

**.EFFECT OF COLLOIDAL NANO SILICA ON THE MECHANICAL AND
RHEOLOGICAL BEHAVIOR OF BLENDED CEMENT PASTES**

A Dissertation submitted

*In partial Fulfillment of the Requirements for
the degree of*

MASTERS OF ENGINEERING

IN

CIVIL (STRUCTURAL)

Submitted by

**PRIYANKA KUMARI
(ROLL NO. 801222012)**

UNDER THE GUIDANCE OF

Dr. SHWETA GOYAL

Assistant Professor

Civil Engineering

Thapar University Patiala



CIVIL ENGINEERING DEPARTMENT

THAPAR UNIVERSITY, PATIALA 147004

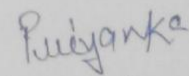
JULY 2014

DECLARATION

I, Priyanka Kumari, hereby declare that this thesis report entitled "Effect of Colloidal Nano Silica on the Mechanical and Rheological Behavior of Blended Cement Pastes" submitted in the partial fulfillment of the requirements for the award of degree of Master of Engineering in Structural Engineering, in the Civil Engineering Department, Thapar University, Patiala, is wholly my own work. This matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.

Date:

Place:



Priyanka Kumari

801222012

CERTIFICATE

This is to certify that above statement made by the student concerned is correct and true to the best of my knowledge & belief.



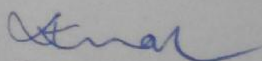
Dr. Shweta Goyal

Assistant Professor

Civil Engineering Department

Thapar University, Patiala

Countersigned by

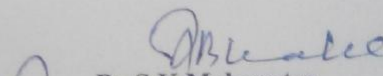


Dr. Naveen Kwatra

Associate Professor and Head

Civil Engineering Department

Thapar University, Patiala



Dr. S.K. Mohapatra

Dean Academic Affairs

Thapar University, Patiala

ACKNOWLEDGMENT

First of all, praise is due to almighty God who taught humankind everything they knew not and giving me the opportunity to step in the excellent world of technology.

It gives me immense pleasure to express my sincere regards and deep sense of gratitude to my supervisor, **Dr Shweta Goyal** Assistant Professor Department of Civil Engineering Thapar University, Patiala, for her thoughtful guidance, continuous enthusiasm, and warm encouragement throughout the course of work. Apart from the subject of my work, I learnt a lot from her, which I am sure, will be useful in different stages of my life.

Sincere gratitude to **Dr. Naveen Kwatra**, HOD, Civil engineering department, for having made available the requisite facilities during the course of study.

My deepest gratitude goes to my parents for their unflagging love, constant encouragement, helpful advice, and a constant support during my study program and this thesis would certainly not have existed without them.

I would like to convey my sincere gratitude to my friends, colleagues and all the staff member of Civil Engineering Department.

Priyanka Kumari

801222012

ABSTRACT

The nano-materials and nanotechnologies have highlighted the potential use of those materials in various fields such as medicine, construction, automobile industry, energy, telecommunications and informatics. The present works investigates the use of nano silica in cementitious pastes to improve the Rheological properties of the pastes along with this its effect on compressive strength of mixes is studied.

Result reveal that colloidal nano silica reduced the setting time of cement paste made by using ordinary Portland cement (grade-43), Portland pozzolonic cement and slag cement. It is clearly observed the use of nano silica have reduced the initial setting time and final setting time of mixes by accelerating the cement hydration. NS also made the cement matrix stiff, hence making the use of superplasticizer compulsory. However, there is a particular level of superplasticizer beyond which, any further increases in superplasticizer dosage does not reduce the flow time of cement paste further. The effect of nano silica addition is large on the early age compressive strength of pastes.

CONTENTS

CONTENT		PAGE NO.
CERTIFICATE		i
ACKNOWLEDGEMENT		ii
ABSTRACT		iii
CONTENTS		iv
LIST OF TABLES		v
LIST OF FIGURES		vi-viii
CHAPTER-1		1-10
INTRODUCTION		
1.1	General	1
1.2	Application of nano technology in the construction industry	2
1.3	Area of neon technology application in the construction industry	3
1.4	Use of nano silica in construction	5
	1.4.1 Concrete	5
	1.4.2 Carbon Nanotube	6
	1.4.2.1 Application of Carbon Nanotube	6
	1.4.3 Titanium Dioxide Nanoparticles (TiO ₂)	7
	1.4.4 Silicon Dioxide Nanoparticles (SiO ₂)	7
	1.4.5 Zinc Oxide Nanoparticles (ZnO)	7
	1.4.6 Silver Nanoparticles (Ag)	7
	1.4.7 Aluminium Oxide Nanoparticles (Al ₂ O ₃)	8
	1.4.8 Zirconium Oxide Nanoparticles (ZrO ₂)	8
	1.4.9 Zirconium Oxide Nanoparticle	8
	1.4.10 Wolfram (Tungsten) Oxide Nanoparticles (WO ₃)	8
	1.4.11 Nanotechnologies for Construction	9
1.5	Nanotechnologies for Concrete	9
1.6	Nanotechnologies for concrete	9
1.7	Organization of work	10
CHAPTER-2		
INTRODUCTION TO NANO SILICA		11-15
2.1	Introduction	11
2.2	Nano Silica	12
2.3	Forms of nano silica	13
	2.3.1 Properties of colloidal nano-silica	13
	2.3.2 Manufacturing process of colloidal nano-silica	13
2.4	Production methods of nano silica	13
2.5	Application of neon silica	15
CHAPTER-3		
LITERATURE REVIEW		16-32
3.1	General	16
3.2	Effect of nano silica on setting time of cement paste	16
3.3	Effect of nano-CaCO ₃ on the properties of fresh cement paste	19

