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Use of Nano Silica for improvement of porous fly ash and silica fume mortars

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Abstract: Portland cement requires water-cement (w/c) ratio of about 0.38 to achieve matrix with zero capillary porosity on complete hydration and hence, any w/c ratio beyond 0.38 will always add to porosity, thereby also to permeability. Thus, cement matrix with w/c of 0.51 necessarily is expected to possess high degree of porosity, which can be further increased to reduction in Portland cement content by partial replacement by mineral admixture such as Fly ash and also by reduced curing. Experimental work on use of 'nano-silica solution' (nSS) and silica fume (SF) to improve degree of impermeability of such matrix is presented in this paper. It was observed that the curing regime adopted in this study could impart estimated maturity of only about 48% when compared with 28 days of conventional curing. It was found that external treatment of nanosilica in the cured matrix produce hydration product comparatively much faster rate thereby causing reduction in capillary pores as seen from 70% reduction of co-efficient of water absorption of matrix without Fly ash and 60% reduction in with fly ash matrix. Incorporation of 2% nano silica by mass of cementitious materials increased compressive strength of Fly ash mortars at the age of 3, 7 and 28 days by 20%, 38 % and 18% respectively. SEM pictures examinations indicate that nano scale silica behaves not only as a filler to improve microstructure but also as an activator to promote pozzolanic reaction.

Keywords: Portland cement, nano silica, permeability, Fly ash, silicafume, compressive strength

Introduction

The nano-Silica (nS), siliceous material, pozzolanic in nature, consisting of an amorphous SiO₂ core with a hydroxylated surface with improved properties from conventional grain-size materials of the same chemical composition. Nanosilica is commonly used for reinforcement of polymer to increase the hardness, modulus, weatherability and flammability^{1,2}. Many studies on use of it as a mineral admixture into cement concrete mix aimed at achieving high mechanical strength are extensively reported^{3,4,5,6,7}. However, its use in

India is not widely reported, though there was a report recently on utility of nS to improve properties of recycled concrete aggregate by external treatment and in cementitious materials^{8,9}. Portland cement reacts with water to form free lime (CH) and C-S-H gel, a nano-sized product, provides the binding action in the composites. But, the porosity is generated by presence of capillary and gel pores (besides entrapped and entrained air) which contribute towards permeability to external aggressive agencies such as water, oxygen, CO₂, chlorides, sulphates, etc.¹⁰. If the w/c ratio > 0.38, the capillary pores does remain, as the products of cement hydration would not be able to fill the capillary pores. Usually silica (SiO₂) reacts with free lime of the hydrated cement matrix to form secondary C-S-H gel which acts as pore filling as well as pore-size refining material. Therefore, the nano-silica (nS), due to its extreme small size, besides being amorphous, can act both physically and chemically in the cement matrix to improve matrix and reduce its degree of impermeability. This aspect was taken up in the present study and the degree of permeability was measured by determining the 'coefficient of water absorptivity' (COA) which is based on rate of water absorption by capillary action and compressive strength¹¹.

Extensive research efforts have been directed to enhance the mechanical property and durability by using supplementary cementitious materials, which partially replace ordinary cement, including Fly ash, natural pozzolans, ground granulated blast furnace slag. The main concern about fly ash concrete, particularly that containing Class F fly ash, has been its slow rate of strength development compared to normal concrete^{12,13}. Numerous studies have been conducted to explore different solutions for this issue, but concrete comprising Class F fly ash is sometimes not preferred for applications where early strength is required, such as in case of repairs and rapid construction. The activity of silica fume at early ages is low according to the literature report^{14,15} and C-S-H formation is very low upto 7 days and extensive C-S-H formation had occurred after 120 days. Investigation showed that only 75% of SF was consumed by a cement after 90 days of hydration. This aspect was also considered while conducting the present study on the effect of nano-Silica incorporation in mortar with single OPC, binary (OPC + fly ash) and (OPC+ silica fume) binders on the mechanical strength, water absorption, micro structural examination through scanning electron microscopy.

Scope of present study

A high water-cement ratio of 0.5 was chosen to produce a porous cement mortar matrix by adopting a curing regime to give about estimated 48% maturity as compared to 28 days of water curing. Two more porous mortars were obtained by replacing 25% and 50% of cement by Class F fly ash. After curing the mortar specimens, they were oven dried and then impregnated with 'nano-silica solution' (nSS) by simple soaking in nSS. The permeability of nSS treated specimens was evaluated by determining the COA.

In another study, to achieve reduced permeability of cement matrix, the addition of 5% and 10% of SF to the cement mortar itself during mix preparation was explored. This addition of SF was found to be also highly effective.

