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Short Term V/S Long Term Optimizations of Nano-Additions on Ordinary Portland Cement

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ABSTRACT

Cement reacts with water and derives its strength by its hydrated products. This hydration is a complex process; it takes usually 20-25 days for 90% of the hydration to get completed. But the long term complete hydration, generally takes a long time to complete. In this paper, an attempt has been made to study both the short term and long term effects of optimized Nanomaterial additions in ordinary cement mortar of cement: sand =1:3 ratios with water added as per the standard consistency as stipulated in IS 4031(Part 6):1988.Nanomaterials viz. Nanosilica (nS), Carbon Nanotubes (CNT) and Nano Titanium Dioxide (n-TiO_2) were added in various dosages which is expressed as % with respect to the weight of cement added and were casted in 70.7mm cubes and tested for its cube strength in the laboratory, at various ages of cement mortar like 7 days,28days,90days,180days and 365days respectively. Optimizations were obtained out after studying the test results; for nS the optimization was found to be 0.75%, CNT optimization was found to be 0.02% and n-TiO_2 optimization was found to be 1% w.r.to cement wt at 28 days i.e. these specific dosages got the maximum compressive strength in the cube testing machine. However the long term results showed different results except for n-TiO_2.

Key words: Cement, cube, nanomaterial, short term, long term

INTRODUCTION

Cement is the only binder in concrete and consists of four major compounds like Alite(C_3S),Belite(C_2S),Celite(C_3A) and Felite(C_4AF) where C=CaO(Calcium Oxide),S=SiO_2(Silicon Di-Oxide),A=Aluminum Oxide(Al_2O_3) and F=Iron Oxide(Fe_2O_3).It gets its strength by reacting with water forming hydrated products of very low solubility. Nanomaterials increases the rate of hydration by increasing the surface area required for the hydration of cement and thus increasing the hydrated products which in turn increases the strength of cement. Cement is also one of the most widely used materials in construction industry. In 2014, the expected total worldwide production of cement was more than 4000 million tons. China is the largest producer accounting for >2 billion tons in production with India in second position (>210 million tons) followed by the USA (>68 million tons). Despite being widely used, cement-based materials have poor mechanical properties and are highly permeable to water and other aggressive chemicals, which reduce their durability. Moreover, cement industry is one of the significant sources of CO_2 emissions, which accounts for 5–6% of global man-made CO_2 emission annually. However, the increasing demand for high-performance structural materials and components has led to the rapid development of new classes of materials [6-7]. Nanotechnology (NT) can play a significant role in the construction industry and stands at eighth position in terms of most significant areas of applications in nanotechnology. Nano-engineering of cement-based materials can result in outstanding or smart properties. Introduction of nanotechnology in cement industry has the potential to address some of the challenges such as CO2 emissions, poor crack resistance, long curing time, low tensile strength, high water absorption, low ductility and many other mechanical performances. A remarkable improvement in the mechanical properties and durability of cementitious materials can be observed with incorporation of nanomaterials such as nano-SiO_2, ZnO_2, Al_2O_3, TiO_2, carbon nanotubes, nanoclays, carbon nanofibers and other nanomaterials [8-9].

The objects produced using NT have unique characteristics such as super connectivity, high strength, low friction, high thermal insulation, specific beam frequency selectivity, quantum effects, extreme water repellence and self-assembling geometric patterns like nanotubes, nanospheres and nanooctagons. There have been many successful NT based applications which could have been almost impossible without utility of nano sized particles. For example, anti-scratch paints, anti-bacterial paints, anti-fouling concrete, dirt repellant textiles, clothes that need no ironing, non-reflective glasses, wonder drugs etc. are only the tip of the ice-berg. The emergence of nano silica, carbon nanotubes and Nano titanium oxide in the last decade have proved their worth as far as building materials is concerned and the motivation to find an effective solution to catch their long-term efficiency is now on the anvil [2–5].

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 nanomaterials (viz., nanosilica, carbon nanotubes and nanotitanium oxide). The following Tables (1 to 3) show the specific properties of nanosilica, carbon nanotubes and titanium dioxide used.

