li 2002).

3.1.2 Split tensile strength

Figs. 6-7 show the split tensile strength of blended mortars for different ratios varying from 0.5 % to 2 % of NS and NMK. It is observed that nano metakaolin and nano silica enhances the tensile strength of hardened cement mortar. The measurements were made as per the standard test methods in ASTM C496 (2001). It is also found that NS performance in tensile strength shows to be better than NMK in all the mixes studied.

Basically two mechanisms are involved in the enhancement of split tensile strength of hardened cement mortar and it can be explained as below:

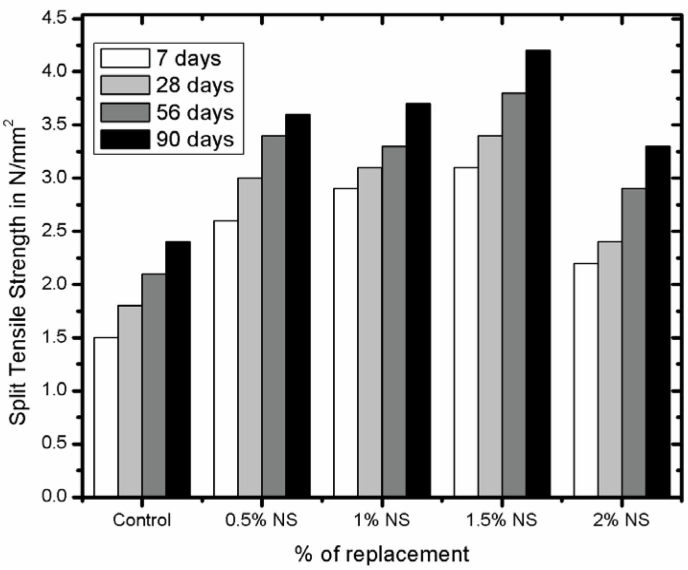

Fig. 6 Split tensile strength for nano silica

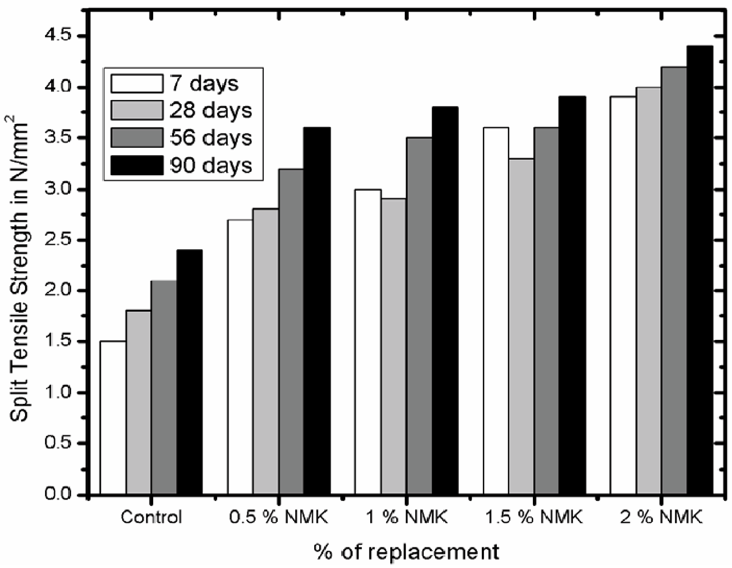

Fig. 7 Split tensile strength for nano metakaolin

The filler effect of NMK into interstitial spaces leads to a micro-cracks resistance which enhances strength. This mechanism holds good for both NMK and NS. Morsy (Morsy *et al*. 2010). The second mechanism is the pozzolanic effect. NMK produces anhydrous alumino-silicate (Al_2SiO_5) which is mainly amorphous material and behave highly reactive artificial pozzolana. The reaction of alumina silicate in NMK with lime liberated during cement hydration leads to the bond strength and solid volume and thus resulting in higher tensile strength.

3.2 Durability aspects

3.2.1 Sulphate attack

Sulphate attack on cement mortar matrix is generally characterized by sulphate ions with cement hydration products, which causes expansion, cracking and spalling as well as loss of mass and strength. Fig. 8 depicts the results of the expansions due to sulphate attack on mortar mixed with NS and NMK. The curing was carried out for 28 days immersed in 5% Na_2SO_4 solution.