3.4	Effect of nano silica on compressive Strength of cement and mortar	21
	3.4.1 Compressive strength of cement paste	21
	3.4.2 Compressive strength of mortar	24
3.5	Effect of nanosilica particle size on compressive strength	25
3.6	Literature review on XRD	31
3.7	Concluding Remarks	32
CHAPTER-4 EXPERIMENTAL PROGRAM		33-44
4.1	General	33
4.2	Experimental Program	33
4.3	Material system	33
	4.3.1 Ordinary Portland cement	33
	4.3.2 Pozzolonic Portland Cement	34
	4.3.3 Slag Cement	36
	4.3.4 Nano Silica	37
	4.3.5 Superplastiser	37
	4.3.5 Water	39
4.4	Preparation of paste mixes	42
	4.4.1 Introduction to Marsh Cone Test	40
	4.4.2 Test Procedure of marsh cone test	41
	4.4.3 Selection of superplastisizer	42
4.5	Casting and curing of the specimen	44
4.6	Cube Compressive Strength	44
4.7	Concluding Remarks	44
CHAPTER-5 RESULTS AND DISCUSSIONS		45-66
5.1	General	45
5.2	Optimum dosages of superplasticiser	45
	5.2.1 Effect of water cement ratio	45
	5.2.2 Effect of cement type	46
	5.2.3 Effect of percentage of nano silica	46
5.3	Fluidity loss	47
5.4	Effect of nano silica on setting time of different mixes	57
5.5	Cmpressive strength of cement mixes	58
	5.5.1 Effect of ns addition on compressive strength	58
	5.5.2 Effect of cement type on compressive strength	59
CHAPTER 6 CONCLUSION		68
6.1	main conclusion	68
6.2	6.2 scope for further	68
REFERENCES		69-71

LIST OF TABLE

S.NO	TITLE	PAGE NO
1.1	Areas of the construction industry in which nanotechnology is the main source of influence	4
3.1	Influence of NC on the performance of fresh cement paste	20
3.2	compressive strength of cement mortar	24
4.1	Physical Properties of OPC	33
4.2	Chemical properties of ordinary Portland cement	34
4.3	Compressive Strength of OPC (Grade-43)	34
4.4	Physical properties of PPC	35
4.5	Chemical composition of PPC	35
4.6	Compressive strength of PPC (cement sand ratio is 1:3)	35
4.7	Physical properties of Slag cement	36
4.8	Chemical composition of Slag Cement	36
4.9	Compressive strength of slag cement	38
4.10	Properties of Colloidal nano silica	39
4.11	Physical Properties of superplasticizer	38
5.1	Initial setting time and final setting time of different types of cement Pastes	57
5.2	Compressive strength of OPC with 0.45, 0.40 and 0.35 water cement ratio.	58
5.3	Compressive strength of PPC with 0.45, 0.40 and 0.35 water cement ratio.	59
5.4	Compressive strength of slag cement with 0.45, 0.40 and 0.35 Water cement ratio.	60

LIST OF FIGURE

FIGURE NO	TITLE	PAGE NO
1.1	Colloidal Nano Silica	10
2.1	Microscopic view of nano silica	12
3.1	Evaluation of setting time	17
3.2	influence of NC on the setting time of cement paste	21
3.3	Compressive strength of control NC1, NC2, and NC3 samples at 7 and 28 days.	23
3.4	Compressive strength at age of 7 days of cement mortar with opc, cement mortar with various particle sizes of ns, and cement mortar with sf.	27
3.5	Variation of 28 days compressive strength.	31
3.6	XRD of cement paste compare with nano silica and silica fume.	32
4.1	colloidal nano silica used in the study	37
4.2	Superplasticizer SP430 observed in the laboratory.	36
4.3	Marsh cone apparatus used in the laboratory.	40
4.4	Marsh cone test procedure	41
4.5	DIGI Mortar Mixer used for preparation of cement pastes	42
4.6	compressive strength test	43
5.1	Marsh cone apparatus	45
5.2	Flow time at different w/c ratios of cement pastes using OPC made at 0% NS.	47
5.3	Flow time at different w/c ratios of cement pastes using OPC made at 1% NS.	48
5.4	Flow time at different w/c ratios of cement pastes using OPC made at 2% NS.	59

5.5	Flow time at different w/c ratios of cement pastes using PPC made at 0% NS.	50
5.6	Flow time at different w/c ratios of cement pastes using PPC made at 1% NS.	51
5.7	Flow time at different w/c ratios of cement pastes using PPC made at 2% NS.	52
5.8	Flow time at different w/c ratios of cement pastes using slag cement made at 0% NS.	53
5.9	Flow time at different w/c ratios of cement pastes using slag cement made at 1% NS.	54
5.10	Flow time at different w/c ratios of cement pastes using slag cement made at 2% NS.	55
5.11	Development of Compressive strength of cement paste made by OPC at w/c ratio of 0.45	61
5.12	Development of Compressive strength of cement paste made by OPC at w/c ratio of 0.40	61
5.13	Development of Compressive strength of cement paste made by OPC at w/c ratio of 0.35	62
5.14	Development of Compressive strength of cement paste made by PPC at w/c ratio of 0.45	64
5.15	Development of Compressive strength of cement paste made by PPC at w/c ratio of 0.40	64
5.16	Development of Compressive strength of cement paste made by PPC at w/c ratio of 0.35	63
5.17	Development of Compressive strength of cement paste made by slag cement at w/c ratio of 0.45	64
5.18	Development of Compressive strength of cement paste made by slag cement at w/c ratio of 0.40	64
5.19	Development of Compressive strength of cement paste made by slag cement at w/c ratio of 0.35	65
5.20	Development of compressive strength of cement paste made by OPC, PPC& slag cement at w/c=0.45	65
5.21	Development of compressive strength of cement paste made by OPC, PPC& slag cement at w/c=0.40	65
5.22	Development of compressive strength of cement paste made by OPC, PPC& slag cement at w/c=0.35	66

CHAPTER 1

INTRODUCTION

1.1 GENERAL

In the present time nanotechnology is in its growing stage. In general, all of today's practical nanotechnologies are those using nano-sized particles in called nonomaterial's and nanometer-size features on integrated circuits. Generally a nanomaterial refers to materials with nanoscale dimensions or bulk materials containing nanosized particles. Nanoparticles are defined particles having diameter is less than 100 nm. Those materials to demonstrate characteristics such as extraordinary strength or unsuspected electrical, physical or chemical properties that are completely different from those established by the same products with larger dimensions. On the basis for this can be found in the increased relative surface area of minute particles. Chemical reactions involving solids happen mainly at their surface (where chemical bonds are also often incomplete). If nanoparticles are incorporated with traditional building materials, the new materials might possess outstanding or smart properties for the construction of different parts and uses in civil structure.