Table -1 Specific Properties of Nanosilica (SiO_2) Used

Sample (Brand Name)	% Content (Lit.)	Specific Gravity(Lab.)	% Content(Lab.)	Specific Gravity (Lit.)
XLP	14-16%	1.12	0.214	1.08-1.11
XTX	30-32%	1.16	0.4074	1.20-1.22
XFXLa	40-43%	1.24	0.41935	1.30-1.32

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

Item	Description
Diameter	20-40nm
Length	25-45nm
Purity	80-85%(a/c Raman Spectrometer
Amorphous Carbon	5-8%
Residue(Calcination in	5-6% by Wt.
Average interlayer	0.34nm
Specific surface area	90-220 m2/g
Bulk density	0.07-0.32gm/cc
Real density	1-8 gm/cc
Volume Resistivity	0.1-0.15 ohm.cm(measured at

Table -3 Specific Properties of Nanotitanium Oxide (TiO_2) Used

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

And the following Figures (1– 3) show the XRD images of nanosilica, carbon nanotubes and titanium dioxide used.

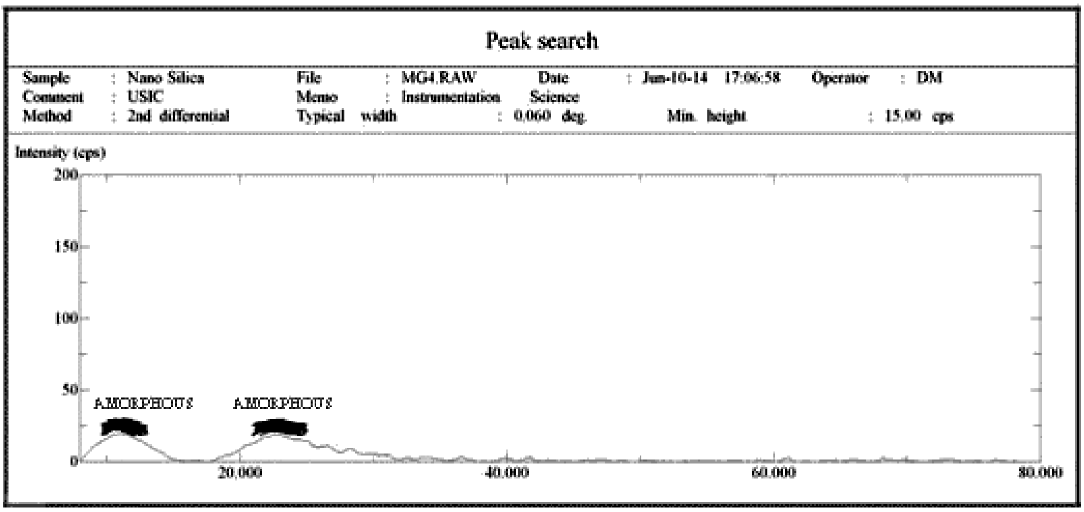

Fig. 1 XRD Image of Nanosilica Used

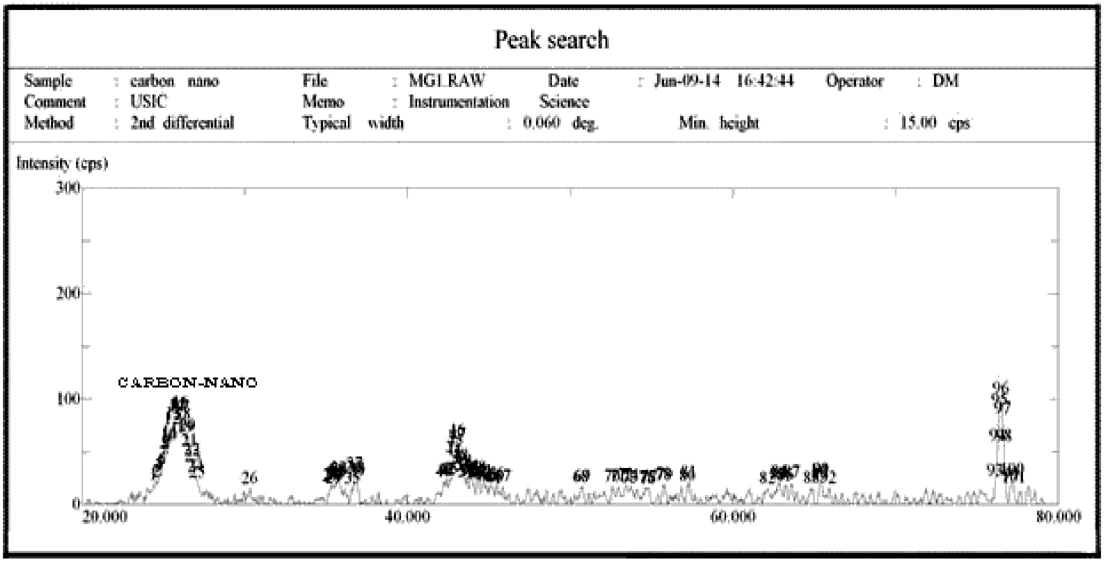

Fig. 2 XRD Image of Carbon Nanotubes Used