In this test control mix was compare with the combination of 1.5% NS + 2% NMK which was the higher strength found from compressive and split tensile strength test. The expansion of the nano silica and nano metakaolin combination mix at the initial days and at the end of the test period was found in percentage varying from 0% to 0 0.033%. As per the ASTM C1012 (1995) the specified expansion of the mortar bar should not increase by 0.1%. From our study it is conformed that the test results are well within the permissible limit as per the ASTM standard. Finally, the conclusion can be drawn such that the mixes has a property of having resistance to sulphate attack due to lesser porosity and not allowing more sulphate ion penetration through the mortar mix.

3.2.2 Acid attack

Fig. 9 indicates the results of acid attack test carried out with the combination of 1.5% NS and 2% NMK which was the level found from our strength study. The mix was compared with control and with partial replacement of NS and NMK in cement mortar. After 28 days of immersion in 5% H_2SO_4 solution and the weight loss in percentage was found. From Fig. 9, the weight loss at the end of 28 days was found to be 12.15%. The results obtained were well within the acceptable limit as per the ASTM C 267 (2012) standard. As per the standard, weight loss should not surpass 15%. When compared with control mix it was found to be 35.79%. It should be noted that the test specimens initially gain weight followed by the weight loss. The weight gain cannot be attributed to the saturation of specimens since the specimens were oven-dried prior to weighing. The reaction

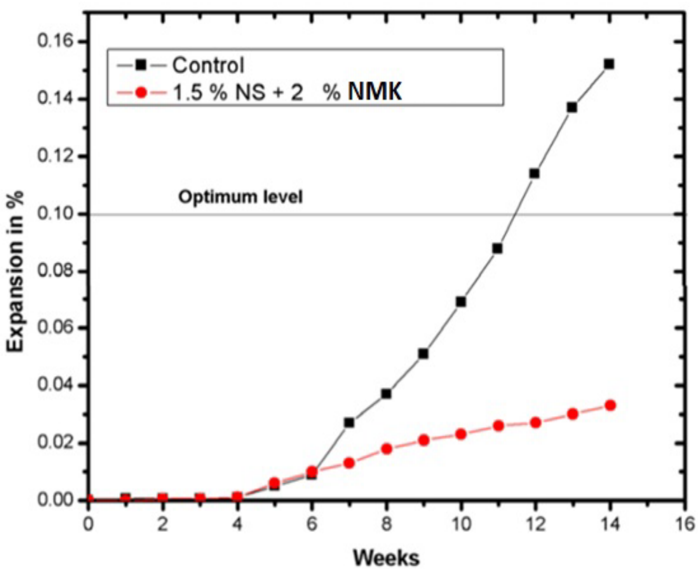

Fig. 8 Expansions for sulphate attack

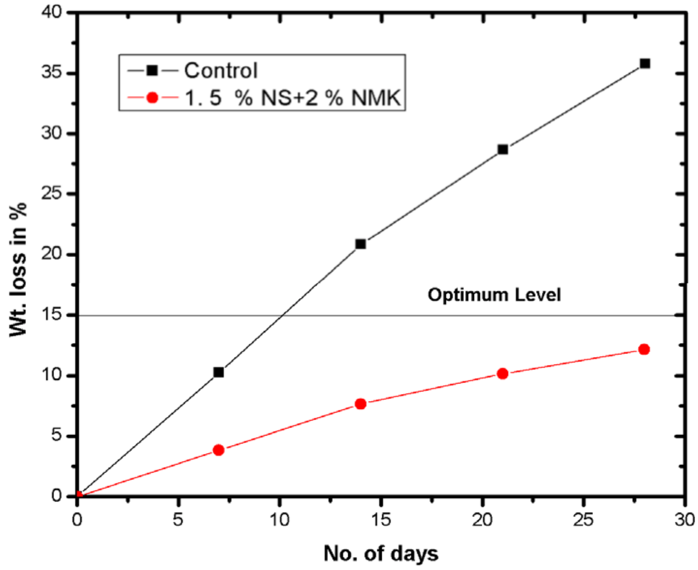

Fig. 9 Weight loss for acid attack

between sulphuric acid and the cement constituent of mortar results in the conversion of calcium hydroxide to calcium sulphate (gypsum) which, in turn, may be converted to calcium sulfoaluminate (ettringite). The formation of calcium sulphate leads to softening (decrease in density) of the mortar, Emmanuel. The combination of hybrid incorporation of NS and NMK performed superior than the control system.