The introduce of nanoparticles into the cementitious materials may be as spherical materials (e.g., nano-SiO₂ (NS), Nano-TiO₂ (NT), nano-Al₂O₃ (NA), nano-Fe₂O₃ (NF), nano-Fe₂O₄, nano-ZrO₂, nano-Cu₂O₃, nano-CuO, nano-CaCO₃, etc.) or as nanotubes or fibers (e.g., carbon nano tubes (CNT) and carbon nanofibers (CNF), respectively) and nano-clay (NC). Nanomaterials could be defined as those physical substances with at least one dimension between 1...150 nm (1 nm = 10⁻⁹ m). The nanomaterials properties can be very different from the properties of the same materials at micro (10⁻⁶ m) or macro scale (10⁻⁶...10⁻³ m). The nanoscience represents to study of phenomena and the manipulation of materials at nano scale and is an extension of common sciences into the nanoscale. The nanotechnologies could be defined as the design, characterization, production and application of structures, devices and systems by controlling shape and size of the nanoscale. Nanotechnology requires advanced imaging techniques for studying and improving the material behavior and for designing and producing very fine powders, liquids or solids of materials with particle size between 1 and 100 nm, known as *nanoparticles*, (Gogotsi, 2006).

Currently, the use of nanomaterials in construction is reduced, mainly for the following reasons: the lack of knowledge concerning the suitable nanomaterials for construction and their behavior; the lack of specific standards for design and execution of the construction elements using nanomaterials; the reduced offer of nanoproducts. The lack of detailed information regarding the nanoproducts content; high costs; the unknowns of health risks associated with nanomaterials. In order to be able to use in the construction industry the nanomaterials at wide scale it is necessary that the researches to be conducted following the next stages: the choice of nanomaterials with potential use in construction and the study of their characteristics; the behavior study of the building elements that contain nanomaterials under various loads; the development of specific design and construction standards.

1.2 APPLICATIONS NANOTECHNOLOGY IN THE CONSTRUCTION INDUSTRY

The ever-growing population, increased number of constructions and the limited resources and building materials being used, the demand of using new materials in the construction industry had increase. Attempts that are made to find solutions for improving the quality, increasing the efficiency of building materials along with reducing the consumption of energy and raw materials have led to applying novel technologies in this industry. In recent years, researchers, who are active in the construction industry, have shown interest in the various applications of nanomaterials with the purpose of improving the characteristics of building materials.

The introduction of nanotechnology-based production for accompanied with a giant leap toward well-being and the quality of life and has resulted in huge economic movements. Different nanomaterials can improve the fundamental characteristics of building materials such as include quality, strength, durability and being light-weighted on one hand and to provide important characteristics and functions such as heat insulation, self-cleaning and anti-fogginess. Also using this technology helps saving energy and eventually, economizing in the whole construction industry. In the present research, it has been tried to study those building materials that are both structural and nonstructural, are manufactured by nanotechnology and are optimized based on this knowledge along with the advantages of using this technology in producing new construction products.

The new forms of today's buildings, which are proportional to mankind's modern needs, are not only due to different designs, but the application and type of building materials that are used in the construction, also has a significant effect on modern buildings' being different. People's new points of view on preserving the environment and saving energy is the outcome of this perspective that without building materials, there won't be any new products. In buildings that were built in the past two decades, both technical and aesthetic considerations were taken into account. Meanwhile, new material engineering progresses have caused technological facilities to increase and just like the aesthetic aspect of building materials, they are considered an opportunity to design. Common building materials that are used in today's constructions are bricks, stones, glass, and plaster, steel and concrete; with the main effect of natural building materials being taken quite seriously in recent years. Translucent concrete, composites, colorful refractory bricks, etc. are some of these examples. At the moment, the ever-increasing need of the society to houses and buildings has made the need for applying new methods and building materials with the purpose of increasing the construction speed, using lighter materials, the useful life of buildings and strengthening them against earthquakes more urgent. Alongside.

1.3 AREAS OF NANOTECHNOLOGY APPLICATIONS IN THE CONSTRUCTION INDUSTRY

Construction industry is one of those industries in which nanotechnology can have many applications. With its requirements in terms of strength, resistance, durability and high efficiency, this industry is considered as one of the main users of nanostructures. It is expected that in a not too distant future, nanotechnology would make the functional extent of building materials take a huge leap in areas like energy conservation, light, safety and being smart. Perhaps, the early stages and steps of progress in the world of nanotechnology could be able to change the nature of building materials and even evolve our construction methods in a way that buildings would be constructed to be more compatible with the environment and users. Undoubtedly, by having reinforced building materials such as carbon nanotubes, one can reconsider his designing methods and the expected functions of a building. For instance, it might be possible to completely exclude the main difference between the building structure and its shell and also, with the help of strong building materials that can act as both the skeleton and the outer shell, many of the limitations with which engineers are faced can be removed. Some of the areas

of the construction industry in which nanotechnology can cause developments could be summarized as follows Producing strong and smart building materials besides repairing and reconstructing the existing structures.

- A new and innovative system which causes the ‘Design-Production-Operation-Destruction’ chain in construction to optimize. This is achieved by developing new tools based on information technology.
- New technologies to process multi-cultural products/functions.
- New methods to produce substances and building materials that have a significant effect on reducing water and energy consumption and would produce much less wastes. Moreover, developing environment sustainability-based production methods that can recycle constructional products and by-products is one of the areas which nanotechnology has influenced. Those who are in charge and active in the field of construction, predict that in 10-15 years time, nanotechnology would be able to have important effects on the construction industry.
- Increased understanding of architects of the nanoscale and its effects.
- Modified nanoscale substances and building materials.
- Strong and super-strong structural building materials.
- Multi-purpose thin films, coatings and paints.
- Multi-purpose building materials and compounds.

Table-1.1 Areas of the construction industry in which nanotechnology is the main source of influence.

Area of technology and research that are related to nano technology	Application	Desired qualities
Nanostructure stance and building materials <ul style="list-style-type: none"> ➤ Porous nano materials(often cement or wood based) ➤ Polymers 	Generally in building materials insulation, carrier building material.	<ul style="list-style-type: none"> ➤ Being multi functional ➤ Increased resistance-wt ratio ➤ More durability and stability ➤ Fire resistance

<ul style="list-style-type: none"> ➤ composites 		<ul style="list-style-type: none"> ➤ Self cleaning ➤ Improve quality of the air inside and outside building recyclable
<p>Nano structure surfaces(coating and films</p> <ul style="list-style-type: none"> ➤ causing chemical changes in surfaces ➤ causing physical changes in surfaces 	<p>Every application in construction and development projects(except for reconstruction and renovation)</p>	<ul style="list-style-type: none"> ➤ Being multi-functional ➤ Increased resistance and hardness ➤ Durability ➤ Improved quality of the air inside the building ➤ Self cleaning

1.4 USES OF NANO MATERIAL IN CONSTRUCTION

All these nano-properties actually affect the materials behavior at macro-scale and, from this point; the power of nanotechnology is emphasized: if the elements are proper manipulated at the nanoscale, the macro-properties are affected and new materials and processes can be developed (Ge & Gao, 2008). The following most important nonmaterial with potential use in construction is presented.

