A STUDY ON APPLICABILITY ASPECTS OF NANO MATERIALS IN CEMENT-CONSTRUCTION

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Abstract

A broad range of challenges faced by the construction industry today deals with both the short term & long term effects of new material use in cement. This paper aims to explore the fact that that small addition of nano particles viz. Nanosilica (nS), Carbon Nanotubes (CNT) & Nano Titanium Oxide (TiO_2) in ordinary Portland cement have enhanced both the short term & medium term strength of cement mortar when added in optimized quantities with respect to the weight of cement & water added as per the normal standard consistency formula of the Indian standards. However, in the long term (90 days & above) it is seen that with increase in the quantities of all the nanoparticles from the optimized one to a bit little further, further increases the same. With the increase of the optimized nS to 1% showed a strength gain of more than 12% and 8% at 180 days and 365 days and with the increase from optimized CNTs to 0.1% saw a strength gain of more than 23% at 180 days and 69.21% at 365 days. However, increased addition of optimized TiO_2 w.r.to its optimized quantity did not serve any better results.

***Keywords:** Cement, Composites, Nano, Optimize, Strength*

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1. INTRODUCTION

Progress of world economy can only be balanced by continuous industrial development supported by sustained agricultural production. But Industrial development is related to uncontrolled release of toxic and harmful agents into the surroundings with the by-products of farming practices adding to it. These have adverse effects as pollution-related syndrome like climate change on living beings and as environmental pollution -- which needs to be mitigated at any cost. If corrective actions are not taken then, Times of India, Mumbai edition of 20th September,2013 rightly highlighted that "In 1.8 billion year Earth will become too hot as seas will evaporate". The same paper in Mumbai edition of 21st October,2013 stated that "World average temperature will rise by at least 4°C by the year 2100 and at least by 8°C by 2200." The main sources of air pollution throughout the world are emissions from vehicular traffic and operating industries namely cement industry, power plants, steel industry(1 ton of steel releases approximately 1.9 tons of CO_2),paper & pulp industry, aluminum & metal industry etc. Also the farmers' fields can be a bigger source of contamination than factory effluent if not checked properly [1]. The exhaustions which cause air pollution could be trapped and CNTs may be manufactured from it[34]. Also rice husk which is a biological waste from agricultural fields can be synthesized to extract Nano Silica by feeding worms with rice husk as developed by Estevez et al.(2009). While Nano Titanium dioxide is now manufactured at a large scale by the Govt. of Kerala from beach sand in Kerala, India.

Concrete particularly its binder cement production releases approximately 0.9 tons of CO_2/ton of cement and as a consequence cement production accounts for 5-8% CO_2 in world. Hence, when we aim of producing sustainable concrete, our aim is for minimum emission of carbon dioxide. The projected CO_2 emissions from the global cement industry through 2050 (assuming no change in current practices) are given in Table 1 but as agreed by all nations (196 numbers) in Climate Conference in Paris (COP 21) on Dec.12, 2015 that it is mandatory for every nation to reduce CO_2 emission to the level 2005 by the year 2030.A tall order but Indian Government is confident.

Table -1: Projected CO_2 emissions [Source: Battelle Memorial Institute; in *Agenda* for Action,p.21]

Year	Production (in million Tonnes)
1990	=1000
2000	~ 1500
2010	= 2000
2020	~ 3000
2050	~ 5000

