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Applicability & Durability Issues Of Nano-Sized Materials In Cement

Research Article

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Abstract

Nano-sized Materials due to their smaller size exhibits many novel properties which may be absent in their conventional bulk material sizes. Cement is the most standard material among all of the materials used in cement concrete constructions and is the only binding medium. This Paper brings out the various beneficial aspects of Nano-sized Materials when they are applied in ordinary cement mortar. Nano-sized Materials viz. Nano Silica (nS), Carbon Nanotubes (CNT) and Nano Titanium Dioxides (n-TiO2) are non-virgin materials but when applied to a virgin cement medium like OPC not only enhances the mechanical properties but also increases the volume stability of cement-mortars to larger extent. Geo-polymers which are very low workability binders having no cement content, has their workability enhancement with Nano-sized Materials.

Introduction

What a 'Nano' is? Is it 'Tata-Nano'? Could anyone tell why it is called 'Nano'? These are the pertinent questions which come in to everyone's mind when they hear about anything called 'Nano'. 'Nano' as it aptly called, is so as it was the world's smallest car invented till now. That was the marketing side of 'Nano' but this Paper discusses the scientific part of it as applied in cement constructions. 'Nano' is a Greek word which means 'dwarf' having dimensions in the order of 10-9m. Nearly fifty years ago, Richard Feynman who is nicknamed as Albert Einstein-II of this century, is also known as the father of nanotechnology-the technology involving the manufacturing and manipulation of atoms. The construction industry was the only industry to identify nanotechnology as a promising emerging technology in the UK Delphi Survey in the early 1990. ("Application of Nanotechnology in Construction", Materials and Structures, 37, 649 (2004), Springer). But now other industries like tyres, paints, medicines etc have paced ahead lagging construction industry behind. With the on-coming of the 4th industrial revolution as explored by Professor Klaus Schwab, Founder and Executive Chairman, World Economic Forum, also brings up the huge promise of the potentiality of nanotechnology and Nano-sized Materials. Use of CNTs [4, 5, 20], have produced remarkable improvements in the mechanical properties of cement concrete on account of their crack bridging effects at the nano scale [7] and nucleation effects in the formation of different cement hydrates [6, 17] and have replaced the state-of-the-art technologies using fibers which mainly includes steel bars [18], steel fibers [8, 14, 20], glass fibers [2, 12], carbon fibers [22], polypropylene fibers [1, 10], and various others [3]. Literatures [9, 11, 13, 15, 16, 21, 22] are abound highlighting the importance of nano additions in cement concrete.

Materials and Experimental Program

The materials used were cement-OPC (43 grade), fine aggregate (FA)-river sand conforming to zone II of IS:383-1970, potable water, admixture (super plasticizer)-PolyCarboxylate ether and Nano-sized Materials (viz., nanosilica, carbon nanotubes and nanotitanium oxide). The following Tables (3 to 5) show the specific properties of nanosilica, carbon nanotubes and titanium dioxide used.

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Table 1. Specific Properties & XRD image of Nanosilica (SiO2).

Sample/ Brands	% Content (Lit.)	Specific Gravity(Lab.)	% Content(Lab.)	Specific Gravity(Lit.)
XLP	14-16%	1.12	21.4%	1.08-1.11
XTX	30-32%	1.16	40.74%	1.20-1.22
XFXLa	40-43%	1.24	41.935%	1.30-1.32

Table 2. Specific Properties of Multi-Walled Carbon Nanotubes (Industrial Grade).

Item	Description
DIAMETER	20-40nm
LENGTH	25-45nm
PURITY	80-85% (a/c Raman Spectrometer & SEM analysis)
AMORPHOUS CARBON	5-8%
RESIDUE (CALCINATION IN AIR)	5-6% by Wt.
AVERAGE INTERLAYER DISTANCE	0.34nm
SPECIFIC SURFACE AREA	90-220 m^2/g
BULK DENSITY	0.07-0.32gm/cc
REAL DENSITY	1-8 gm/cc
VOLUME RESISTIVITY	0.1-0.15 ohm.cm (measured at pressure in powder)

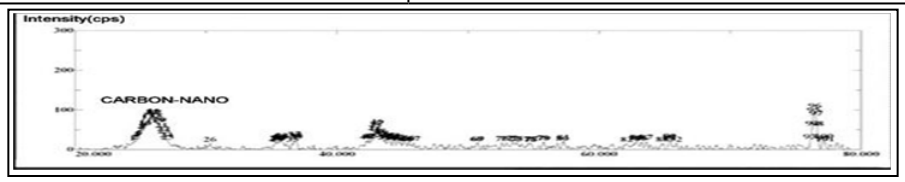
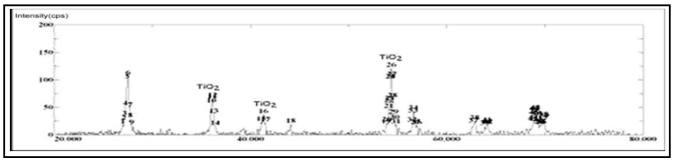


Table 3. Specific Properties of Nanotitanium Oxide (n-TiO2).

