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Study of Effect of Nanomaterials as Cement Replacement on Physical Properties of Concrete

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Abstract - ***In this paper, the significance of nanomaterial for construction industry is emphasized and reviews of recent developments and present state of the application of nano alumina, nano titanium dioxide, nano zinc oxide and nano-silica for sustainable development of concrete industry. This would save not only the natural resources and energy but also protect the environment with the reduction of waste material. Only a limited amount of nano-products make it to the construction site of today, because of this lack of awareness and the fact that nano-sized ingredients are often too expensive to result in competitive products.***

Key Words: *Concrete, nano alumina, nano titania, nano zinc oxide and nano-silica (amorphous silica)*

1. INTRODUCTION

The framework of the next industrial revolution, or nanotechnology, was first introduced in the famous lecture of Nobel Laureate Richard P. Feynman "There's Plenty of Room at the Bottom" given in 1959 at the California Institute of Technology. The past 25 years of revolutionary developments in physics, chemistry, and biology have proved Feynman ideas of controlling matter at an extremely small scale – the level of molecules and atoms. According to Whatmore and Corbett, the subject of nanotechnology includes "almost any materials or devices which are structured on the nanometre scale in order to perform functions or obtain characteristics which could not otherwise be achieved".

Nanoparticles are defined as "engineered" particles (man-made to distinguish them from "natural" nano-sized particles that are formed during i.e. volcano eruptions) at the size of 1- 100nm. These can be soluble or non-soluble. At the moment, only non-soluble particles are addressed by the term nanoparticles because the non-soluble persistent ones are those that are of key interest with respect to potential nano-typical health effects. However, discussion is currently developing around the issue of possible nano-typical health effects by soluble nano-sized particles also because of their nano-typical fate in the environment.

Nanotechnology concerns with the usage of materials falling in range of few to less than 100 nanometers. Constructional structures form a very important part while contributing to the GDP of any economy by rendering services ranging from transportation to living to producing useful products to earning livelihood, and at the same time also commanding a very dominant share of the energy produced for utilization, no wonder that it has been estimated by a certain source that construction industry involving nanotechnology will occupy the eighth position out of the usage of nanotechnology materials while being incorporated in constructional structures would not only help in prolonging their lifetime, but would also keep a check on the energy spent by them and at the same time gauging their reactions and reacting to different agents like fire, corrosion, water penetration, fractures, cracks, etc.

Nanotechnology has changed our vision, expectations and abilities to control the material world. The developments in nano-science can also have a great impact on the field of construction materials. Portland cement, one of the largest commodities consumed by mankind, is obviously the product with great, but not completely explored potential. Better understanding and engineering of complex structure of cement based materials at nano-level will definitely result in a new generation of concrete, stronger and more durable, with desired stress-strain behavior and, possibly, with the whole range of newly introduced "smart" properties.

2. LITERATURE REVIEW

Aiswarya S Lecturer ,Anand Narendran Former PG Student (School of civil engineering, Karunya University, Coimbatore, Tamilnadu India) Prince Arulraj G Professor and Dean (Department of Civil Engineering, SNS College of Technology Coimbatore, Tamilnadu India) worked on nano-metakaolin. An experimental investigation has been carried out to determine the compressive strength, split tensile strength and modulus of elasticity of normal cement concrete and concrete containing Nano-Metakaolin partially replacing cement at various percentages. The mixes were designed as per IS 10262-

2009. The cement was replaced by Nano- Metakaolin at various percentages (2%, 4%, 6%, 8%, 10%, 12%, 14%, 16%, 18% and 20%) for M20, M30, M40 and M50 grades. A comparison between the cost of Normal Concrete and concrete with Nano-Metakaolin is also made. It is found that partial replacement of cement with Nano-Metakaolin has a greater influence on the strength of concrete. The optimum percentage at which cement can be replaced with Nano-Metakaolin is found to be 10%.