1.4.1 Concrete

Concrete is one of the most common and frequently used building materials. Annually, about a ton of concrete is produced for every individual in the world. Consumption of energy and the carbon dioxide which is produced during the production processes of cement, concrete and wastes are the most important environmental issues related to concrete production and use. Nanotechnology has been a great help to researchers in the field of concrete industry. In fact, it has led to the production of new cements, concretes, additives and nano composites. According to conducted studies, adding nano particles would improve the durability of concrete through physical and chemical interactions like concrete pore fillers. By adding fibers that are nanometers to micrometers long and are made of carbon, steel or polymers, researchers have reinforced concrete. Experiments have shown that after 28 days, the compressive strength of these concretes is doubled compared with ordinary concretes that are traditionally reinforced.

Also, the developments of such materials guide building constructors to reduce their cement consumption by 50 percent compared with normal conditions"

1.4.2 Carbon Nano tube

Carbon nanotubes are a form of carbon having a cylindrical shape, the name coming from their nanometer diameter. They can be several millimeters in length and can have one “layer” or wall (single walled nanotube) or more than one wall (multi walled nanotube) (Lu *et al.*, 2010). Nanotubes are members of the fullerene structural family and exhibit extraordinary strength and unique electrical properties, being efficient thermal conductors. For example, they have five times the Young’s modulus and eight times (theoretically 100 times) the strength of steel, whilst being 1/6th the density. Expected benefits of carbon Nanotube are: mechanical durability and crack prevention in concrete, enhanced mechanical and thermal properties in ceramics and real-time structural health monitoring capacity, (Mann, 2006).

1.4.2.1 Application of carbon nano tube

- Carbon nanoparticles have excellent properties because of their high aspect ratio and chemical nature. One of the main uses of nanoparticles is as reinforcing agents or as functional fillers in other materials. Carbon nanoparticles can result in a reduction in material weight and in the obtaining of materials with higher impact strength, electrical conductivity, strength, thermal stability, flame resistance, dimensional stability.
- This enable the use of carbon nanoparticles and their composites in a wide variety of economic sectors: aerospace, construction, energy, cosmetics, electronics, textiles, The construction sector has not yet experienced a massive use of carbon nanoparticles because among other reasons it is a very competitive market which requires a high adjustment in the price of materials. In addition, new materials need to meet stringent construction standards so, often it requires a long time since the materials are developed until they reach the market. Poor knowledge of new materials for applicators also limits its application in high-grade work.
- Nanoparticles are also suitable for the development of structural materials. They may be used in cement and concrete. Until now there have not been reported such commercial

products with nanoparticles but it is believed that CNTs can prevent the propagation of cracks and improve its mechanical properties.

1.4.3 Titanium Dioxide Nanoparticles (TiO₂)

The titanium dioxide nanoparticles are added to concrete to improve its properties. This white pigment is used as an excellent reflective coating. Or added to paints, cements and windows for its sterilizing properties. The titanium dioxide breaks down organic pollutants, volatile organic compounds and bacterial membranes through powerful photo catalytic reactions, reducing air pollutants when it's applied to outdoor surfaces. Being hydrophilic gives self cleaning properties to surfaces to which it is applied, because the rain water is attracted to the surface and forms sheets which collect the pollutants and dirt particles previously broken down and washes them off. The resulting concrete surface has a white color that retains its whiteness very effectively (Mann,2006).

1.4.4 Silicon Dioxide Nanoparticles (SiO₂)

Nano-SiO₂ could significantly increase the compressive strength of concretes containing large fly ash volume at early age, by filling the pores between large fly ash and cement particles. Nano-silica decreases the setting time of mortar when compared with silica fume (microsilica) and reduce bleeding water and segregation by the improvement of the cohesiveness (Sadrumontazi & Barzegar, 2010).

1.4.5 Zinc Oxide Nano particles (ZnO)

Zinc oxide is a unique material that exhibits semiconducting and piezoelectric dual properties. It is added into various materials and products, including plastics, ceramics, glass, cement, rubber, paints, adhesive, sealants, pigments, fire retardants. Used for concrete manufacturing, ZnO improves the processing time and the resistance of concrete against water (Broekhuizen &Broekhuizen, 2009).

1.4.6 Silver Nanoparticles (Ag)

The nanosilver will affect, in contact with bacteria, viruses and fungi, the cellular metabolism and inhibit cells growth. The nanosilver inhibits multiplication and growth of bacteria and fungi,

which causes infection, itchiness and sores. The core technology of nanosilver is the ability to produce particles as small as possible and to distribute these particles very uniformly. When the nanoparticles are coated on the surface of any material, the surface area is increasing several million times than the normal silver foil.

1.4.7 Aluminum Oxide Nanoparticles (Al_2O_3)

Alumina reacts with calcium hydroxide produced from the hydration of calcium silicates. The rate of the pozzolonic reaction is proportional to the amount of surface area available for reaction. The addition of nano- Al_2O_3 of high purity improves the characteristics of concretes, in terms of higher split tensile and flexural strength. The cement could be advantageously replaced in the concrete mixture with nano- Al_2O_3 particles up to maximum limit of 2.0% with average particle sizes of 15 nm, the optimal level of nano- Al_2O_3 . particles content being achieved with 1.0% replacement (Nazari *et al.*, 2010).

1.4.8 Zirconium Oxide Nano particles (ZrO_2)

Zirconium oxide (or Zirconia) nanopowder or nanoparticles are white high surface area particles with typical dimensions of 5...100 nanometers and specific surface area in the 25...50 m^2/g range. Nano zirconium shows good aesthetics (translucency), superior physical resistance (hardness, flexibility, durability), chemical resistance (practically inert) and is a very good insulator.

1.4.9 Zirconium Oxide Nanoparticles (ZrO_2)

Zirconium oxide (or Zirconia) nanopowder or nanoparticles are white high surface area particles with typical dimensions of 5...100 nanometers and specific surface area in the 25...50 m^2/g range. Nano zirconium shows good aesthetics (translucency), superior physical resistance (hardness, flexibility, and durability), and chemical resistance (practically inert) and is a very good insulator.