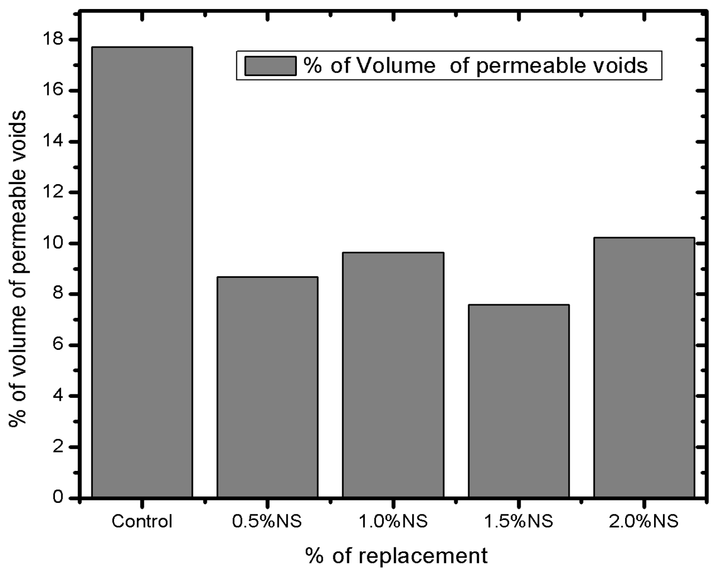

Fig. 10 Water absorption for nano silica

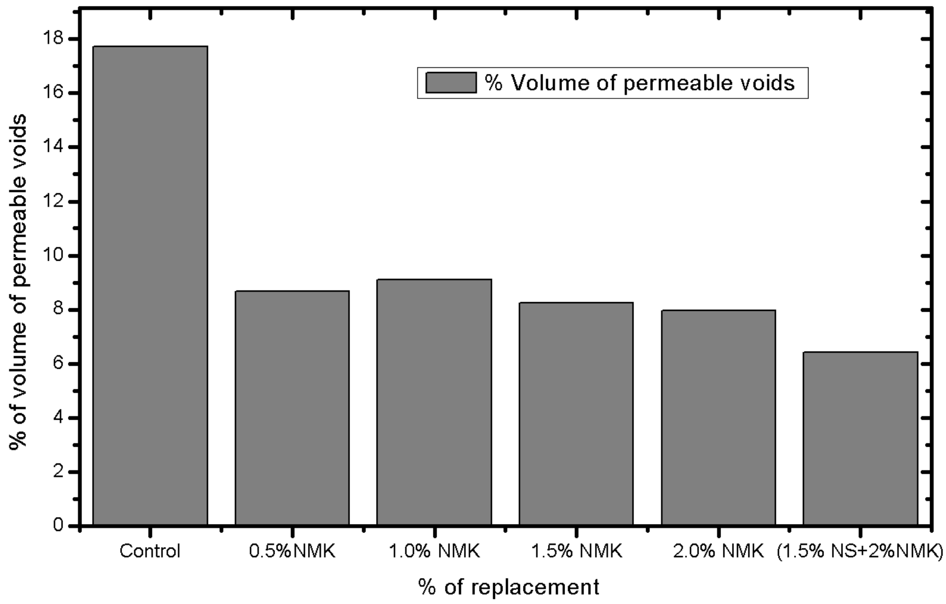

Fig. 11 Water absorption for NMK and combination

3.3 Permeability aspects

3.3.1 Water absorption

The absorption characteristics indirectly represent the porosity through an understanding of the permeable pore volume and its connectivity of these results is in Figs. 10-11 for NS and NMK respectively. The water absorption test was conducted as per ASTM C642 (2006).

The test result shows that the inclusion of NS and NMK can improve considerably in the resistance of water penetration of the mortar mix. A significant reduction in water absorption by marginal replacement of cement was observed. At 28 days curing water absorption values decreased considerably with increase in NS content up to 1.5%. Even at 2% NS, the value was lower compared to that of control. The water absorption amount of all the mixes with replaced nano silica was decreased by more than twice that of the control mix. Similarly, when nano metakaolin used as replacement for cement the water absorption in the mixes was decreased by more than two times compared to control mix. Likewise, the incorporation of NS and NMK leads to substantial improvement in water absorption by about 63.66% decrease when compared with the control mix. The increase in impenetrability can be accomplished by two phenomena. Nano silica particles generate large number of nucleation sites for hydration products and induce a homogeneous distribution of C-S-H gel and hence lesser pore structure. Nano particles act as a retarder or blockage of passages connecting capillary pores and water channels in cement mortar.