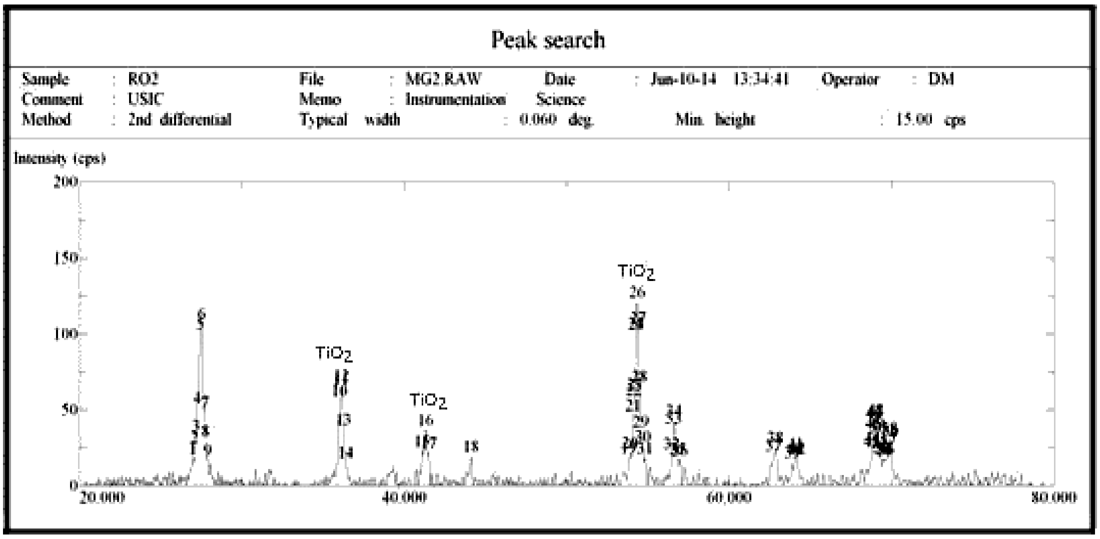

Fig. 3 XRD Image of Nanotitanium Dioxide Used

Tests on Cement Mortar

Mortar cubes of 70.7×70.7×70.7 mm size were casted with 1 part of cement+3 parts of sand with water added as per the normal consistency formula of Indian standards, i.e., according to the standard formula P'=(P/4+3)(1 part cement+3parts sand). Here P'=Quantity of water and P=Consistency of cement used, i.e., amount of water used to make 300 g cement paste to support a penetration of 5–7 mm in a standard Vicat mold with a Vicat needle. Nanosilica was added in various proportions ranging from 0, 0.5, 0.75, 1.0, 1.25, and 1.5% in Ordinary Portland Cement (OPC) , carbon nanotubes added in proportions as per literature review, i.e., 0.02, 0.05 and 0.1% in OPC and nanotitanium oxide added in proportions ranging from 1.0 and 2.5% w.r.t. cement wt. in OPC after proper dissolutions in a suitable Superplastcizer (PolyCarboxylate ether) (for CNTs and 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 7, 28, 90, 180 and 365 days.