While the projected demand for cement production continues to rise exponentially, the demand for water, aggregates and concrete also rises along with. Nano technological applications have the potential to reduce these material demands to a desired level. Concrete is a brittle material which makes cracking rapid thereby making collapse of structures, all of a sudden. The deformation process involves the initiation, propagation and distribution of micro cracks. Various researchers have employed the incorporation of fibers with different shapes and geometries to arrest the cracking phenomenon, which mainly includes steel bars[25], steel fibers[15][21][27], glass fibers[9][19], carbon fibers[31], polypropylene fibers[8][17], and various others[10]. These reinforcing materials exhibit their reinforcement either at a macro-level or a micro-level and therefore cannot arrest the cracks originating at the nano scale. To overcome these drawbacks, investigations have shifted to the use of nano fibers (i.e. CNFs or CNTs).CNFs and CNTs have been the materials of interest for the past few years [11][12][27],and have produced remarkable improvements in the mechanical properties of cement concrete on account of their crack bridging effects at the nano scale[14] and nucleation effects in the formation of different cement hydrates[13][24]. Also as concrete is the most consumable material on earth after water, it gets deteriorated during its service life very easily due to the unreacted free lime of cement hydration process and also due to its exposure to sunlight and effects of altering and increasing polluted environment. Today many of the degraded structures which were built decades ago fail to catch attention for repairing due to staggering rehabilitation costs. It is not surprising that in USA alone 27% of all highway bridges are in need of repair or replacement and think of what India which severe corrosion prone coastal country has to offer. Protection of aesthetic durability of concrete needs continuous maintenance which is expensive, time and energy consuming. Again, long term environmental effects causes substantial financial losses and it requires extensive efforts to limit its impact. To deal with these problems, we need to enable a transformation from traditional cement based materials to multifunctional and more durable competitive materials. These transformations can be effected by using Nanotechnology (NT) at both micro and macro scale level. To deal with NT and its other aspects, it means to integrate expertise in diverse subjects' like, mechanics, chemistry, physics, and material sciences. The literature survey on nanomaterials reveals that these smart nano materials are highly durable materials and have a potential for application in a huge number of areas but its use is still limited, especially in the construction sector, due to its severe cost [32]. Literatures[16],[18],[20],[22],[23][28]&[29] are abound highlighting the importance of nano additions in cement concrete but practical *in-situ* applications [2],[3] are far from satisfactory. Thus, there is an inherent need to develop on these applicapability aspects of nanomaterials.

The construction industry was the only industry to identify nanotechnology as a promising emerging technology in the UK Delphi Survey in the early 1990s… ("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 which may be due to the fact as emphasized in Ministry of Commerce & Industry's (Govt. of India) 14th International Seminar on Cement & Building Materials, December, 2015, New Delhi, that the biggest challenge faced by nanotechnology today is distribution and dispersion. This Paper aims to investigate the economic feasibility of Nanomaterials addition viz. Nanosilica (nS), Carbon Nanotubes (CNT) & Nano Titanium Oxide (TiO_2**)** in cement composites, apart from its short term and long term implications. The following Table shows the basic data for the energy (also called Embodied Energy, EE) consumed to produce the Nanomaterials. Embodied energy is the sum of all the energy required to produce any goods or services.

Table -2: Data for Embodied Energy computations [Source: ICI Journal, Vol. 15, Jan-March, 2015, p.12]

Cement Mortar / Ingredients	Without Nanomaterials	With nS	With CNT	With Nano TiO_2
Ordinary Portland Cement	4.79801MJ/Kg	4.79801 MJ/Kg	4.79801 MJ/Kg	4.79801 MJ/Kg
Water	0.2004 MJ/Kg	0.2004 MJ/Kg	0.2004 MJ/Kg	0.2004 MJ/Kg
Sand	0.08106 MJ/Kg	0.08106 MJ/Kg	0.08106 MJ/Kg	0.08106 MJ/Kg
Processing	0.014 MJ/Kg	0.014 MJ/Kg	0.014 MJ/Kg	0.014 MJ/Kg
Nanomaterials	**--**	1.45 MJ/Kg[5]	880 MJ/Kg[6]	116 MJ/Kg[7]
Total Embodied Energy**(**EE)	5.09346 MJ/Kg	6.5436 MJ/Kg	885.0935MJ/Kg	121. .0934 MJ/Kg
% increase in Energy Expenditure	--	28.47%	17,277%	2,277.41%

For the table above, it is seen that by using Nano Silica one have to expend 28.47% more energy w.r.to ordinary cement mortar and by using CNTs & Nano TiO_2 the expenditure level is much much higher up in the range of 17,277% & 2,277% but the fact may be compensated by considering the short term & long term mechanical properties of nano materials in cement as discussed in this Paper but it also needs a considerable research effort to effect a desirable perception change in nanomaterials for large scale construction usages.