3.3.2 Rapid Chloride Penetration Test (RCPT)

It was observed from the Table 3, that NS incorporated mortar specimens remarkably lower the permeability than the control mix. 1.5% and 2% replacement levels were considered to be the best which have lesser coulombs transferred through the media. The total electrical charge (Coulombs) passed in control mix is 2666.13 coulombs, whereas the mix of 1.5% and 2% NS showed lesser

Table 3 RCPT values for nano silica

System	Q_s (Coulombs)	Free chloride (PPM)	J (Mol/cm^2.sec)	D (m^2/sec)
Control	2666.13	212.718	29.37×10^{-9}	1.23×10^{-10}
0.5% NS	4850.54	212.718	29.37×10^{-9}	1.23×10^{-10}
1% NS	6448.65	248.171	3.426×10^{-8}	1.439×10^{-10}
1.5% NS	2189.53	70.9060	9.79×10^{-9}	4.11×10^{-11}
2% NS	2224.48	106.359	14.68×10^{-9}	6.16×10^{-11}

Table 4 RCPT values for NMK and combination

System	Q_s (Coulombs)	Free chloride (PPM)	J (Mol/cm^2.sec)	D (m^2/sec)
Control	2666.13	212.718	29.37x10^{-9}	1.23x10^{-10}
0.5% NMK	2607.60	177.265	24.5x10^{-9}	1.027x10^{-10}
1% NMK	2227.78	106.359	14.68x10^{-9}	0.616x10^{-10}
1.5% NMK	2880.08	212.718	29.37x10^{-9}	1.23x10^{-10}
2% NMK	2179.52	106.359	14.68x10^{-9}	0.616x10^{-10}
1.5%NS+2%NMK	1538.19	70.906	9.79x10^{-9}	0.411x10^{-10}

values i.e., 2189 and 2224 coulombs. Similarly from Table 4, lower permeability values were observed with NMK addition to mortar mix when compared to control. At 2% and 1% NMK replacement levels the total electrical charge (Coulombs) passed in the NMK mix showed lesser values i.e., 2179 and 2227 coulombs.

The Tables 3-4 shows the electrical charge passed through that of NS and NMK mortar exposed in normal water after 28 days. The total electrical charges passed in NS were more than the NMK.

The RCPT result value reflects the interconnected pore's network of mortar in which ions migrate. The improvement in permeability resistance decreases Coulombs charge passed through the NMK that are attributed in the reduction of pore size and an improvement of the interfacial zone which increase the resistance to the ingress of ions present in wastewater. The mechanism of electrical conduction through the hardened cement matters is essentially electrolytic in nature and the principal ions that are responsible for the ionic conduction are Na^+, K^+, Ca^{2+}, OH^- ions present in pore water. During RCPT, the electrical conduction through the specimen is also electrolytic in nature and the majority of electrical conduction. RCPT should be due to chloride ions present in the negative reservoirs of the cell. It is quit logical to experimental part of the electrical conduction during RCPT. The current carrying captions cell Na^+ and K^+, present in pore solution of the specimen can be considered to be insignificant due to the lower ionic conduction, as there migrate in a solvent state Yang (Yang *et al*. 2002). Similarly the Ca^{2+} present in the pore solution should also be negligible due to their presence in low concentration also hinder the inability of Ca^{2+} ion during RCPT.

4. Conclusions

The following broad conclusions were drawn from the above investigation.

- Compressive and split tensile strength of the mortar increases with replacement of NS and NMK, especially at early ages. 1.5% NS and 2% of NMK mixes gives higher strength compared to the other mixes. These results indicate that the pozzolanic activity is greater than that of other mixes studied.
- The water absorption and distribution of chloride ion tests indicate that the NS and NMK mortar have better permeability resistance than the control mix.
- Acid immersion and sulphate immersion studies indicated that nano mortars don't show any deterioration behavior. Also expansions are within the limit as per the ASTM standard.

From the above studies it is concluded that 1.5% of NS and 2% of NMK in mortar was found to be more beneficial and better performance in strength and durability among all other mixes was studied.

Acknowledgments

Authors thank the Director, CSIR-CECRI, Karaikudi for his kind permission to carry out the research work.

References

Amutha, K., Ravibaskar, R. and Sivakumar, G. (2010), "Extraction, synthesis and characterization of Nanosilica from rice husk ash", *Int. J. Nanotech. Appl.*, **4**(1), 61-66.

ASTM C1012-95a (1995), Standard test method for length change of Portland-cement Mortars exposed to a sulfate solution.

ASTM C1202-97 (1997), Standard test method for electrical indication of concrete's ability to resist chloride ion penetration.

ASTM C267 – 01 (2012), Standard test methods for chemical resistance of mortars, grouts and monolithic surfacing's and polymer concretes.

ASTM C39 (2001), Standard test method for compressive strength of concrete specimens, PA, USA.

ASTM C496 (2001), Standard test method for splitting tensile strength of concrete specimens, PA, USA.

ASTM C642-06 (2006), Standard test method for density, absorption and voids in hardened concrete.