Sakshi Gupta Assistant Professor, Civil Engineering Department, Dronacharya College of Engineering, Gurgaon, Haryana, India concluded that Nanotechnology has the potential to be the key to a brand new world in the field of construction and building materials. The role and application of the nano and micro silica particles with cementitious materials have been reviewed and discussed in details. It is evident from the literatures reviewed that none of the researchers have carried out extensive or comprehensive study of the properties of paste and mortar, with nano silica, micro silica and their simultaneous use. There is a limited knowledge about the mechanisms by which nano silica & micro silica affects the flow properties of cementitious mixes. In India, the research work on use of nano silica is still in elementary stage. Thus, a need arises to study extensively the various properties of paste, mortar, and concrete containing various percentages of nano silica, micro silica alone as partial replacement of cement and then studying their combined percentage effects. As the properties of nano-silica and micro-silica reported in literatures relate with those manufactured or exported from abroad, there is urgent need to study the effect of these materials (manufactured in India) on various properties of cement paste, mortar and concrete. Major parties in the construction materials industry should divert more funds to research work on incorporating nanotechnology in construction materials. Thus, the main motive is to provide practical information, regarding the strength, sustainability & durability properties of nano silica, micro-silica and their simultaneous use in paste, mortar and concrete. Also, the aim is to carry out the extensive studies to conceive the general purpose of testing new sustainable building processes and modern production systems, aimed at saving natural raw materials and reducing energy consumption. Taking advantage of nanostructure and microstructure characterization tools and materials, the simultaneous and also separate optimal use of micro-silica and nano-silica will create a new concrete mixture that will result in long lasting concrete structures in the future. Thus, there is a gap or room available for further research towards the fruitful application of especially nano-silica for construction with different nano structure characterization tools, which will be enable to understand many mysteries of concrete.

Mr. Davoud Tavakoli and Mr. Ali Heidari concluded that The combination of silica fume with nano-SiO2 as a replacement for cement has been investigated in this study. The silica fume was used in quantities of 5 and 10 percent and nano-SiO2 was 0.5 and 1 percent of the cement. The following conclusions can be drawn from the study:

- Silica fume and nano-SiO2 can lead to the improvement of concrete strength. Moreover, given the less water absorption as a result of using these two materials, it can be maintained that these materials enhance the concrete durability in the long term.
- Nano-SiO2 in low amounts can exert positive and desirable impacts on concrete. Therefore, the necessity to do further studies is strongly felt.
- The simultaneous use of silica fume and nano-SiO2 increase noticeably the strength and durability of concrete compared with their single use, besides, in view of the two materials, influence process in the case of their simultaneous use in concrete, all defects of concrete in all ages will be covered and caused them to strengthen each other.

In recent Mr. Anwar Khitab and Muhammad Tausif Arshad Department of Civil Engineering, Mirpur University of Science and Technology, Allama Iqbal Road, Mirpur, Azad Kashmir, Pakistan, concluded that

1. Nanotechnology has tremendous potentials in construction industry. The examples are germ-free laboratories and hospitals, waterproof buildings, urban environmental protection.
2. The important developments made in concrete technology are ultra high strength concrete, photocatalytic concrete, self-heating concrete, bendable concrete and concrete containing CNTs.
3. Nano Silica Concrete incorporates nano silica instead of micro silica particles or well known silica fumes. This concrete results in higher initial and final compressive strengths, higher workability, and lower permeability. Additionally, higher tensile strength and segregation resistance are also achieved. The new concrete is named as Ultra High Strength Concrete. The advantages of this concrete are numerous: the column sections in buildings can be reduced. The amount of steel reinforcement in concrete can also be reduced. And in highways and railway tunnels, thinner tunnel segments can be constructed leading to a great saving in excavations.
4. It is a well known fact that nano TiO2 on UV irradiation can be used as an effective way to reduce the contaminants and enhance environmental safety.
5. Photocatalytic concrete is a green material. With this concrete, structures looking new for decades can be constructed. Inside hospitals and laboratories, the spread of germs can be minimized and urban air quality can be improved.
6. Serious health issues related to the use of nano materials must be well understood and remedies are mandatory.

7. The investigation for various applications of nanotechnology to build up novel building materials continues. It is by now obvious that the science of the very small is creating big changes, with various economic benefits to the construction industry.

3. WHY WE USED

3.1 Nano Alumina

The role of nano Alumina in increasing the mechanical properties of cement has been carried out by few researchers. The optimized level of usage of nano particles to attain the ultimate strength was reported. Further, the potential of nano materials for activation of the initial strength of belite cements. The study concluded that an addition of nano particles notably increases the early strength (7 days) and the nano particle can be used as an agent for activating hydraulic properties of belite cement thereby changes in microstructure causes improved mechanical property. The nano Alumina fill the ITZ of cement- sand and some capillary in the matrix and hence the elastic modulus and compressive strength of mortars were increased. But, no significant improvement in compressive strength was noticed due to insufficient filling of pores in the cement matrix under experiment condition. Alumina imparts quick setting properties to the cement. It acts as a flux and it lowers the clinkering temperature.