2. 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 (3 to 5) show the specific properties of nanosilica, carbon nanotubes and titanium dioxide used.

Table -3: Specific Properties of Nanosilica (SiO_2) Used[28][29]

Sample	% 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-4: Specific Properties of Multi-Walled Carbon Nanotubes (Industrial Grade) Used[28][29]

ItemItemIIItem	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-5: Specific Properties of Nanotitanium Oxide (TiO_2) Used[28][29]

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.

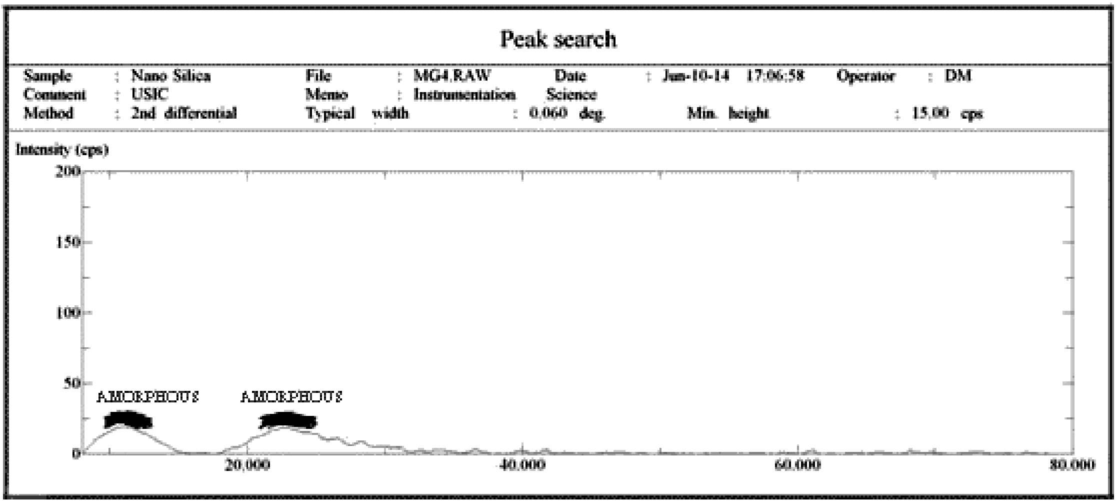

Fig -1: **:** XRD Image of Nanosilica Used[28][29]

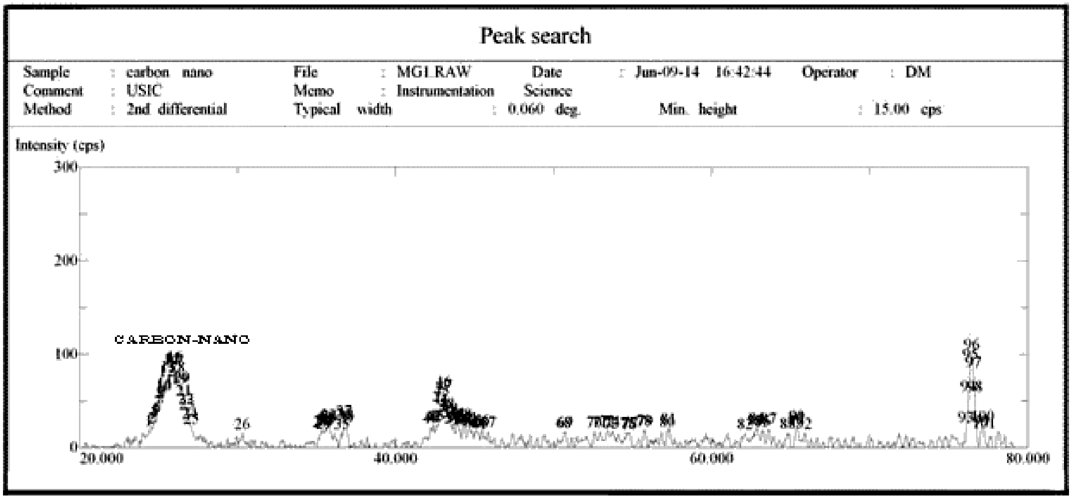

Fig -2: XRD Image of Carbon Nanotubes Used[28][29]