1.4.10 Wolfram (Tungsten) Oxide Nano particles (WO_3)

In recent years, tungsten trioxide has been employed in the production of electro chromic windows, or smart windows. These windows are electrically switchable glass that change light

transmission properties with an applied voltage. This allows the user to tint their windows, changing the amount of heat or light passing through.

1.5 NANOTECHNOLOGIES FOR CONSTRUCTION

Nanotechnology can generate products with many unique characteristics that can improve the current construction materials: lighter and stronger structural composites, low maintenance coatings, better cementitious materials, lower thermal transfer rate of fire retardant and insulation, better sound absorption of acoustic absorbers and better reflectivity of glass (Lee *et al.*, 2010).

1.6 NANO TECHNOLOGIES FOR CONCRETE

Concrete is a macro-material strongly influenced by its nano-properties. The addition of nano-silica (SiO_2) to cement based materials can control the degradation of the calcium-silicate hydrate reaction caused by calcium leaching in water, blocking water penetration and leading to improvements in durability.

(Mann, 2006). Nano-sensors have a great potential to be used in concrete structures for quality control and durability monitoring. (To measure concrete density and viscosity, to monitor concrete curing and to measure shrinkage or temperature, moisture, chlorine concentration, pH, carbon dioxide, stresses reinforcement corrosion or vibration). Carbon Nanotube increases the compressive strength of cement mortar specimens and changes their electrical properties which can be used for health monitoring and damage detection. The addition of small amounts (1%) of carbon Nanotube can improve the mechanical properties of mixture samples of Portland cement and water. Oxidized multi-walled Nanotube show the best improvements both in compressive strength and flexural strength compared to the reference samples.



Fig. 1.1 Colloidal nanosilica (www.googleimage.com)

1.7 ORGANIZATION OF WORK:-

Chapter 1 discuss general introduction of nano materials, application of nano materials, uses of nano materials in concrete .different types of nano materials. Application of carbon Nanotube.

Chapter 2 Explain in details about the nano silica such as application of nano silica, introduction of nano silica, Properties of nano silica, manufacturing process of colloidal nano silica

Chapter 3 presents a thorough literature review on effect of nano silica on hardened properties of cement, mortar and concrete. Also a thorough review of literature on rheological properties of cementineous paste and compressive strength cement paste, mortar.

Chapter 4 represents the experimental program, wherein all test procedure and measures to be followed during experiments are explained in detail.

Chapter 5 deals with results and discussions where findings of the experimental program are explained in detail.

Chapter 6 is the concluding chapter. This chapter is followed by the list of references

Used in the present study.

CHAPTER 2

INTRODUCTION TO NANO SILICA

2.1 INTRODUCTION

Concrete is known to be the most used man made material. In the last few years, the total annual worldwide production of concrete exceeded 2600 million tons. The most important material in production of concrete is cement. The cement industry is considered to be one of the most energy consuming industries, with a high rate of carbon dioxide (CO₂) emissions. Every year, it is responsible for approximately 5% of the global manmade CO₂ emissions, 50% of these emissions are caused by chemical manufacturing processes and 40% are due to burning fuel.

Extensive research efforts have been directed to reducing the effect of the cement industry on greenhouse gases either by improving the efficiency of the cement manufacturing process or by using supplementary cementitious materials (SCMs), which partially replace ordinary cement. A method to reduce the cement content in concrete mixes is the use of mineral admixtures. Various mineral admixtures like fly-ash, silica fume and GGBS etc are used now- a-days as partial replacement of cement. One of the silica fines with high potential as cement replacement and as concrete additive is nano-silica.

Experimental results indicated that the performance of concrete is generally improved by adding nano-silica Said et al. (2012). At first it was believed that the improvement in concrete performance due to the addition of nano-silica is attributed to its filler effect and its pozzolonic reaction Aly et al. (2011). Recently, however, it has been reported that the small particle size of nano-silica provides a larger surface area, which speeds up the rate of cement hydration and pozzolonic reactions Qing et al. (2005). This chapter deals with the basic introduction to nano silica with some of its properties.

2.2 NANO SILICA

Nano silica is nano particles of silicon dioxide. They are available in colloidal as well as in amorphous forms. The microscopic view of nano silica is shown in Fig 1.1. The working principal of nano silica in concrete is explained in the following section.

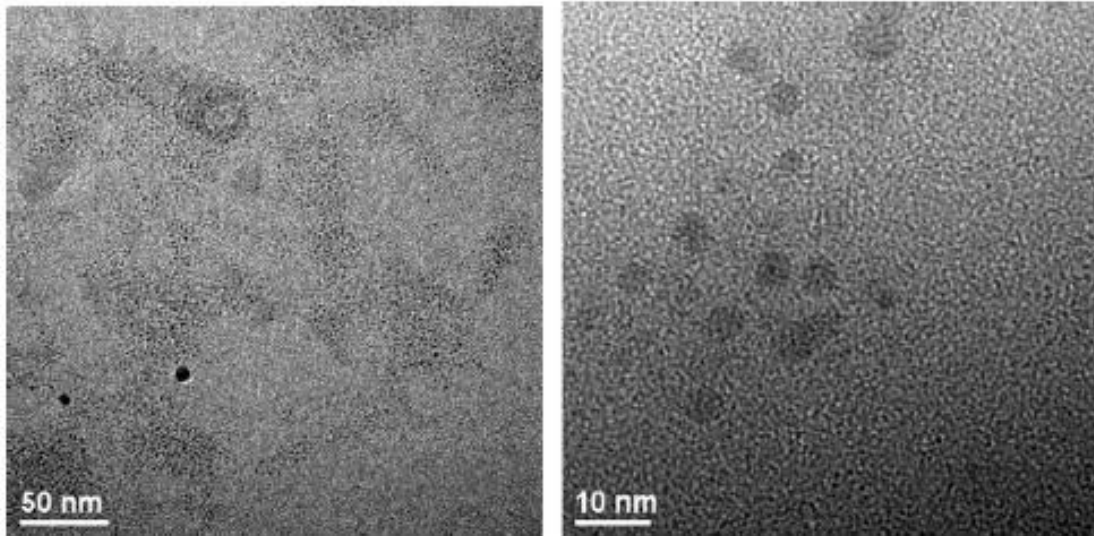


Fig. 2.1 Microscopic view of nano silica Peng-kun Hou et al. (2012)

In concrete, nano-silica works on two levels. The first one is the chemical effect: the pozzolonic reaction of silica with calcium hydroxide forms more CSH gel at final stages. The second function is physical one, because nano-silica is about 1000 times smaller than cement. Nano-silica can fill the remaining voids in the young and partially hydrated cement paste, increasing its final density. It is found that the addition of 1 kg of micro-silica permits a reduction of about 4 kg of cement, and this can be higher if nano silica is used. Nano-silica addition in cement paste and concrete can result in different effects. The main mechanism of this working principle is related to the high surface area of nano silica, because it works as nucleation site for the precipitation of CSH gel Dunster, (2009).