It was seen that the nano-silica (nS), a product of modern nano-technology, can improve the degree of impermeability of a highly porous cement matrix after curing of the matrix, whereas the SF needs to be incorporated during mixing of cement mortar itself.

Materials and Methods

(i) Ordinary Portland cement (OPC) had Fineness (based on test on IS sieve of 90 μ) 9%; Specific gravity was 3.15, normal consistency of cement was 29%; Initial and Final setting times (IS: 4031-1968 Part 5) were 120 minutes and 285 minutes respectively.

(ii) The nano-Silica aqueous solution (with density of 1.20 g/ml) had 30% solid content and was reported to contain average particle sizes of 15-30nm.

(iii) The super plasticizer was a commercial carboxylic acid ester with density 1130 kg/m³ and it is a non-ionic surfactant. The SP dosage was adjusted for each mixture to ensure that the mix is self compacting in nature without any segregation and bleeding.

(iv) River sand had Specific gravity of 2.65, water absorption of 0.5%, Fineness Modulus of 2.4 and Bulk density of 1550 kg./m³.

(v) The fly ash used in the study was Class F, from Ennore Thermal Power plant with the major chemical composition being SiO₂ (60%); Al₂O₃ (21%); Fe₂O₃ (18%); alkalis equivalent Na₂O 0.54%; LOI:1.06 %. Fineness (Blaine) 3435 cm²/gm, Specific gravity: 2.2: Bulk density 950 kg/m³

(vi) The silica fume powder is procured from ChemConTechsys, Chennai. Specific gravity:2.2, particle size :150 nm., SiO₂ (90%);

Mixing procedure adopted

The liquid components such as nS, superplasticisers (SP), and water, were premixed thoroughly using a flexible shaft stirrer. This liquid mix was added slowly to dry mix of sand and binder consisting of OPC, FA, SF. The mixing using trowel was continued for a minimum period of about 10 minutes to obtain a flowing, self compacting type of mix. The water available in SP and nS was accounted for computing the total water content of the mix and this was used to compute net water cement ratio of the mix. Since the quantity of material used in each batch was very small and careful hand mixing was found to be adequate in getting uniformly fresh mortar mixtures. The mix proportion for the mortar is shown in Table 1.

Table 1.0 Mix proposition for the mortars (water / binder = 0.51)

Mix ID	Binder type	Cement (gm)	Water (gm)	Super plasticizer (ml)	sand	SCM (gm)	nS (gm)
CM	Control –OPC	1300	658	13	2600	0	0
CM2ns	OPC+ 2% nSS	1292	658	13	2600	0	8
25 FAM	OPC+25% FA	975	658	13	2600	325	0
25FAM2ns	OPC+25%FA+2%nSS	967	658	13	2600	325	8
50FAM	OPC+50%FA	650	658	13	2600	650	0
50FAM2ns	OPC+50%FA+2%nSS	642	658	13	2600	650	8
5SFM	OPC+5%SF	1235	658	13	2600	65	0
5SFMns	OPC+5%sf+2%ns	1227	658	13	2600	65	8
10SFM	OPC+10%SF	1170	658	13	2600	130	0
10SFMns	OPC+10%SF+2%ns	1162	658	13	2600	130	8

SCM= Supplementing Cement Material (FA:SF)

Casting of Test Specimens and Curing:

Since the mortar mixes produced were self compacting type, the fresh mix could be easily placed into disposable cylindrical moulds (size 50 mm D *100 mm H.), without any need for external application of vibration for compaction. The specimens could be de-moulded after 24 hrs. of casting and they were placed in water tanks for effective curing.

Testing procedure:

The compressive strength of mixes was determined at different ages by testing each time a minimum of 5 specimens. In order to get the idea of morphology, the hydration products were examined by scanning electron microscopy (SEM) with Quanta 200 FEG instrument under 15 kV accelerating voltage conditions. Water absorption measurements were carried out with the oven dried (105° C for 48hr) specimens, weighed before and after soaking in water for a period of 60 minutes. The Coefficient of Water Absorption, COA, was computed using the formula: $COA = (Q / A)^2 / t$, cm²/sec, where, Q = Water penetrated in 60 minutes, cm³, and A-Total surface area of cylinder: t-time. External nS treatment of 3 and 7 days cured matrix was done by soaking the oven dried specimens for 16 hrs in nano –silica solution and then allowing them to dry at ambient conditions.

Results and Discussion:

Compressive Strength

The compressive strength of specimens at different curing period is given Fig.1. The strength of the control specimen cured for 28 days was 38.8 MPa. The compressive strength gain (3, 7, 28 days, 56 days and 1 year) were compared for control and 25%, 50% Fly ash-cement mortars with and without 2% nS addition. The compressive strength of specimens at different curing period is given in Fig. 1.