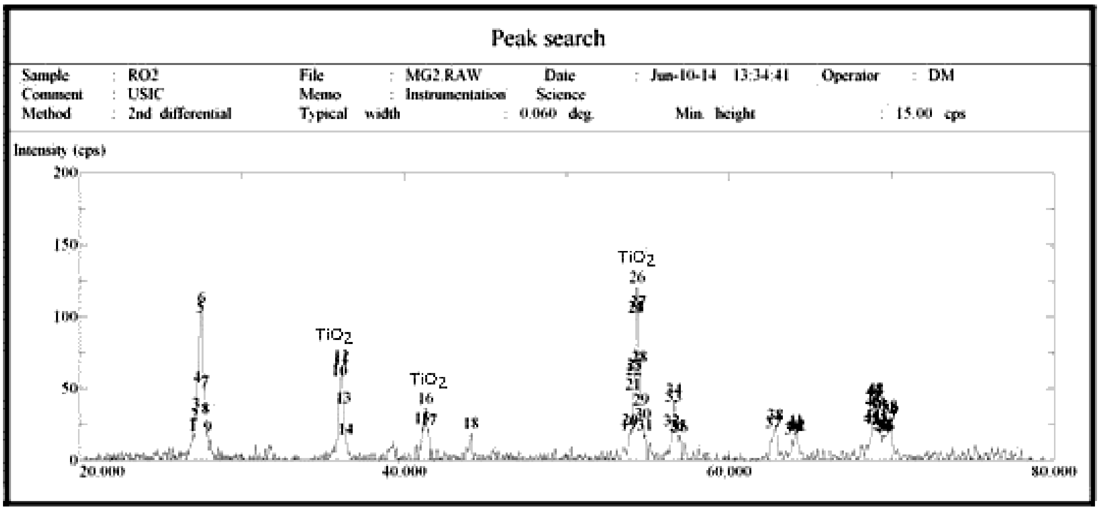

Fig -3*:* XRD Image of Nanotitanium Dioxide Used[28][29]

2.1 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) and 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)(PCE) (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.

2.2 Test Data

A) Sp. gravity of cement=3.08 (as lab. experiment suggests)
B) Chemical admixture=SuperPlastcizer (PolyCarboxylate Ether)=solid content=30%.

3. RESULTS

Table 6 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 4–7.

Table-6: 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
1.	OPC (0 % nS/CNT/ TiO_2)	21.33 21.08 20.83	21.08	Control Sample	35.20 28.57 31.89	31.89	Control Sample	24.14 38.26 31.20	31.20	Control Sample	23.81 36.22 30.01	30.01	Control Sample	29.01 30.01 31.01	30.01	Control Sample
2.	OPC(0.5% nS)	21.82 25.87 23.85	23.85	13.1 %	29.68 41.33 35.51	35.51	11.4 %	41.93 40.67 41.30	41.3	32.7 %	28.17 26.79 27.47	27.47	-9.2%	25.76 26.76 27.76	26.76	-4.3%
3.	OPC(0.75% nS) (optimized @ 28 day)	28.06 27.39 27.73	27.73	31.5 %	46.28 38.26 42.27	42.27	32.5 % ⇧	51.75 47.95 49.85	49.85	59.8 %	40.24 24.80 32.52	32.52	8.4%	30.5 31.5 32.5	31.5	4.7%
4.	OPC(1.0 % nS)	25.15 25.00 25.07	25.07	18.9 %	31.57 43.15 37.36	37.36	17.2 %	41.32 44.64 42.98	42.98	37.7 %	29.59 37.78 33.68	33.68	12.2 %	31.41 32.41 33.41	32.41	8.0% ⇧
5.	OPC(1.25% nS)	21.52 24.73 23.17	23.17	9.9%	23.47 38.23 30.85	30.85	3.3%	33.27 45.63 39.45	39.45	26.4 %	44.46 26.02 35.24	35.24	17.4 %	30.3 31.3 32.3	31.3	4.3%
6.	OPC(1.5% nS)	24.15 23.47 23.81	23.81	12.9 %	40.89 34.70 37.79	37.79	18.5 %	34.69 32.14 33.42	33.42	7.1%	31.63 30.82 31.23	31.23	4.1%	29.12 29.12 29.12	29.12	-3.0%
7.	OPC(0.02% CNT)(optimized @ 28 day)	16.86 20.12 16.10	17.69	-10.4 %	42.35 44.63 44.27	43.75	38.7 % ⇧	34.60 35.59 36.60	35.59	15.5 %	34.69 33.13 24.85	30.89	10%	22.83 34.18 28.57	28.53	-4.9%
8.	OPC(0.05% CNT)	32.56 24.86 24.14	27.19	-16.1 %	41.95 31.35 31.35	34.88	37.2 %	41.24 24.13 30.18	31.85	14.1 %	54.30 31.18 30.18	38.55	3.0%	34.21 41.69 49.17	41.69	38.9 %
9.	OPC(0.1% CNT)	24.14 20.54 20.41	21.69	28.9 %	23.00 27.00 24.49	24.83	9.4%	28.17 30.61 35.71	31.50	2.1%	27.78 32.09 30.61	30.16	23.6 %	49.60 40.24 62.50	50.78	69.2 % ⇧