Test Data

A) Sp. gravity of cement=3.08 (as lab. experiment suggests)
B) Chemical admixture=Superplasticizer (polycarboxylate ether)=solid content=30%.

RESULTS

Table 4 shows the strength development at various ages including short term(7 days),medium term(28 days), and long term(90 days,180 days and 365 days), in ordinary cement mortar with and without nano additions.. Some apparatus used for mortar castings is shown in Figures 7-8.

Table -4 Strength (N/mm^2) for Various Proportions/Ages of Nano-added OPC Mortar (% Increase w.r.to Ordinary Control Cement Cubes)

Sl. No.	% Nano additions in Cement (OPC)	7 day strength			28 day strength			90 day strength			180 day strength			365 day strength		
		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
		21.33			35.20			24.14			23.81			29.01		
1.	OPC (0% nS/CNT/ TiO_2)	21.08	21.08	Control Sample	28.57	31.89	Control Sample	38.26	31.20	Control Sample	36.22	30.01	Control Sample	30.01	30.01	Control Sample
		20.83			31.89			31.20			30.01			31.01		
		21.82			29.68			41.93			28.17			25.76		
2.	OPC(0.5% nS)	25.87	23.85	13.1%	41.33	35.51	11.4%	40.67	41.3	32.7%	26.79	27.47	-9.2%	26.76	26.76	-4.3%
		23.85			35.51			41.30			27.47			27.76		
		28.06			46.28			51.75			40.24			30.5		
3.	OPC(0.75% nS) (optimized)	27.39	27.73	31.5%	38.26	42.27	32.5%	47.95	49.85	59.8%	24.80	32.52	8.4%	31.5	31.5	4.7%
		27.73			42.27			49.85			32.52			32.5		
		25.15			31.57			41.32			29.59			31.41		
4.	OPC(1.0% nS)	25.00	25.07	18.9%	43.15	37.36	17.2%	44.64	42.98	37.7%	37.78	33.68	12.2%	32.41	32.41	8.0%
		25.07			37.36			42.98			33.68			33.41		
		21.52			23.47			33.27			44.46			30.3		
5.	OPC(1.25% nS)	24.73	23.17	9.9%	38.23	30.85	3.3%	45.63	39.45	26.4%	26.02	35.24	17.4%	31.3	31.3	4.3%
		23.17			30.85			39.45			35.24			32.3		
		24.15			40.89			34.69			31.63			29.12		
6.	OPC(1.5% nS)	23.47	23.81	12.9%	34.70	37.79	18.5%	32.14	33.42	7.1%	30.82	31.23	4.1%	29.12	29.12	-3.0%
		23.81			37.79			33.42			31.23			29.12		
		16.86			42.35			34.60			34.69			22.83		
7.	OPC(0.02% CNT)(optimized)	20.12	17.69	-10.4%	44.63	43.75	38.7%	35.59	35.59	15.5%	33.13	30.89	10%	34.18	28.53	-4.9%
		16.10			44.27			36.60			24.85			28.57		
		32.56			41.95			41.24			54.30			34.21		
8.	OPC(0.05% CNT)	24.86	27.19	-16.1%	31.35	34.88	37.2%	24.13	31.85	14.1%	31.18	38.55	3.0%	41.69	41.69	38.9%
		24.14			31.35			30.18			30.18			49.17		
		24.14			23.00			28.17			27.78			49.60		
9.	OPC(0.1% CNT)	20.54	21.69	28.9%	27.00	24.83	9.4%	30.61	31.50	2.1%	32.09	30.16	23.6%	40.24	50.78	69.2%
		20.41			24.49			35.71			30.61			62.50		
		24.45			38.70			33.61			29.59			42.47		
10.	OPC (1% TiO_2)(optimized)	26.02	25.24	19.7%	36.71	36.71	12.6%	35.92	35.92	15.1%	33.42	33.42	11.4%	39.86	41.16	37.2%
		25.24			34.72			38.23			32.25			41.16		
		20.05			36.73			35.21			39.24%			25.51		
11.	OPC (2.5% TiO_2)	20.62	20.34	-3.5%	33.20	34.97	9.6%	37.80	37.80	21.2%	442.66	40.95	36.5%	30.81	28.16	-6.2%
		20.34			34.97			40.40			40.95			28.16		