It was observed that the incorporation of nano-Silica in the plain cement matrix improves the strength of mixes at all ages up to 1 year. The strength of 25% FAM and 50% FAM as expected have shown lower strength value compared to control specimen, at strength curing time require more curing time to get 28 day strength of control. At early ages of curing (3 and 7 days), by the addition of 2% nano-Silica, the strength increases by 20% and 38% respectively on low volume (25%) fly ash replacement but for 50% FAM replacement it was found to above 20%. At 28 days of curing, increase in strength was further improved up to 20%. Addition of nano-Silica in Fly ash mixes thus leads to increases of both short term and long term strength. Comparatively, mixture containing fly ash without nano-Silica matched the compressive strength of control mixes after 360 days. This suggests that addition of fly ash leads to higher porosity at short curing period, while nano-SiO₂, acting as an accelerating additive, leads to more compact structures. The results are consistent with earlier workers^{16,17}. However the enhancing effect gradually decreased over the time and the compressive strength was found to be more or less equal to that of control mixes after 1 year.

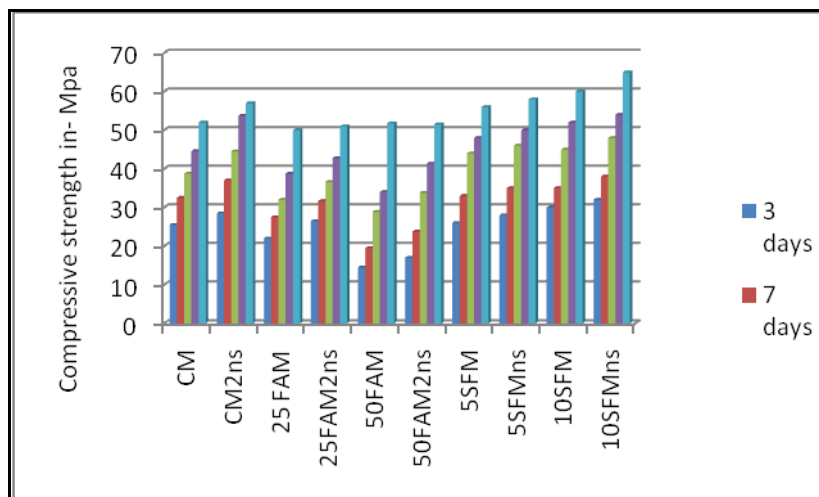


Fig. 1 Compressive strength of mortar mixes at difference ages

Silica fume has a high pozzolanic activity and is normally considered as the best mineral addition used for concrete up to now. When SF is added to cement or concrete, it acts both as chemical inert filler, improving the physical structure and providing nucleation sites for hydration products, and as a pozzolan, reacting chemically with CH formed during hydration of cement, which will probably improve the paste-aggregate bond. However, the pozzolanic activity of SF at early ages is low according to the literature^{18,19}. It is reported that the pozzolanic reaction between SF and CH formed during cement hydration begins to occur after 3 days of hydration. In the present study, with increasing silica fume content (5 to 10%), mortar strengths were slightly higher than those of control sample at early ages. But at ages of 28 days and above, strengths are increasing than those of control. The strength of silica fume with addition of nano silica, in the ternary mixes are found to be more, an increase 20% and 25% at ages of 50 days and 1 year respectively.

However, the effect of addition of nano silica in fly ash mixed matrices is more pronounced showing higher strength. This may be due to the presence of many unsaturated bonds, --Si-O-, Si-, in the nano silica surface and faster the reaction between SiO₂ and Ca(OH)₂ compared to that of silica fume, which is having more saturated bonds. Further, in the cement-water system, the bond between Si-O of Silica fume is not easy to break down owing to its higher bond energy. Hence the reaction with silica fume with water is slower than that

of nano silica. So nano silica can accelerate the cement setting and hardening, thereby increasing the strength at early ages and can improve the interface structure.

Water permeability

Effect of nano silica addition during mixing and its external treatment in the matrices

Mixes without nS, viz, CM, 25FAM, 50FAM, the COAs were 6.9×10^{-6} , 7.9×10^{-6} , and 9.1×10^{-6} cm²/sec; in contrast, due to nSS addition, the COAs increased to 8.7×10^{-6} , 8.6×10^{-6} , 10.6×10^{-6} cm²/sec which are about 26%, 9% & 16% more respectively. Similarly, saturated water absorptions of the mortars increased from 8.8% , 7.9% , 9.1% to 9.9%, 10.3%, 11.2% on addition of nSS in the mix. Thus, nS containing mortar matrix seems to generate more porosity and increased permeability. Thus, the increased porosity due to higher w/c ratio (0.51) could not be compensated by addition of 2% of highly pozzolanics solids.