3.2 Nano Titania & Zinc Oxide

Anatase, rutile, brookite are some of the crystalline forms in which Titania exists in nature. High refraction index is one of the properties of Titania. Titania also known as titanium oxide, is a naturally occurring oxide of titanium, having chemical formula TiO_2. Titanium dioxide has excellent ultraviolet (UV) resistant qualities and is used as sunscreen in cosmetics. Nano titania particles have found to be stable, anticorrosive and possess photocatalytic properties. Many researchers have credited this photocatalytic activity of titania particles to their high surface area. Nano-layers of titania are being put on the glass of windows so that they are self-cleaning. It has also been proved that nano-titania containing paints are easy to clean and have much larger design life. Apart from paints, nano Titania particles have also been added in concrete. The manufactured concrete is named as self cleaning concrete or photocatalytic concrete or smogeating concrete or Green Concrete due to its self cleaning properties. The applications of nano photocatalytic concrete also include environmental pollution cleansing and self disinfecting. Titania disintegrates organic pollutants into harmless CO_2 and water, in the presence of light. Products of reaction are easily removed by rain or simple rinsing. Buildings stay cleaner and more beautiful. One major disadvantage of using Titania is that UV light is required to activate the photo catalysis and initiate the killing of the bacteria and viruses.

3.3 Nano Silica

Nano silica having a low cost budget, high compressive & tensile strength, high surface area, ability to prevent silicosis, reducing percentage of CO_2, nanosilica also helps in checking solid waste pollution when mixed with recycled concrete aggregates. As micro silica fumes are added in concrete to fill in the voids, decrease the concrete alkalinity, and increases its resistance against the chemical attack. Cement and water undergo chemical reactions known as hydration reactions: A cement particle is composed of four chemical compounds namely, Tricalcium sulfide (C_3S), Dicalcium sulfide (C_2S), Tricalcium Aluminate (C_3A), and Tetra calcium Alumino-ferrite (C_4AF). The hydrations of the first two compounds with water lead to the formation of calcium-silicate-hydrate (CSH) gel and calcium hydroxide (CH) also known as Portlandite. The CSH gel is a strong bond and forms strong connection between the concrete particles. On the other hand, Portlandite is a soluble product and leaches out in water. It is a weak link between the concrete particles. The addition of silica particles in concrete mix converts the weak CH into stronger CSH. Silica fumes refine the properties of concrete by two means: its fine size fills the voids between cement particles and the voids between cement particles and aggregates; and secondly they react Pozzolanically with CH to produce CSH gel, increasing the binding quality and decreasing the capillary porosity of concrete. Thus it is well established that silica fumes increase the strength of concrete and produce a denser and more homogeneous matrix. This effect of silica fume has been proved by electron microscopy measurements. Silica fumes as discussed above are micro particles. It imparts strength to the cement due to formation of dicalcium and tricalcium silicates. If silica is present in excess quantity, the strength of cement increases but at the same time it setting time is prolonged. It compacts concrete, making it more strong and more durable under alkaline conditions like marine environments. It can also be added to concrete to stabilize fillers like fly-ash, to a coating material resulting in a very strong matrix, or used as fire retardant agent. Typical applications are UHPC (Ultra High Performance Concrete), scratch resistant coatings and fire resistant glass.

4. PROBLEM FORMULATION

In 2003, R&D specialists shared high expectations about the near future developments of nano-products for the construction industry. However, only little of the products expected that time really made it to the construction site of today. Various reasons can be appointed. The most important ones will be discussed in the sections below.