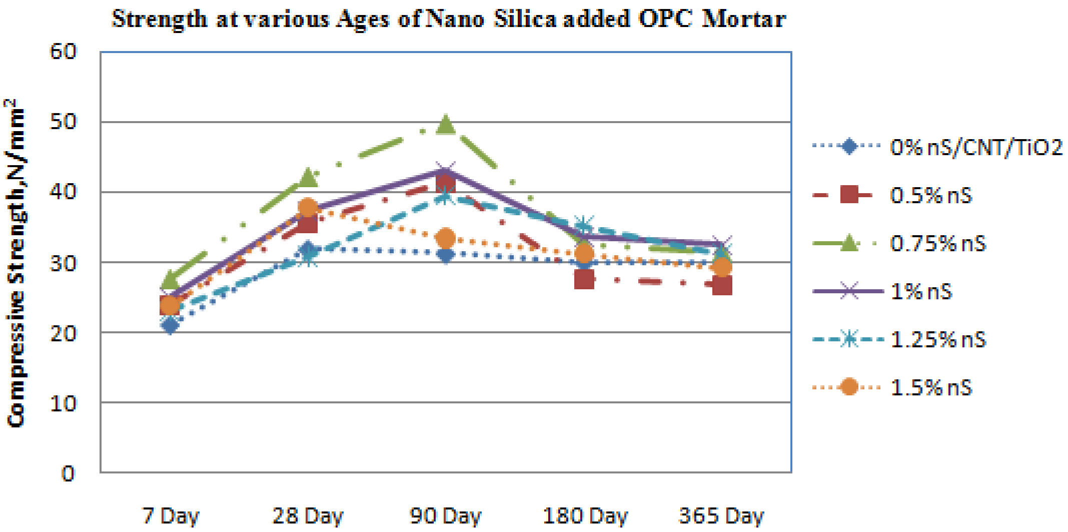

Fig. 4 Chart showing strengths at various ages of different % of nS addition in OPC Mortar

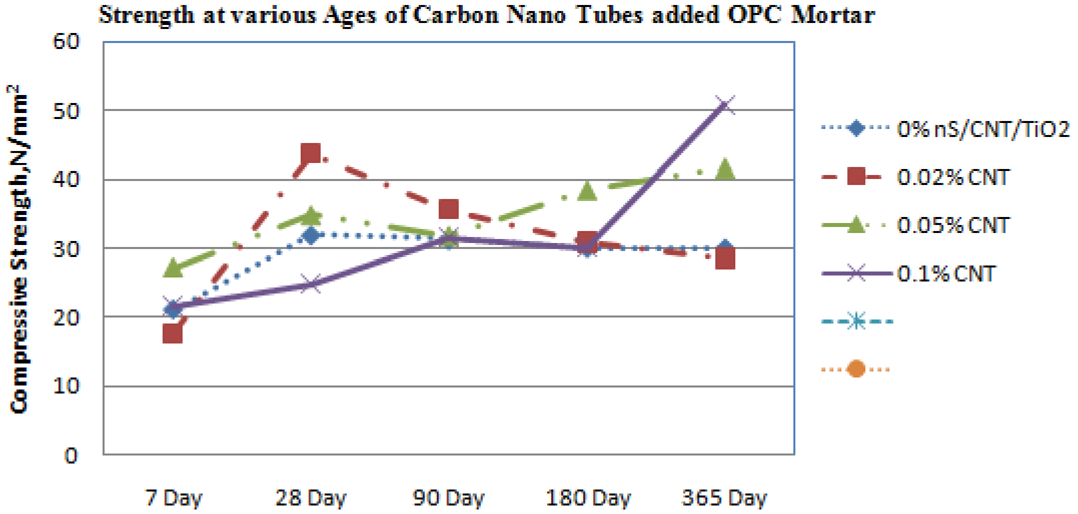

Fig. 5 Chart showing strengths at various ages of different % of CNT addition in OPC Mortar