NANO TITANIUM OXIDE %	97
RUTILE CONTENT %	98
PH	7
AVERAGE PARTICLE SIZE (TEM)	30-40 nm
TREATMENT	Nil
MOISTURE %	1.75-2
BULK DENSITY	0.31gm/cc
WATER SOLUBILITY	In-soluble



Tests On Hydrated Cement Paste:

Cement paste containing water added as per normal consistency is taken in a mould (25mmx25mmx282mm) is boiled for a fixed time (3 hrs) at a temperature of 100°C under a pressure of 2.1 N/mm^2 in a Autoclave machine and subsequent removing of the specimen & cooling it in room temperature and measuring the cement paste's dimensions to record any volume change as per IS:4031.

Tests On Cement Composites:

Mortar Cubes of 70.7mmx70.7mmx70.7mm size were casted with 1 part of cement +3 parts of sand with water added as per

Table 4. Strength (N/mm²) for Various Proportions/Ages of Nano-added OPC Mortar.

Sl. No.	% Nano additions in Cement (OPC)	7 daystrength			28 daystrength			90 daystrength			180 daystrength			365 daystrength		
		Individual Cube Strength	Avg.	% increase	Individual Cube Strength	Avg.	% increase	Individual Cube Strength	Avg.	% increase	Individual Cube Strength	Avg.	% increase	Individual Cube Strength	Avg.	% increase
1	OPC(0% nS/CNT/ TiO_2)	21.33	21.08	Control Sample	35.20	31.89	Control Sample	24.14	31.20	Control Sample	23.81	30.01	Control Sample	29.01	30.01	Control Sample
		21.08			28.57			38.26			36.22			30.01		
		20.83			31.89			31.20			30.01			31.01		
2	OPC (0.5% nS)	21.82	23.85	13.1%	29.68	35.51	11.4%	41.93	41.3	32.7%	28.17	27.47	-9.2%	25.76	26.76	-4. 3%
		25.87			41.33			40.67			26.79			26.76		
		23.85			35.51			41.30			27.47			27.76		
3	OPC (0.75% nS) (optimized @ 28 day)	28.06	27.73	31.5%	46.28	42.27	32.5% ↑	51.75	49.85	59.8%	40.24	32.52	8.4%	30.5	31.5	4.7%
		27.39			38.26			47.95			24.80			31.5		
		27.73			42.27			49.85			32.52			32.5		
4	OPC (1.0% nS)	25.15	25.07	18.9%	31.57	37.36	17.2%	41.32	42.98	37.7%	29.59	33.68	12.2%	31.41	32.41	8.0% ↑
		25.00			43.15			44.64			37.78			32.41		
		25.07			37.36			42.98			33.68			33..41		
5	OPC (1.25% nS)	21.52	23.17	9.9%	23.47	30.85	3.3%	33.27	39.45	26.4%	44.46	35.24	17.4%	30.3	31.3	4. 3%
		24.73			38.23			45.63			26.02			31.3		
		23.17			30.85			39.45			35.24			32.3		
6	OPC (1.5% nS)	24.15	23.81	12.9%	40.89	37.79	18.5%	34.69	33.42	7.1%	31.63	31.23	4.1%	29.12	29.12	-3.0%
		23.47			34.70			32.14			30.82			29.12		
		23.81			37.79			33.42			31.23			29.12		
7	OPC(0.02% CNT) (optimized@ 28 day)	16.86	17.69	-10.4%	42.35	43.75	38.7% ↑	34.60	35.59	15.5%	34.69	30.89	10%	22.83	28.53	-4.9%
		20.12			44.63			35.59			33.13			34.18		
		16.10			44.27			36.60			24.85			28.57		
8	OPC (0.05% CNT)	32.56	27.19	-16.1%	41.95	34.88	37.2%	41.24	31.85	14.1%	54.30	38.55	3.0%	34.21	41.69	38.9%
		24.86			31.35			24.13			31.18			41.69		
		24.14			31.35			30.18			30.18			49.17		
9	OPC (0.1% CNT)	24.14	21.69	28.9%	23.00	24.83	9.4%	28.17	31.5	2.1%	27.78	30.16	23.6%	49.60	50.78	69.2% ↑
		20.54			27.00			30.61			32.09			40.24		
		20.41			24.49			35.71			30.61			62.50		
10	OPC (1% TiO2) (optimized @ 28 day)	24.45	25.24	19.7%	38.70	36.71	12.6% ↑	33.61	35.92	15.1%	29.59	33.42	11.4%	42.47	41.16	37.2% ↑
		26.02			36.71			35.92			33.42			39.86		
		25.24			34.72			38.23			32.25			41.16		
11	OPC (2.5% TiO2)	20.05	20.34	-3.5%	36.73	34.97	9.6%	35.21	37.8	21.2%	39.24%	40.95	36.5%	25.51	28.16	-6.2%
		20.62			33.20			37.80			442.66			30.81		
		20.34			34.97			40.40			40.95			28.16		