10.	OPC (1% TiO_2)(optimized @ 28 day)	24.45 26.02 25.24	25.24	19.7 %	38.70 36.71 34.72	36.71	12.6 % ⇧	33.61 35.92 38.23	35.92	15.1 %	29.59 33.42 32.25	33.42	11.4 %	42.47 39.86 41.16	41.16	37.2 % ⇧
11.	OPC (2.5% TiO_2)	20.05 20.62 20.34	20.34	- 3.5%	36.73 33.20 34.97	34.97	9.6%	35.21 37.80 40.40	37.80	21.2 %	39.24 % 442.66 40.95	40.95	36.5 %	25.51 30.81 28.16	28.16	- 6.2%

Fig. 4: Some Apparatus used in Mortar Cubes Castings

4. DISCUSSION OF TEST RESULTS

1. Nano-Additions never resulted in any appreciable change in physical characteristics_of Cement – colour, shape, size, weight, density.
2. Nano-Additions in PCE for CNT/TiO_2 reduced the setting time[From 3 Days to 1.5 Day]
3. 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. 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]. Optimized TiO_2 indicated no such appreciable gain in strength. In the Long term @ 365 days, an interesting fact emerges. From Table 6 and from Figures 5,6 & 7 it is found that a small amount of nS(1% w.r.to cement wt.) and CNT(0.1% w.r.to cement wt.) addition results in maximum strength gain of 8% in the former and 69% of the latter, in the long term @ 1 year.