In order to explore different options of using nSS, external treatment of specimens by nSS was undertaken. After oven drying for 48 hours at 105 C, the specimens were soaked in nSS for 16 hours. Test data has been tabulated as shown in Table 2.0 .Such nSS treated specimens indicated COAs of mixes, CM, 25FAM, and 50FAM to be 2.1×10^{-6} , 1.9×10^{-6} , 2.2×10^{-6} , cm²/sec which are less than those recorded before nSS treatment, by about 70%, 59%, 76%, respectively. Thus, even though, use of nS as mineral admixture in the mix with FA was not useful, but its use as impregnant for the hardened matrix was highly useful. In the case of silica fume matrices the reduction is found to be 53% for 5% silica fume and 34 % for 10% .SF

Table 2.0 :Comparison of silica fume mortars with nSS treated mortars

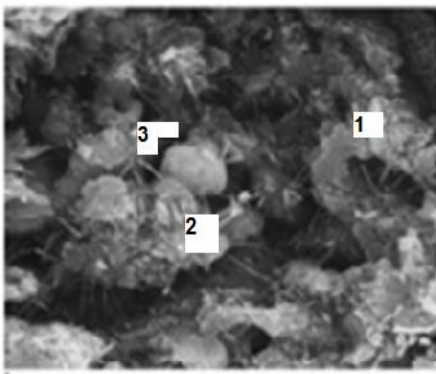
Mix ID	CM	25FAM	50FAM	5SF	10SF
COA*10 ⁻¹² (cm ² /s)	6.9	7.9	9.1	5.5	3.2
%nSS Absorption after soaking for 16hrs	5.9	4.0	3.4	3.8	4.0
COA*10 ⁻¹² (cm ² /s)	2.1	1.9	2.2	2.2	2.3
% COA reduction	70	59	76	53	34

The amount of nSS absorbed by the cement mortar in the present study was about 5.9% (by mass) which is equivalent to presence of about 1.8% of nS solids in the matrix. This small quantity of nS solids was sufficient to effectively reduce the permeability of the matrix. The nSS being similar to water in viscosity, was able to penetrate easily into the matrix even by simple soaking and fill physically the capillary pores of the cement matrix. Moreover, the hardened cement mortar matrix has free lime generated as a result of cement hydration and this could easily chemically react with SiO₂ of the nS solids due to the very high specific surface area of nS resulting in formation of secondary C-S-H gel which now acts as filler in capillary pores. Thus, both physical and chemical actions of nS reduce porosity and causes pore size refinement. This leads to reduced permeability of the matrix thereby increased resistance to penetration of water. This was confirmed by reduced water absorption and decreased COA value for nSS treated specimens.

SEM

The effect of nano-Silica on hydration of ordinary Portland cement and fly ash particles, silica fume and its interfaces with cement paste at different ages were studied using Back Scattered Scanning Electron Microscopic (BSEM) images.

SEM examinations performed for the CM, cement mortar at 7 days of curing with and without addition of nano silica is shown Fig 2.(A&B.). In the control specimen, it was found that CSH gel existed in isolation, surrounded by and connected with many needle hydrates..



CM, 7 days:1-crystals:2-C-S-H:3-pore

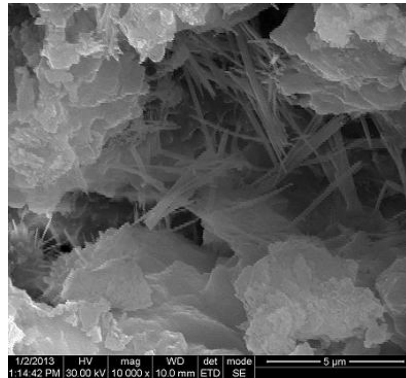


Fig : 2 B. SEM picture of CMns (7 days)

Fig : 2.A SEM picture of CM (7 days)

Very thin and long needle-like ettringite was detected mainly inside the pores as seen. On the other hand, the microstructure of mixes containing nano silica revealed a dense, compact formation of hydration products and reduced number of CH crystals. The formation of ettringite is still in progress

Addition of nano silica were found to influence hydration behaviour of fly ash matrices and led to differences in the microstructure of hardened matrices. Figure 3.(A& B) are SEM pictures of Fly ash cement matrices with and without addition of nano silica at 28 days. In fig 3.A fly ash particles in the control specimen are severely eroded and an abundance of hydration products can be found coating the fly ash particles surface. The well compacted rods and grains are typical hydration products of cement pastes. The addition of nano silica in the fly ash matrix, shows fly ash particles are smooth and featureless, indicating less pozzolanic activity. However, fibroids and compacted grains which are the products of nanosilica and CH, may hinder the hydration of fly ash particles at this age of curing.