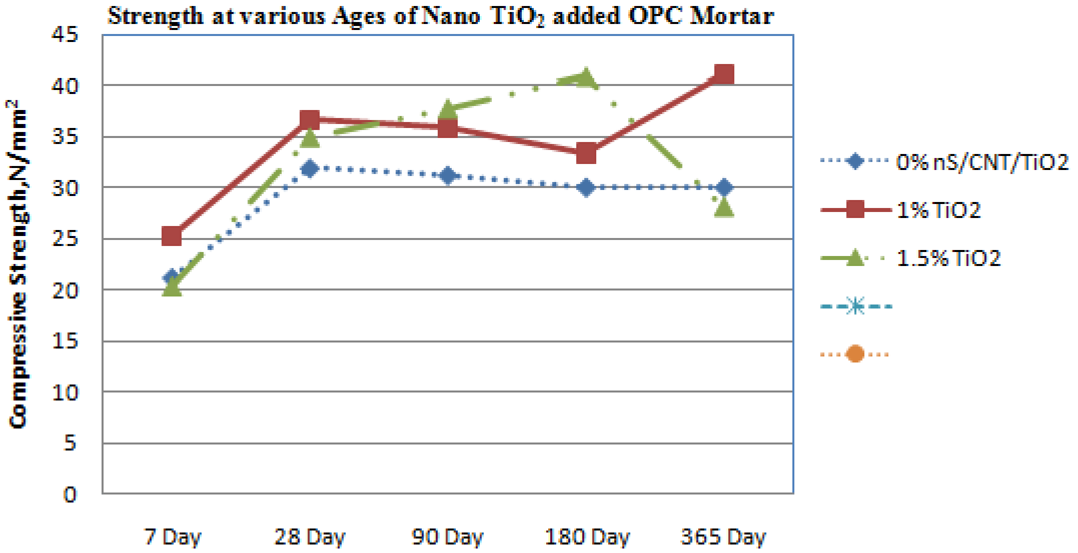

Fig. 6 Chart showing strengths at various ages of different % of n-TiO_2 addition in OPC Mortar

Fig. 7 Curing Chamber

Fig. 8 Compression Testing Machine

DISCUSSION OF TEST RESULTS

- The OPC mortar compressive strength determined as per IS:4031 shows a 32.55% increase in strength at 0.75% nS[optimized addition]addition at 28 days, with the rate of strength gain increasing up to 59.8% at 90 days but then the gain falling by 8.4% at 180 days at same optimization as shown in Fig.4.In the long term i.e. at 365 days it is seen that 1% nS is giving more strength gain(8%) than the optimized one(4.7%)
- For CNTs, the gain in strength was 38.7% at 28 days but the gain falling to 15.48% at 90 days and 10% at 180 days for 0.02%CNT addition [optimized addition] as shown in Fig.5. Here in the long term i.e. at 365 days it is seen that 0.1% CNT is giving more strength gain(69%) than the optimized one(-4.9%).

Optimized TiO_2 indicated no such appreciable gain in strength at 28 days as shown in Fig.6 and its optimization remained fixed at 1% both for short and long term as found by other researchers [11].In the short term the gain is 12.6% but in the long term the strength gain is 37%.

CONCLUSIONS

- The results showed that the optimizations for nanomaterials in OPC mortar are nS=0.75%, CNT=0.02% and TiO_2=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 in OPC mortar the long term strength gain increases appreciably, except for n-TiO_2.
- Further research on micro structural studies is necessary for characterization of nanomaterials in cement.

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