4.1 Price competition

The very first reason why nano-products may be successful in society but still do not make it in the construction industry is the costs involved. At the moment, nano-materials and consequently nano-products are still significantly more expensive than their non-nano alternatives because of the technology required to produce them. For the construction sector, this implies that already at the R&D phase of a product, initiatives are stopped when is foreseen that the nano-product to be produced will never reach competitive pricing. Largely this is due to the fact that construction products almost always come in large volumes and small price differences at the kg level add up to enormous increase in total costs when the total volume of the construct is considered. As a result, manufacturers of construction materials are reluctant to develop nano-products and those nano-products that are developed are only applied upon specific request. This inparticular holds for the larger volume products like concrete or mortar and for construction coatings. However, for e.g. insulation materials and architectural and glass coatings, the current societal focus on the improvement of energy management in the context of climate change and the reduction of greenhouse gasses does stimulate their further market introduction.

4.2 Technical performance

The technical performance of the product is a second limiting factor for large scale nanoproduct introduction. The technical performance should thoroughly be proven to meet the technical standards for that material. Obviously, this does depend on the market sector. For concrete for example this is a major issue. For self cleaning window coatings, this issue is much less important as the safety standards for instance are much lower.

4.3 Awareness within the sector

Awareness (or the lack thereof) is another key element hampering the introduction of nanoproducts in construction works. Without awareness one simply doesn't know there is anything new to apply or explore. Within Europe, knowledge about nanotechnology in construction is very limited and at this moment is still the property of a small number of key players that develop the market. The 2009-survey set out by the FIEC and EFBWW to monitor the awareness of construction workers and their employers, showing that the majority of respondents (~75%) were not aware if they do work with nanoproducts. This result is based on 28 returned questionnaires, where it was aimed at 3 returns by each FIEC or EFBWW member from each of the 24 EU countries approached (a total target of 144 returns).

5. SOLUTION

The use of nanotechnology for improved material study and development requires a strong R&D department with the possibility to use expensive equipment worked on by skilled people. However, since the construction industry never has been strongly R&D oriented, R&D activities with respect to nano mainly take place at large multi-national producers like BASF, AKZO-NOBEL, DuPont, Heidelberg and ItalCementi or at specialized Research Institutes (either university based or private). This indirectly implies that SME's play little to no role in the present pioneering nano activities within the construction sector. Exceptions are SME spin-offs that do have a contract that allows them to use the research facilities of their more large "mother" company, SMEs that were set-up as University spin-offs (and can make use of the university based facilities) focused on specific nano-niche markets like for example the production and design-on-demand of specific nano-materials, and a small amount of SMEs that succeeded in using the successes and break troughs of the more large companies to innovatively develop their own product lines. At present though, this situation is changing in the coating sector. Nano-coatings are typically 'far' in their development with respect to other construction products like concrete or insulation materials and methods to apply nano-materials are becoming more and more 'common knowledge' among product manufacturers. It is therefore that in the field of paint and coatings SME's are starting to play a role too and fabricate their own nano-product line.

6. METHODOLOGY

1. Samples are prepared by adopting 10 % replacement of cement by weight with nano products available.
2. Cube samples of size 0.15x0.15x0.15cm are prepared for testing of compressive strength of concrete for 7 and 14 days.
3. Cube samples of size 70.6x70.6x70.6mm are prepared for testing of compressive strength of cement for 7 and 14 days.
4. Workability of different cement concretes are determined and compared with normal concrete by various methods at different water –cement ratio.
5. Durability of cement is measured by finding % weight loss of 7 days samples of different nano products.
6. All the materials used to prepare the samples are as per IS specifications.
7. All the tests performed are as per IS specifications.

7. RESULTS

7.1 Compressive Strength Test

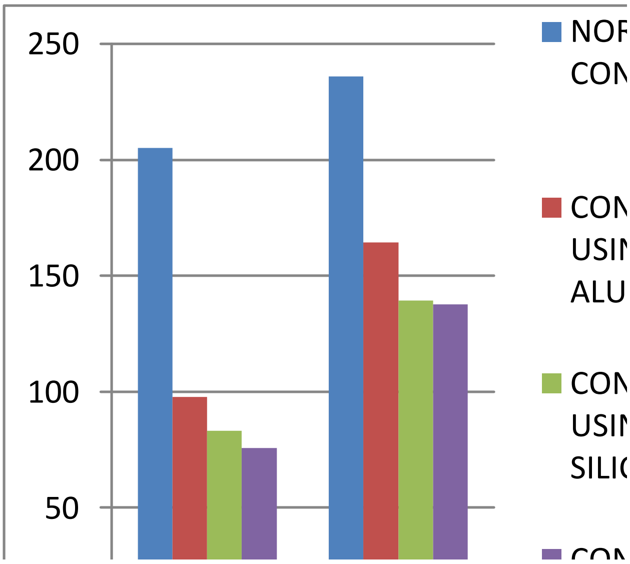
Table I
Compressive Strength Of Cube Samples Prepared (kg/cm²)