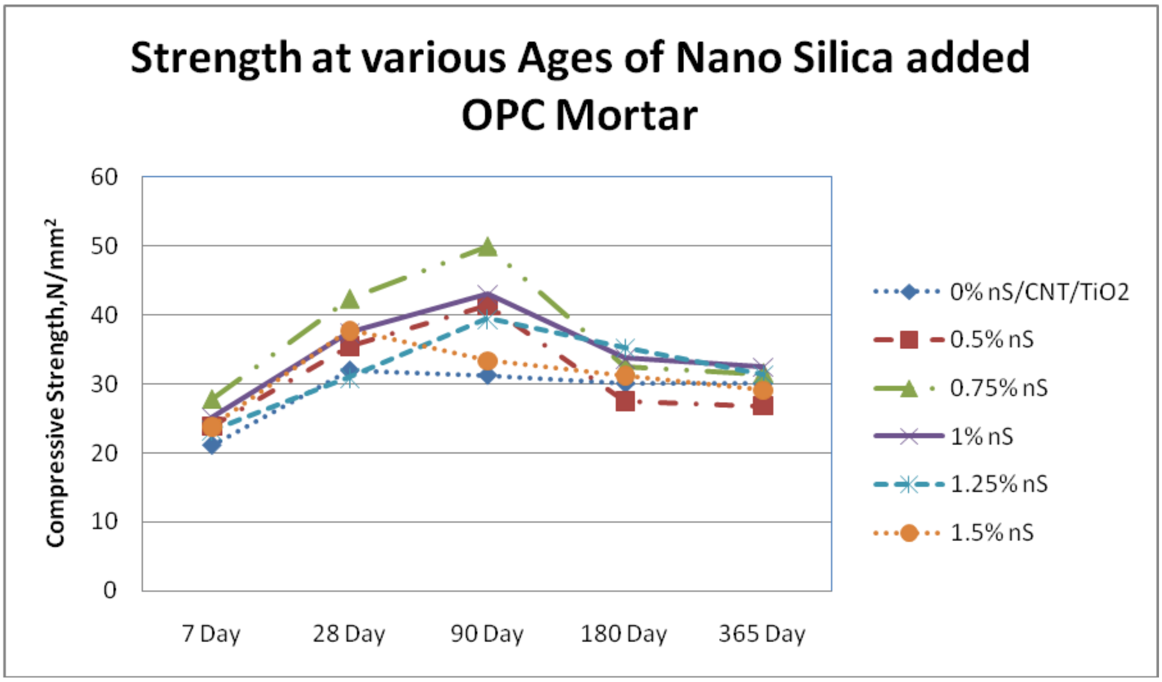

Fig.5: Chart showing strengths at various ages of different % of nS addition in OPC Mortar

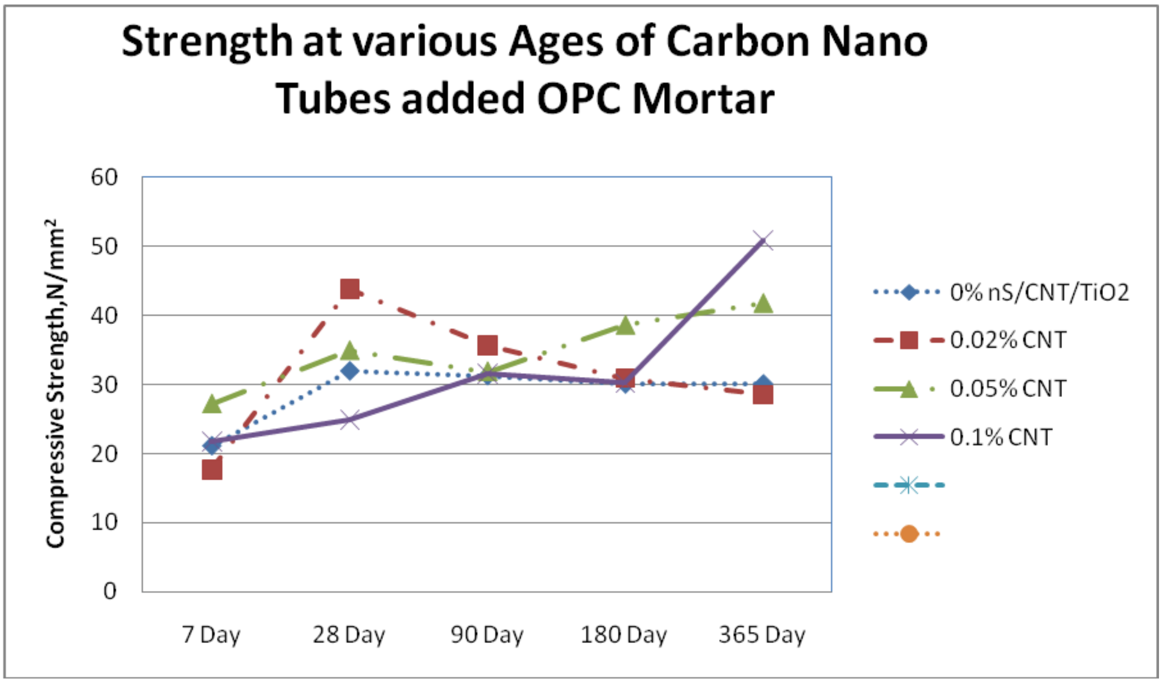

Fig.6: Chart showing strengths at various ages of different % of CNT addition in OPC Mortar