2.3 FORMS OF NANO SILICA

Nano silica is available in two basic forms: colloidal nano silica and amorphous nano silica. Colloidal nano silica is in suspension form while amorphous nano silica is in powdered form. Most of the research work till date is carried out by using colloidal nano silica. Therefore; the following section explains colloidal nano silica in details.

2.3.1 Properties of colloidal nano-silica

Colloidal nano silica is suspensions of fine amorphous, nonporous, and typically spherical silica particles in a liquid phase. Usually they are suspended in an aqueous phase that is stabilized electro statically. Colloidal nano silica exhibits particle densities in the range of 2.1 to 2.3 g/cm³.

Most colloidal silica is prepared as mono-disperse suspensions with particle sizes ranging from approximately 30 to 100 nm in diameter. Poly-disperse suspensions can also be synthesized and have roughly the same limits in particle size. Smaller particles are difficult to stabilize while particles much greater than 150 nanometres are subject to sedimentation.

2.3.2 Manufacturing Process of Colloidal Nano-Silica

Colloidal silica are most often prepared in a multi-step process where an alkali-silicate solution is partially neutralized, leading to the formation of silica nuclei. The subunits of colloidal silica particles are typically in the range of 1 to 5 nm. Whether or not these subunits are joined together depends on the conditions of polymerization. Initial acidification of a water-glass (sodium silicate) solution yields Si(OH)₄.

If the pH is reduced below 7 or if salt is added, then the units tend to fuse together in chains. These products are often called silica gels. If the pH is kept slightly on the alkaline side of neutral, then the subunits stay separated, and they gradually grow.

2.4 PRODUCTION METHODS OF NANO SILICA

Nowadays, there are different methods to produce nano-silica products. Some of the methods have been explained in the following sections.

- SOL-GEL process (organic or water route) at room temperature. In this process, the starting materials organo metallics are added in a solvent, and then the pH of the solution is changed, reaching the precipitation of silica gel. The produced gel is aged and filtered to become a xerogel. Sakka, et al. (2000). This xerogel is dried and burned or dispersed again with stabilized agent (Na, K, NH₃, etc.) to produce a concentrated dispersion (20 to 40% solid content) suitable for use in concrete industry.
- An alternative production method is based on vaporization of silica between 1500 to 2000°C by reducing quartz (SiO₂) in an electric arc furnace. Furthermore, nano-silica is produced as a by-product of the manufacture of silicon metals and ferro-silicon alloys, where it is collected by subsequent condensation to fine particles in a cyclone. Nano-silica produced by this method is a very fine powder consisting of spherical particles or microspheres with a main diameter of 150 nm with high specific surface area (15 to 25 m²/g) Dunster, (2009).
- Dunster, (2009) developed a biological method to produce a narrow and bimodal distribution of nano-silica from the digested humus of California red worms (between 55nm to 245nm depending of calcinations temperature). By means of this method, nano particles having a spherical shape with 88% process efficiency can be obtained. These particles were produced by feeding worms with rice husk, biological waste material that contain 22% of SiO₂.
- Nano-silica can also be produced by precipitation method. In this method, nano-silica is precipitated from a solution at temperature between 50 to 100 °C (precipitated silica). It was first developed by Iller (1954). This method uses different precursors like sodium silicates burned rice husk ash (RHA), semi-burned rice straw ash (SBRSA), magnesium silicate and others. In addition, nano-silica is being developed via an alternative production route.
- Basically, olivine and sulphuric acid are combined, whereby precipitated silica with extreme fineness but agglomerate form is synthesized (nano-size with particles between 6 to 30 nm), and even cheaper than contemporary micro-silica.

2.5 APPLICATION OF NANO SILICA

At present nano-silica, because of its price, is only used in the manufacture of high performance concretes (HPC), eco-concretes and self compacting concretes (SSC) Sobolev, et al. (2006). For the last types of special concretes (eco-concrete and SCC), the application of these materials is a necessity. Also, some explorative applications of nano-silica in high performance well cementing slurries, specialized mortars for rock-matching grouting Green, (2006) and gypsum particleboard can be found Wen, 1(2006). The application of these concretes can be anywhere, both in infrastructure and in buildings.

Nano-silica is applied in HPC and SCC concrete mainly as an anti-bleeding agent. It is also added to increase the cohesiveness of concrete and to reduce the segregation tendency. Dunster et al. (2009) used colloidal nano-silica (2% by weight of concrete) to produce HPC concrete with compressive strength of 85 MPa, anti-bleeding properties, high workability and short demolding times (10 h).

Eco-concretes are mixtures where cement is replaced by waste materials mainly sludge ash, incinerated sludge ash, fly ash or others supplementary waste materials. One of the problems of these mixtures is their low compressive strength and long setting period. This disadvantage is solved by adding nano-silica to eco-concrete mixes to obtain an accelerated setting and higher compressive strength.

Sari,(1999) applied particulate nano-silica in oil well cementing slurries in two specific ranges of particles sizes, one between 5 to 50 nm, and second between 5 to 30 nm. Also they used nano-silica dry powders in encapsulated form and concentrations of 5 to 15% by weight of concrete. The respective test results for the slurries demonstrate that the inclusion of nano-silica reduces the setting time and increases the strength (compressive strength, tensile strength, Young's modulus and Poisson's ratio) of the resulting cement in relation with other silica components (amorphous 2.5 to 50 μm , crystalline 5 to 10 μm and colloidal suspension 20 nm, types silica) that were tested.

CHAPTER-3

LITERATURE REVIEW

3.1 GENERAL

This chapter represents the review of literature on effect of nano material on hardened properties and rheological properties of the cementitious material. In this chapter the effect of nano silica on initial and final setting time was observed.