Days	NORMAL CONCRETE	NANO ALUMINA CONCRETE	NANO SILICA CONCRETE	NANO TITANIA CONCRETE
7	204.44	93.33	80.00	71.11
	208.88	102.22	84.44	80.00
	204.44	97.78	84.44	75.55
14	240.00	168.89	142.22	133.33
	235.55	164.44	137.77	142.22
	231.11	160.00	137.77	137.77

Figure : Sample of nano Alumina concrete

Figure : Sample of nano Titania concrete

Figure : Sample of nano Silica concrete



Note: X- axis shows Time and Y- axis shows compressive strength in kg/cm^2

7.2 Workability Test of Concrete

a. **Slump Cone Test**

Table II
Slump of Concrete Samples Prepared (mm)

W/C Ratio	NORMAL CONCRETE	NANO TITANIA CONCRETE	NANO ZINC OXIDE CONCRETE	NANO ALUMINA CONCRETE
0.50	65	69	71	74
060	78	83	86	85
0.70	92	97	101	104
0.80	108	115	123	124

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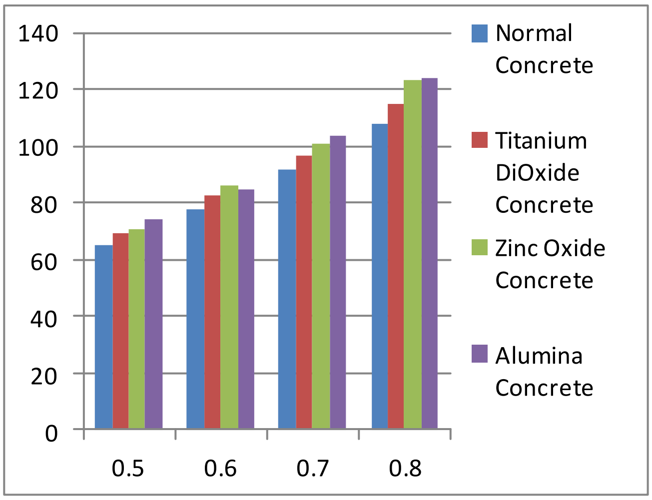
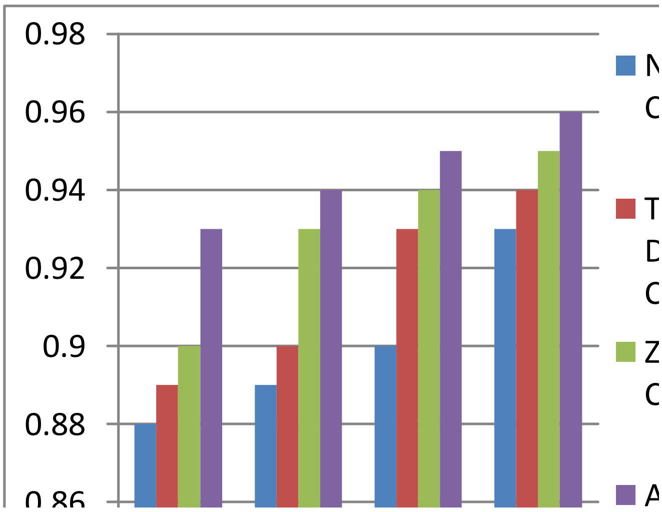


Note: X- axis shows W/C ratio and Y- axis shows slump in mm

b. Compaction Factor Test

Table III
Comparison of compaction factor

W/C Ratio	NORMAL CONCRETE	NANO TITANIA CONCRETE	NANO ZINC OXIDE CONCRETE	NANO ALUMINA CONCRETE
0.50	0.88	0.89	0.90	0.93
060	0.89	0.90	0.93	0.94
0.70	0.90	0.93	0.94	0.95
0.80	093	0.94	095	0.96