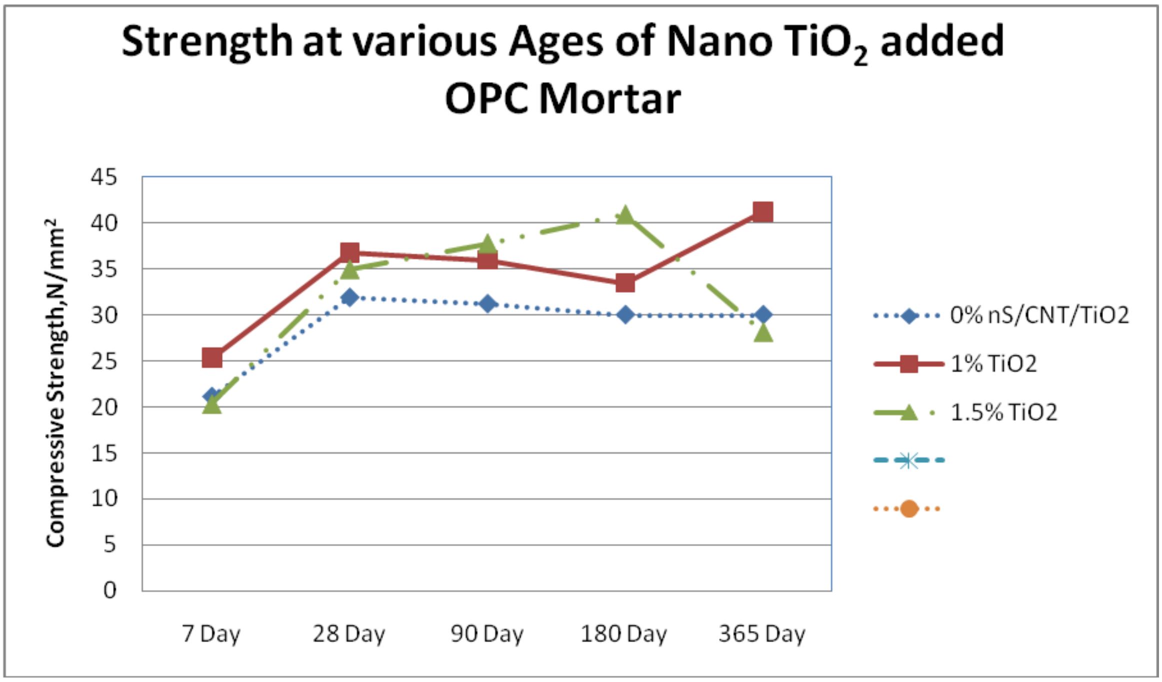

Fig.7: Chart showing strengths at various ages of different % of TiO_2 addition in OPC Mortar

4. The Embodied Energy calculation for nS shows an extra energy of 28.47% w.r.to ordinary cement mortar is needed to produce its composites but the optimized strength gain of 32.55% is comparatively much more. For TiO_2 the expenditure on Embodied Energy is 2277% more w.r.to ordinary cement mortar but considering the long term strength gain of 37.15% & other synergistic effects like application in high performance concrete[32] & its photocatalyst effects[33] ,its application may turn out to be eco-friendly and cost-compatible. For CNTs expenditure on Embodied Energy is 17,277% more but as CNT is a 'wonder material'[4] having multiple functions as per existing literatures, so this huge cost effect may get subdued with more leapfrogging research work.

5. CONCLUSION

1. 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.
2. 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.
3. The 28day strength for optimized Nano Titanium dioxide never varied with increased addition of TiO_2 in the long term. That is 1% optimized TiO_2 as found by others [32] holds good for both short & long terms respectively.
4. Further research on micro structural studies is necessary for characterization of nanomaterials in cement.

ACKNOWLEDGEMENT

The authors would like to acknowledge the Structural Waterproofing Co., Kolkata-Chryso, and Ambuja Cements & UltraTech Cements for providing financial assistance to carry out the research work.

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