Askarinejad, A., Pourkhorshidi, A.R. and Parhizkar, T. (2012), "Evaluation the pozzolanic reactivity of sonochemically fabricated nano natural pozzolan", *Ultrasonics Sonochemistry*, **19**(1), 119-124.

Attiogbe, E.K. and Rizkalla, S.H. (1988), "Response of concrete to sulfuric acid attack", *ACI Mater. J.*, **85**(6), 481-488.

Bonakdar, A. and Mobasher, B. (1994), "Multi-parameter study of sulphate attack in blende cement materials", *Cement Concrete Res.*, **24**(4), 735-742.

Borsoi, A., Collepardi, S., Coppola, L., Troli, R. and Collepardi, M. (2000), "Sulphate attack on blended portland cements", *Proceedings of the 5th CANMET/ACI International Conference on Durability of Concrete*, Barcelona, Spana Am, Coner. Int., SP-192 Vol. 1, pp. 417-432.

Irassar, E.F. (2000), "Sulphate attack on cementitious materials containing limestone filler and natural pozzolana review", *Cement Concrete Compos.*, **22**(5), 361-368.

Irassar, E.F., Bonavetti, V.L. and Gonzalez, M. (2003), "Microstructural study of sulphate attack on ordinary and limestone Portland cements at ambient temperature", *Cement Concrete Res.*, **33**(1), 31-41.

IS 8112 (2000), Revised 43 grade ordinary portland cement – specification.

Jo, B.W., Kim, C.H., Tae, G.H. and Park, J.B. (2008), "Characteristics of cement mortar with nano-SiO_2 particles", *Constr. Build. Mater.*, **21**(3), 153-157.

Lin, K.L., Chang, W.C., Lin, D.F., Luo, H.L. and Tsai, M.C. (2008), "Effects of nano-SiO_2 and different ash

particle sizes on sludge ash-cement mortar", *J. Environ. Manag.*, **88**(4), 708-714.
Lin, Q., Xu, Z., Lan, X., Ni, Y. and Lu, C. (2011), "The reactivity of nano silica with calcium hydroxide", *J. Biomed. Mater. Res. Part-B Appl. Mater.*, **99**(2), 239-246.
Ltifi, M., Guefrech, A., Mounanga, P. and Khelidj, A. (2002), "Experimental study of the effect of addition of nano-silica on the behaviour of cement mortars", *J. Funct. Polym.*, **15**(3), 271-275.
Morsy, M.S., Alsayed, S.H. and Aqel, M. (2010), "Effect of nano-clay on mechanical properties and Microstructure of ordinary Portland cement mortar", *Int. J. Civil Environ. Eng.*, **10**(1), 21-25.
Morsy, M.S., Alsayed, S.H. and Aqel, M. (2011), "Hybrid effect of carbon nanotube and nano clay on physic-mechanical properties of cement mortar", *Constr. Build. Mater.*, **25**(1), 145-149.
Qing, Y., Zenan, Z., Deyu, K. and Rongshen, C. (2007), "Influence of nano-SiO_2 addition On properties of hardened cement paste as compared with silica fume", *Construct. Build. Mater.*, **21**(3), 539-545.
Sadrmomtazi, A. and Barzegar, A. (2010), Assessment of the effect of nano silica on physical and mechanical properties of SCC containing rice husk ash", *Proceedings of the 2nd International Conference on Substainable Construction Materials and Technology*, Ancona, Italy, June.
Sadrmomtazi, A., Fasihi, A., Balalaei, F. and Haghi, A.K. (2009), "Investigation of mechanical and physical properties of mortars containing silica fume and Nano- SiO_2", *Proceedings of the 2nd International Conference on Substainable Construction Materials and Technology*, Ancona, Italy, July.
Thuadaij, N. and Nuntiya, A. (2008), "Preparation of nanosilica powder from rice husk ash by precipitation method", *Chiang Mai J. Sci.*, **35**(1), 206-211.
Tseng, D.H., Pan, S.Z. and Li, Z. (2002), "The study of the characteristics of sewage sludge ash and the development of reclamation techniques", *Proceedings of the 12th Annual Meeting Sanitary Engineering*, Taipei, Taiwan, pp. 221-232.
Yang, C.C., Cho, S.W. and Huang, R. (2002), "The relationship between charge passed and the chloride-ion concentration in concrete using steady-state chloride migration test", *Cem. Concr. Res*, **32**(2), 217-222.
Zhang, Y.L. and Li, C.D. (2002), *Nano-Structured Technology and Nano-Structured Plastics*, China Light Industry Press, Beijing, China, pp. 8-15, 386-389. [In Chinese]

JL