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Application of Nanomaterials in Cementitious Systems

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Abstract— Nanomaterials are advanced materials derived from nanotechnology which can address much of the present-day world's problems if used in optimum quantities. Nanotechnology is ruling in electronics, medicines, water-purification, textiles, cosmetics, mobiles, computers and health-care fields. This Paper focus on the effect of adding nanomaterials in cement-sand mortar at various dosages by weight of cement at different ages starting from short term to long term via. medium term. Comparing the results of nano-additive cement mortars with that of ordinary cement mortars it has been found that nano-additions has resulted in a higher strength gain.

Keywords *— Cement; Mortar; Nanomaterials.*

1. Introduction

Nanomaterials are the derived product of Nanotechnology and are being increasingly used in multi-disciplinary fields for process-product improvement. American Concrete Institute (ACI) defines nanomaterials are those materials that are less than 100 nanometres (nm). 'Nano' is actually a *Greek* word which means 'Dwarf' and is mathematically represented as 10^{-9}m. Due to their very small size they offer unique novel properties in various systems through *quantum effects* which include cementitious matrices. *Quantum Effect* is very much different than Newtonian effects or Newtonian Mechanics which is associated with mechanical properties of conventional building materials. With small additions of nanomaterials i.e. less than 1% by weight of cement in the cementitious systems we get such increase like 30 to 40% in mechanical properties of the advanced nanomaterial doped system like compressive strength, tensile strength, flexural strength, Elasticity etc. when compared to the ordinary cementitious systems. Various literatures suggest that nanomaterials like Nano-Silica (NS), Carbon Nano-Fibres (CNF), Carbon Nanotubes (CNT), Nano Titanium Dioxide or Nano Titania (NT) etc. are in a revolutionary way to address the advanced material deficiency of 21st century. These nanomaterials increase the nucleation sites responsible for cement hydration which increases the space available for cement hydration resulting in much more hydration products [14].

The hydration products are very complex structures at the nano level in the cementitious matrix constitute the backbone for its mechanical strength. NS increases the pozzolanic activity of cementitious systems leading to lesser pore sizes, reduced permeability which ultimately gives a higher strength gain [2,3,4,5] and like Silica Fumes(micro-silica), NS can also be used in the production of High Performance Concrete.CNF or CNT have proved to be the strongest material in earth and even harder than diamond and can be used in cementitious matrices for crack bridging effects resulting in much improved cementitious systems [6,12] while NT are possessed with excellent self-healing properties[1,11]and at present NTs are the most consumed nanomaterial followed by NS. Though US is not poised to become a world leader in the field of Nanotechnology as China & Germany are becoming the top two countries in the use of nanotechnology-based products in the building industry. India is lagging despite investing in nanotechnology from 2002 onwards. Despite an increase in research publications (see Fig.1) which includes India as well, the world today is polarised into nano have & have-nots. So, more research work is needed in the field of nanotechnology to reveal more on the novel aspects of nanomaterials.

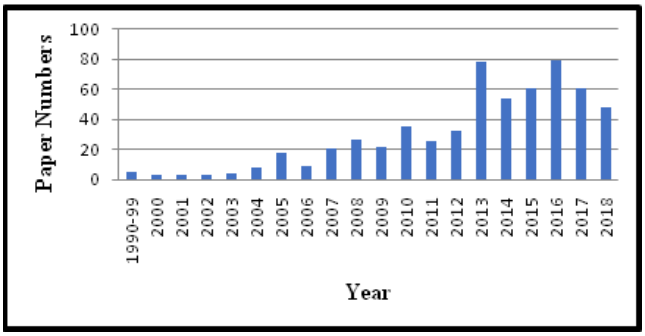

Fig.1: Published papers indexed to Scopus database

Figure 1 shows the number of published papers indexed to Scopus database, which include the terms cement and nanotechnology or nanomaterials in the title, abstractor keywords, subjected to the fields of engineering and materials science. (Source: Scopus Support (ELS)

2. Literature Survey

Nanotechnology was prevalent in the pages of history and evidence of use of nanomaterials can be found dating back to the fourth century AD in the form of the *Lycurgus Cup*[15]having unusual optical properties, *Damocles' Sword*, *Ajanta Paintings* ,etc. Since Richard Feynman's

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lecture "There's Plenty of Room at the Bottom" in 1959, nanotechnology has evolved as the "bottom-up" approach for controlling matter at 1 and 100 nanometres.