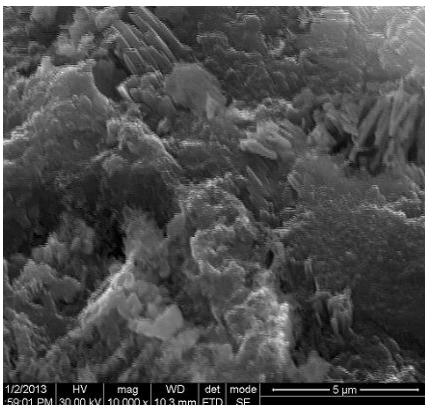


Fig:3.A SEM picture of 50FAM (28 days)

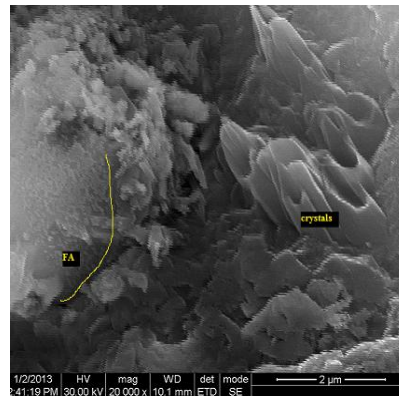


Fig: 3.B SEM picture of %0FAMns.

However, at the age of 1 year, the microstructure of the mixture containing nano-SiO₂ in both fly ash and silica fume matrices, revealed a dense, compact formation of hydration products and a reduced number of Ca(OH)₂ crystals as seen from the picture Fig 4 A & B. It is attributed to dispersion of nano-Silica among cement fine grain, seems to act as 'nucleuses for the hydration products development especially on lime which will accelerate the hydration reaction^[20-21]. Thus good micro structure has been formed with uniformly distributed conglomeration.

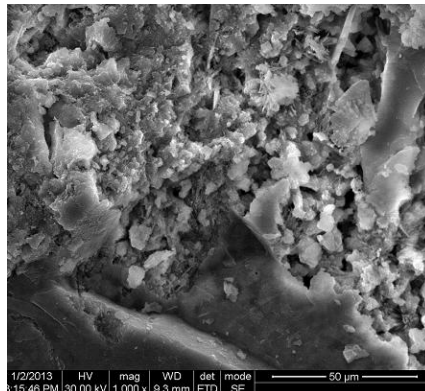
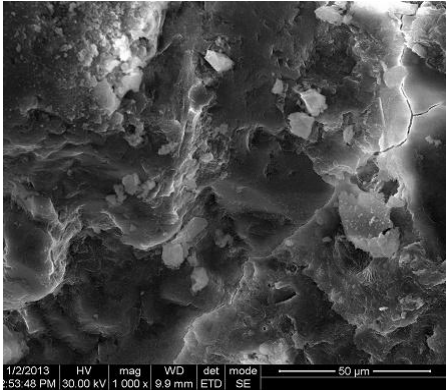


Fig :4 A SEM picture of 50FAMNs (1 year) Fig :4. B SEM picture of SFns (1 year)

Conclusion

Nano silica has potential for very fast reaction with free lime and this causes the high benefits in cement matrix in the form of increased strength, reduced permeability, dense microstructure.

At all curing ages the strength generally increased with the addition of nano silica and particularly, considerable strength development occurred at 28 days in fly ash matrices. It indicates that that the inherently slower rate of strength development of concrete containing Class F fly ash can be controlled by the addition of small dosages of nano-silica which can be utilized for production of high strength .

The porous microstructure of fly ash matrices at earlier ages can be modified by external treatment with nS solution.

Extremely low Ca(OH)_2 , free lime crystal and hardly detected the needle like ettringite crystals were found in nano silica incorporated specimens against normal OPC.

The pore size refinement, as a result of the pozzalanic reaction, led to a significant enhancement of the compressive strengths.

The test results indicate that nSS can be used to improve the microstructure of any cement composites near the exposed surface, thereby reducing the rate of entry of aggressive agents [such as O_2 , CO_2 , H_2O , Cl^- , SO_4^- etc] resulting in enhanced durability. Thus, any precast products and ferrocement units have potential for getting benefitted easily by nS treatment.

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