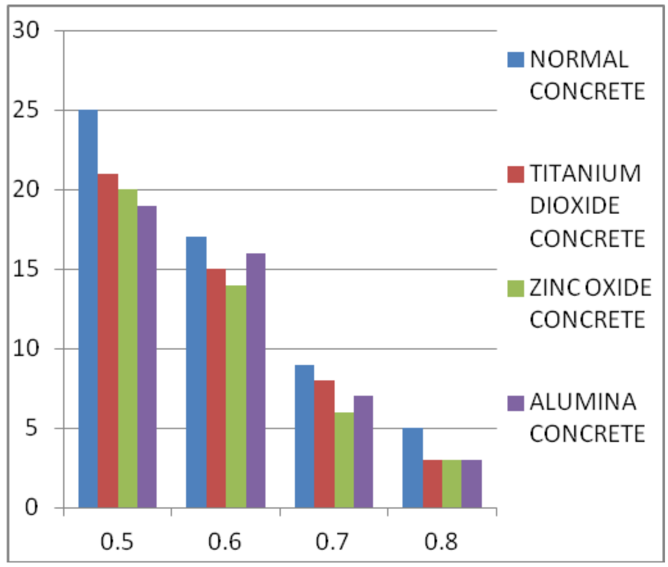


Note: X- axis shows W/C ratio and Y- axis shows Compaction factor.

c. Vee Bee Consistometer Test

Table IV
Comparison of Vee Bee Time in Sec

W/C Ratio	NORMAL CONCRETE	NANO TITANIA CONCRETE	NANO ZINC OXIDE CONCRETE	NANO ALUMINA CONCRETE
0.50	25	21	20	19
060	17	15	14	16
0.70	9	8	6	7
0.80	5	3	3	3



Note: X- axis shows W/C ratio and Y- axis shows time in second.

7.3 Compressive Strength of Cement Test

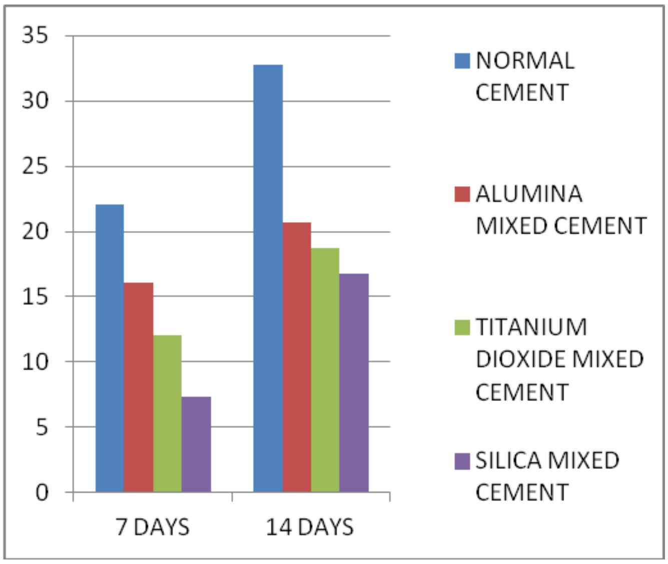
Table V
Compressive Strength of cement cubes in MPa

Days	NORMAL CEMENT MORTAR	NANO ALUMINA MORTAR	NANO TITANA MORTAR	NANO SILICA MORTAR
7	20.062	14.043	12.037	8.025
	22.069	18.056	10.031	6.018
	24.075	16.050	14.043	8.025
14	32.100	20.062	18.056	18.056
	34.106	22.069	18.056	16.05
	32.100	20.062	20.062	16.05