3.2 EFFECT OF NANO SILICA ON SETTING TIME OF CEMENT PASTE

The researchers investigated the effect of nano silica on initial and final setting time on hardened properties of cement pastes. Nano silica reduce the setting time of cement was observed in the laboratory. Recently, nano-particles have attracted great interests due to their four major effects including size effect, quantum effect, surface effect and interface effect. By adding nano-particles into cement, the performance and properties of materials could be improved. Some researches on adding nano-particles into cementitious materials were reported.

Ltifi et al. (2011)

They investigated the influence of nano-SiO₂ addition on setting time of fresh cement paste. With increasing the nano-SiO₂ content, the setting of fresh pastes was slightly accelerated but the difference between the initial and the final time decreased with increasing the NS content. It appears that by adding nano-SiO₂, at the beginning the setting is anticipated and the dormant period is reduced. So that it is possible to establish a relationship between initial setting time and the time for the beginning of the acceleration period during cement hydration. Setting time of cement was observed in the Fig. 3.1.

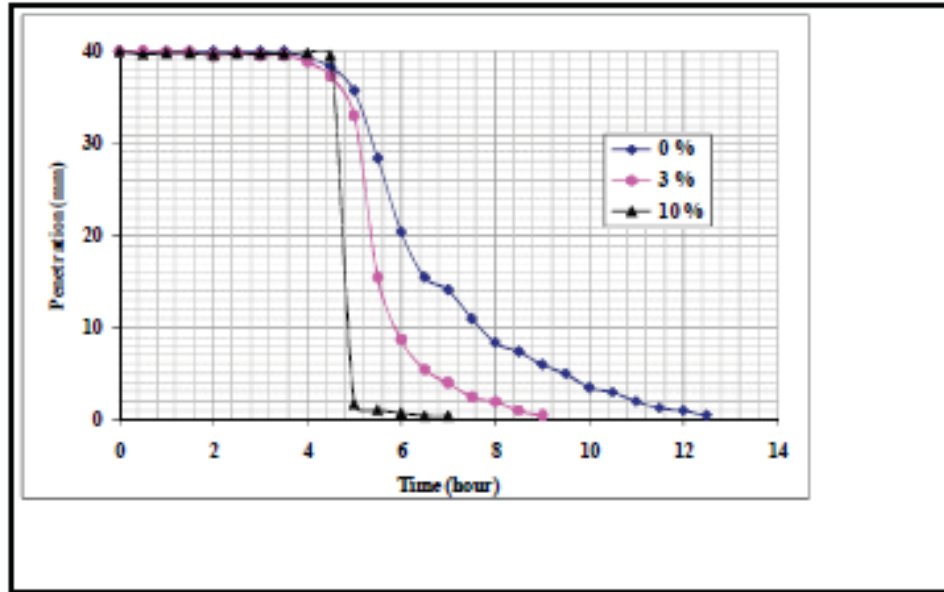


Fig. 3.1 Evaluation of setting time. Ltifi et al. (2011)

Qing Ye et al. (2005)

The researchers presented the overview of the influence of nano-SiO₂ (NS) addition on properties of hardened cement paste (HCP) as compared with silica fume (SF) has been studied through measurement of compressive and bond strengths of HCP, and by XRD and SEM analysis. It was observed that the influence of NS and SF on consistency and setting time of fresh cement paste shows different results. NS made cement paste thicker and NS accelerated the cement hydration process. Compressive strengths of HCP and bond strengths of paste–aggregate interface incorporating NS were obviously higher than those incorporating SF, especially at early ages. And with increasing the NS content, the rate of bond strength increase was more than that of their compressive strength increase.

Zhang et al. (2011)

This paper presented an experimental study to evaluate the effects of nano-silica (NS) on rate of cement hydration, setting time and strength development of concretes with about 50% fly ash or slag. Results indicate that length of dormant period was shortened, and rate of cement and slag hydration was accelerated with the incorporation of 1% NS in the cement pastes with high volumes of fly ash or slag. The incorporation of 2% NS by mass of cementitious materials

reduced initial and final setting times by 90 and 100 min, and increased 3 and 7 day compressive strengths of high-volume fly ash concrete by 30% and 25% respectively.

Stefanidou et al. (2012)

The researchers investigated the effect of nano-SiO₂ produced by pyrolysis and with specific area of 200 m²/g has been added at different percentages (0%, 0.5%, 1%, 2% and 5%) to high-strength cement pastes. These pastes were tested for their mechanical and structural properties at different ages. Nanoparticles act as nuclei for crystallization and large, idiomorphic crystals of Ca–Si composition were formed assisting, up to a certain percentage, in producing materials with dense structure, reduced porosity and improved strength.

Nano-SiO₂ appears to affect the mechanical properties and the structure of high-strength cement pastes even in low concentration. The addition of nanosilica (in specimens labeled –N) seems to create two competing mechanisms in terms of the overall chemo mechanical response of cement pastes. On one hand the addition of extra water to the paste increases the w/c ratio with all the well-established consequences while the addition of nanoparticles tends to primarily increase the mechanical response. In this case, 0.5% up to 2% w/w of cement nanoparticles can cause 20–25% strength increase despite the increased demand in water in the fresh state. In the second set of specimens (labeled –G) the above mentioned problem is restricted. The addition of superplasticiser in 1% w/w of cement reduces the water demand and the strength increase varies from 30% to 35%. Impressive changes were also recorded in the structure of nano modified samples as the calcium silicate crystal size is larger in samples with high nano-SiO₂ content. This is obvious in pastes with 5% nanoparticles where crystals of 1.2 μm average size were formed at 14 days while at the same age, in pastes with 1% nano-SiO₂ the average crystal size was 600 nm. Microstructure observation also recorded a denser structure in nano-modified samples.

Senff et al. (2009)

Observed the amorphous nano-silica (NS) particles (0–2.5 wt %) by cement were incorporated in cement pastes and mortars, and their effect on the fresh state behaviour was analyzed. Rheological tests showed that after 75 min of mixing, the mortar having 2.5 wt% NS shown insufficient flow ability to allow its continuous monitoring in a Viskomat PC viscometer. The influence of nano silica content was better observed on yield stress as compared with plastic viscosity values (the first increased about 66.5% while the later stages just increased by 3.6%). With nano silica addition, spread, setting time and the moment to reach the maximum temperature decreased 33%, 60% and 51.3%, respectively, when compared with samples without nano silica. X-ray diffraction shows the presence of calcium hydroxide.