2.1 Effect of Nano-Silica

Belkowitz, S. J. and Armentrout. D.[2] developed relationships to distinguish the benefits when using different sizes of nano-silica(NS) in cement hydration paste through experimenting & measuring the heat of hydration of multiple mix designs and showed that as silica particles decreased in size with increased size distribution the C-S-H became more rigid and successively increasing the compressive strength. Quercia, G. & Brouwers, H. J. H. [3]aimed to present in their paper the NS production process from olivine dissolution, their addition and their application in concrete.

Valipour.M et al [4] studied the influence of NS addition on properties of concrete in comparison with silica fumes(SF) through measurement of compressive strength, electrical resistivity & gas permeability. The results show that replacement of some of SF with NS is more active in early age thanks to larger specific surface & fineness and can also improve the sturdiness aspects of HPC. Jemimath, C.M. &Arulraj, G. [5] reported that cement replaced with nano cement (NC), nanoflyash (NFA) and nano silica fume(NSF) showed a unaffected consistency but it had been found that addition of NC decreases the initial and final setting times while the addition of NFA and NSF increases the setting times.

Maheswaran,S et al [7] attempted to highlight the influence of Ns towards pore filling effect and its pozzolanic activity with cement for improvement of mechanical properties and durability aspects and development of crack free concrete. Yang,H [8] presented the laboratory investigations that when nano silicon powder mixing content is 0.5%,0.75% & 1.0% compared with ordinary concrete ,the bending tensile strength at 28 days were increased by 3.2%,7.5% & 4.0% .

Yuvraj,S [9] explains that, NS is added to make concrete less alkaline as C-H in concrete, which reduces the corrosion of steel bars. He also focused that more C-S-H is produced at the Nano scale and so it increasing the compressive strength. Abyaneh, M.R.J. et al [10] described the compressive strength, water absorption and electrical resistivity of the concrete containing NS and micro-silica at 7,14,28 days and identified that concrete with micro-silica and NS have high compressive strength than concrete with only micro-silica. He also identified that that specimens with 2% NS and 10% micro-silica have less water absorption and more electric resistance. Rajmane, N.P. et al [13] showed that NS cannot be used as an admixture to improve the microstructure of the cement composites (with and without 5% SF) at the w/c ratio of 0.5.

2.2 Effect of Carbon Nano Tubes

Kumar,S. et al [6] difined the effect of Multiwalled Carbon Nanotubes (MWCNT) on strength characteristics of hydrated portland cement paste by mixing different proportions of MWCNT and an increase was found in compressive and tensile strength of 15% and 36% at 28 days. Madhavi,T. et al [12] found an increase in compressive and split-tensile strengths of samples with increasing MWCNT.0.045% of MWCNT has improved the 28 days compressive strength by 27% while the split lastingness increased by 45%.Crack propagation was reduced and water absorption decreased by 17% at 28 days curing.

2.3 Effect of Nano-Titanium Dioxide

Jayapalan,A.R. et al [1] throwed light on the effect of nano-sized titanium dioxide on early age hydration of Portland cement. He said that the addition of TiO2 to cement modifies the hydration rate primarily thanks to dilution, modification of particle size distribution & heterogeneous nucleation. But when the dosage is increased, cement dilution is resulted with a rise in w/c ratio. Lucas. et al [11] concluded that photo catalytic activity of TiO_2 increases with increase in dosage but its mechanical strength decreases for addition of more than 1% wt. of TiO_2.

3. Materials and Methods

The materials used were Ordinary Portland Cement (OPC) of 43 Grade of *Ambuja* make, natural river sand, drinking water and nanomaterials viz. Nano Silica (NS), Multi-Walled Industrial Grade Carbon Nanotubes (CNTs) & Nano-Titanium Oxide (TN).

Fig.2: Curing of cement mortar cubes in Curing Chamber of Indian Institute of Engineering Science & Technology, Shibpur's(IIESTS) Concrete Laboratory

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3.1 Test Methods

Mortar cubes of 70.7 mm X 70.7 mm X 70.7 mm dimensions are filled with one part of Cement plus three parts of River Sand with Water added, according to the standard formula P'=(P/4 +3)(1 part Cement+3parts Sand). Where, 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 Vicatmould with a Vicat needle. Nanomaterials like NS at dosages ranging from 0.5%,0.75% & 1.0% b.w.c.; CNT at dosages ranging from 0.02%,0.05% b.w.c. & TN at dosages of 1.0% & 2.5% b.w.c. were added as per literature surveys. Three (03) numbers of cubes were casted against each nanomaterial dosage and against specified age. Now, we would be testing the Compressive Strength of both composite & ordinary Cement Mortar cubes after 7days (short term), 28days (medium term) and 90days (long term) ordinary curing (see Fig.2) in a Compression Cube Crushing or Testing Machine.