the normal consistency formula of Indian standards.i.e., according to the standard formula P'=(P/4 +3) (1part Cement+3parts Sand). Here P'=Quantity of water & P=Consistency of Cement used.i.e. amount of water used to make 300gms cement paste to support a penetration of 5-7mm in a standard Vicat mould with a Vicat needle. Nano silica were added in various proportions ranging from 0%, 0.5%, 0.75%, 1.0%1.25%, 1.5%, Carbon Nanotubes added in proportions as per literature review i.e., 0.02%, 0.05% & 0.1% and Nano Titanium Oxide added in proportions ranging from 1.0% & 2.5% w.r.to cement wt. after proper dissolutions in a suitable Super Plastcizer (Poly Carboxylate Ether) (for CNTs & TiO2 as they were insoluble in water) keeping the w/c ratio fixed at 0.4. The cubes were then ordinary cured under water and tested at 7days, 28days, 90days, 180days and 365days as per IS:4031.

For geopolymer concrete, taking alkaline liquid to fly ash ratio by mass = 0.44 & water to geopolymer ratio of 0.25 & assuming that the combined aggregate occupies 79% of the geopolymer concrete (density=2400kg/m3) by mass, a design mix was prepared with & without nS additions as shown in Fig 2.

The Test Results Shows That:

The mortar compressive strength as shown in Table 4 & determined as per IS: 4031 shows a 32.55% increase in strength at 0.75% nS addition at 28 days, with the rate of strength gain increasing up to 59.8% at 90 days but then falling by 8.4% at 180 days at same optimization. However, for long terms the 1% nS addition showed an 8 % increase. For CNTs the gain in strength was 38.7% at 28days but falling to 15.48% at 90 days & 10% at 180 days. But 0.1% CNT shows a strength increase of 69% at 1 year.

So, for long term for nS and CNT it is observed that slight increased dosages from the previous optimized @ 28days gave increased strength. Even Geopolymer concrete which is conventionally believed to be viscous in nature had a desired workability (more than 25% when compared to controlled concrete) when treated with the same optimized dosage of Nano-sized Materials (as per Table 6).

Figure 1. Effect of nanotechnology & Nano-sized Materials in construction sector.

Figure 2. Nano-sized Materials used for Geopolymer concreting and Nanoconcreting in IIESTS Laboratory.

Table 5. Volume Stability of Nano-sized Materials through Autoclaving Tests.

Type of Cements	Original Length of Sample(mm) [Typical]	Expanded Length of Sample(mm) after Autoclaving [Avg.]	Average Expansion(%) after Autoclaving	Resistivity to Volume Expansion (in %)
1. OPC	282	282.138	0.0490%	--
2. OPC + 0.75% ns	282	282.085	0.030%	38.78%
3. OPC + 0.02% CNT	282	282.021	0.0074%	84.90%
4. OPC + 1.0% TiO_2	282	282.042	0.0150%	69.39%

Table 6. Properties of concrete and geopolymer concrete in presence of Nano-sized Materials.

Type of Concrete	Fresh Property (Slump)
Geopolymer Concrete (nS = 0% by wt. of Fly Ash)	100 mm
Geopolymer Concrete (nS = 0.75% by wt. of Fly Ash)	130mm (30% increase)

Conclusion

The results showed that the optimizations for Nano-sized Materials in OPC mortar are nS=0.75%, CNT=0.02% and TiO2=1.0% for cement mortar up to 28 days. In the long-term strength, some contradictions were noticed for which the reasons are not clear.

It is seen that with the increased addition of nano materials like nano-silica (1% by cement wt.) and carbon nanotubes (0.1% by cement wt.) in OPC mortar the long term strength gain increases appreciably.

The optimum percentages based on cement mortar when used in geopolymer concrete produced good results for fresh properties (workability) of geopolymer concrete.

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