Figure : Samples of nano alumina mortar

Figure : Samples of nano silica mortar

Figure : Sample of nano Titania mortar

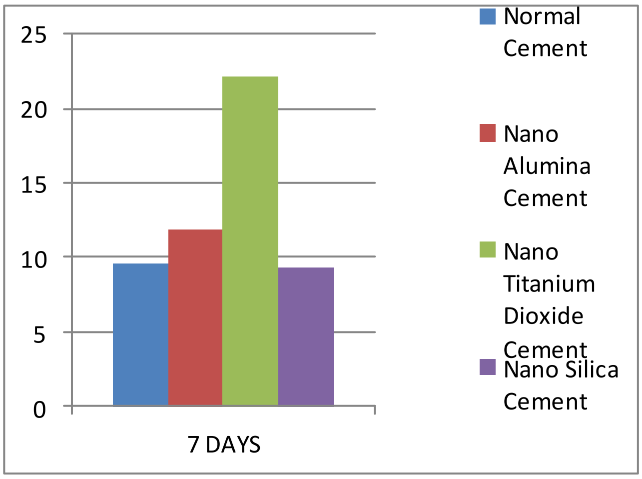


Note: X- axis shows Time and Y- axis shows compressive strength in MPa

7.4 Durability of Cement test

Table VI
Weight Loss in %

AGE OF SAMPLE	NORMAL CEMENT	NANO ALUMINA CEMENT	NANO TITANIA CEMENT	NANO SILICA CEMENT
7 DAYS	09.52	11.90	22.22	9.30



Note: X- axis shows Time and Y- axis shows % weight loss

8. CONCLUSIONS

1. Compressive strength of Nanoconcrete by using nano Alumina as cement replacement 10 % is reduced by 52.52 % for 7 days samples as compare to normal concrete.
2. Compressive strength of Nanoconcrete by using nano Silica as cement replacement 10 % is reduced by 59.71 % for 7 days samples as compare to normal concrete.
3. Compressive strength of Nanoconcrete by using nano Titania as cement replacement 10 % is reduced by 63.31 % for 7 days samples as compare to normal concrete.
4. Compressive strength of Nanoconcrete by using nano Alumina as cement replacement 10 % is reduced by 30.18 % for 14 days samples as compare to normal concrete.
5. Compressive strength of Nanoconcrete by using nano Silica as cement replacement 10 % is reduced by 40.88 % for 14 days samples as compare to normal concrete.
6. Compressive strength of Nanoconcrete by using nano Titania as cement replacement 10 % is reduced by 41.51 % for 14 days samples as compare to normal concrete.
7. Slump of Nanoconcrete by using nano Titania as cement replacement 10 % is increased by 6.15 %, 6.41%, 5.43% and 6.48% at 0.50, 0.60, 0.70, and 0.80 W/C ratio respectively as compare to normal concrete.
8. Slump of Nanoconcrete by using nano Zinc Oxide as cement replacement 10 % is increased by 9.23 %, 10.25%, 9.78% and 13.88 % at 0.50, 0.60, 0.70, and 0.80 W/C ratio respectively as compare to normal concrete.
9. Slump of Nanoconcrete by using nano Alumina as cement replacement 10 % is increased by 13.84 %, 8.97%, 13.04% and 14.81% at 0.50, 0.60, 0.70, and 0.80 W/C ratio respectively as compare to normal concrete.
10. Compaction factor is little increased at different water-cement ratios.
11. Vee Bee Time is also decreased at different water-cement ratios.
12. Compressive strength of Cement by using nano Alumina as cement replacement 10 % is reduced by 27.27% for 7 days samples as compare to normal 53 grade cement.
13. Compressive strength of Cement by using nano Titania as cement replacement 10 % is reduced by 45.45 % for 7 days samples as compare to normal 53 grade cement.
14. Compressive strength of Cement by using nano Silica as cement replacement 10 % is reduced by 66.67 % for 7 days samples as compare to normal 53 grade cement.
15. Compressive strength of Cement by using nano Alumina as cement replacement 10 % is reduced by 36.73% for 14 days samples as compare to normal 53 grade cement.
16. Compressive strength of Cement by using nano Titania as cement replacement 10 % is reduced by 42.85 % for 14 days samples as compare to normal 53 grade cement.
17. Compressive strength of Cement by using nano Silica as cement replacement 10 % is reduced by 48.98 % for 14 days samples as compare to normal 53 grade cement.
18. In durability test, weight loss by using nano Alumina as cement replacement 10 % is 11.90 % for 7 days samples.
19. In durability test, weight loss by using nano Titania as cement replacement 10 % is 22.22 % for 7 days samples.
20. In durability test, weight loss by using nano Silica as cement replacement 10 % is 9.30 % for 7 days samples.
21. As the compressive strength of concrete and cement by using nano products is not achieved up to the desired degree although workability is achieved up to some extent. Also the nano products are not easily available in market at present, So the other alternatives which are easily available are preferable as compare to nano products, in case 10 % replacement of cement is adopted.
22. Nano Products used in this study, are costlier than other additives and admixtures, so use of nano product increases the overall cost of the project.
23. The results obtained in present study are on the experimental basis up to research level only.
24. To get the better results, the study can be done with different parameters.

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