4. Results

The following Table shows the results of cube crushing at time-specified ages.

Table 1: Test results of the cement mortar cube crushing at various ages

Sl No	% Nanomaterial additions in Cement (OPC)	Avg. 7 day cube strength (% increase)	Avg. 28 day cube strength (% increase)	Avg. 90 day cube strength (% increase)
1.	OPC (0% Nanomaterials)	21.08	31.89	31.20
2.	OPC (0.5% nS)	23.85(13.14%)	35.51(11.35%)	41.3(32.7%)
3.	OPC (0.75% nS) (optimized)	23.85(13.14%)	42.27(32.55%)	49.85(59.8%)
4.	OPC (1.0 % nS)	25.07(18.93%)	37.36(17.15%)	42.98(37.7%)
5.	OPC (0.02% CNT)	17.69(-16.08%)	43.75(37.19%)	35.59(14.07%)
6.	OPC (0.05% CNT)	27.19(28.98%)	34.88(9.37%)	31.85(2.08%)
7.	OPC (1.0% n-TiO_2 (optimized)	25.24(19.73%)	36.71(12.59%)	35.92(15.13%)
8.	OPC (2.5% n-TiO_2)	20.34(-3.51%)	34.97(9.58%)	37.80(21.15%)

5. Discussions

For different nanomaterials different behaviours were observed which are discussed as follows.

- At early ages for NS added cement mortar, the gain of strength grew (more than 27%)at 7 days and at medium term the strength grew by more than 30% at 28 days w.r.to the ordinary cement mortar cubes with 0% nanomaterial additions) with the maximum strength development was found to be optimized at 0.75% NS b.w.c. for all ages. For later ages, the strength was maximum to a value of 49.85MPa at 90 days.
- Using 0.02% CNT added cement mortar as the optimized one, the strength was increasing at 7 days, reached the peak at 28 days with 37% increase in strength w.r.to the ordinary cement mortar cubes with 0% nanomaterial additionsand then again increasing at slow rate 90 days.
- Table 1 shows the Compressive Strength results of Ordinary Portland Cement for various percentages of Nano-Titanium Oxide at early ages of 3 & 7 days. It shows that with decreasing the content of Nano-Titanium Oxide from 2.5% to 1% increases the strength by more than 12% at 28 days but at 90 days 2.5% NT shows a strength gain of 21%.

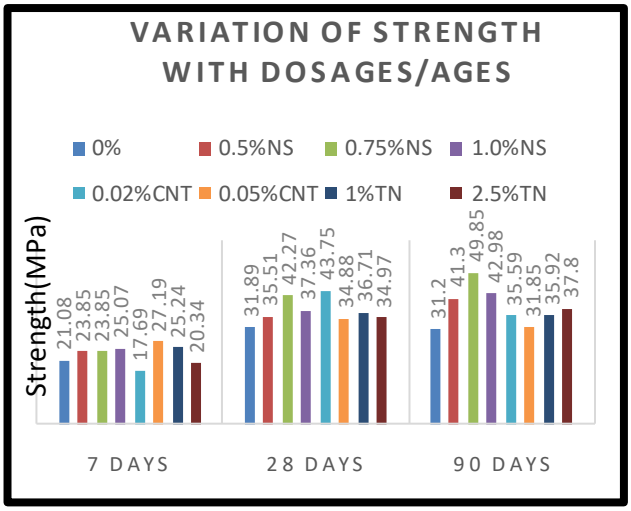

Fig.3: Chart showing the Variation of Strength with Dosages/Ages.

6. Conclusions

From figure 3, it has been found out that the optimizations of NS = 0.75%, CNT=0.02% & NT=1% b.w.c. But with more nanomaterial additions more strength gain is observed at longer terms of 90 days. So, further studies are needed to develop a correlation between dosages and ages along-with the characterization of nanomaterials.

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