Liu et al. (2012)

Studied the effect of nano CaCO_3 (NC) on properties of cement paste. Experimental results shows that NC had no effect on water requirement of normal consistency of cement. However, with the increase of NC content, the flow ability decreased and the setting time of fresh cement paste was shortened. The early hydration of cement was activated by NC. The strength and the early age shrinkage of cement paste were also studied.

3.3 EFFECT OF NANO- CaCO_3 ON THE PROPERTIES OF FRESH CEMENT PASTE

The outhor was observed the effects of nano- CaCO_3 on fresh cement paste with four NC contents were given in Table 3.1. Table 3.1 showed that NC had no effect on water requirement of normal consistency of cement. On one hand, NC filled up the pores of loose net structure around the cement particles, and then part of free water was liberated from the pores. On the other hand, super surface area of NC needed to be covered with more free water. As a result, NC had no effect on water requirement of normal consistency of cement due to the synergetic effect of the two opposite aspects. Guhua Li et al. (2006)

Observed to evaluate the similar results. **Table3.1** shown the influence of NC contents on the workability of cement paste with the water-cement ratio 0.45. There was an obvious decrease of the flow ability when NC was added into the cement. With the increase of NC, the flow ability decreased. It might be explained that the increasing surface requires more water.

Table 3.1 Influence of NC on the performance of fresh cement paste Liu et al. (2012)

S.No	NC(%)	Water required for normal consistency.	Initial setting time	Final setting time	Flowability (mm)
C0	0	132	200	260	163
NC1	1	132	187	232	137
NC2	2	132	139	221	130
NC3	3	132	131	207	120

The initial and final setting time of cement paste with NC were shown in Fig 3.1. It showed that the addition of NC could shorten the setting time. When the content of NC was 2%, the effect of NC on the setting time of cement paste was the most prominent, compared to CO. The initial and the final setting time were shortened by 61 min and 39 min, respectively. The results indicated that NC could promote hydration reaction rate. Due to its surface effect, smaller particle sizes and higher surface energy, Ca_2^+ and OH^- produced by cement hydration could be adsorbed in the surface of NC more easily, and the reduction of Ca_2 and OH in cement paste solution led to speeding up the hydration reaction of cement.

The addition of NC could activate the cement hydration with the increase of NC, the flow ability decreased and the setting time was shortened. However, NC had no effect on water requirement of normal consistency of cement. The flexural and compressive strength of hardened cement paste with NC increased at the age of 7 days and 28 days, and the optimal content of NC was 1%. Adding 1% NC could obviously decrease the early age shrinkage of cement paste.

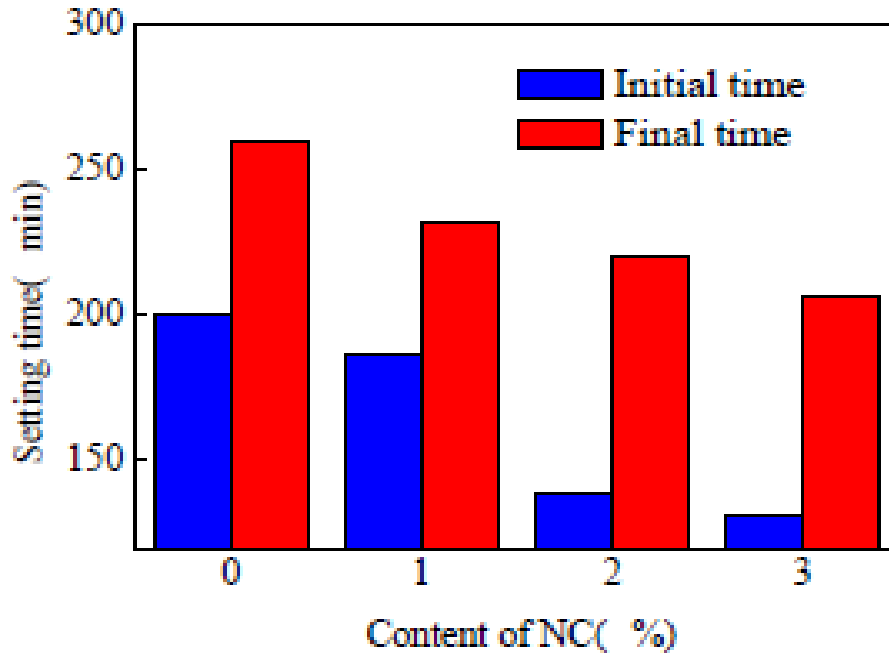


Fig. 3.2 influence of NC on the setting time of cement paste Liu et al. (2011)

3.4 EFFECT OF NANO SILICA ON COMPRESSIVE STRENGTH OF CEMENT AND MORTAR

So many authors were observed and studied the compressive strength of cement and mortar by using nano silica with different percentage of nano silica and variation in water cement ratio. Some people are studied with different mineral admixture and the observed the improvement of compressive strength in 3 days, 7 days and 28 days.

3.4.1 COMPRESSIVE STRENGTH OF CEMENT PASTE

Qing Ye et al. (2005)

Studied that the variation of compressive strength development of hardened cement paste in the NS or SF added. It is found that all paste strengths of sample A-series were obviously higher than those of control sample CO especially at 3 days. Also, with increasing the NS content, paste strengths increased. For example, compared with sample CO, the strengths of sample A3 increased by 6%, 35%, 23% and 11% at ages of 1 day, 3 days, 28 days and 60 days, respectively. However, with increasing the SF content, all paste strengths of sample B-series were slightly lower than those of sample CO at ages of 1 day and 3 days. But at ages of 28 days and 60 days,

strengths with increasing the SF content were obviously higher than those of sample CO, and the strengths were slightly lower than those of sample A-series with the same content of addition. For example, as compared with sample CO, the strengths of sample B3 decreased by 3% and 1% at ages of 1 day and 3 days, and increased by 16% and 10% at ages of 28 days and 60 days, respectively. These results shown that the compressive strength of hardend cement paste is enhanced with NS addition added, especially at early ages, and the pozzolonic activity of NS is much greater than that of SF.

Farzadnia et al. (2013)

Observed that incorporation of 3% nanoclay increased the 28th day compressive strength up to 24% compared to the control samples. Three mechanisms may be attributed to the enhancement of strength in cement mortars containing nanoclay. Firstly, nanoclays might have acted as filler due to their nanosized particles and filled up the voids. Also they might have cross linked the matrix because of their tubular shape and several hydroxyl groups that are present onto the surface of halloysite nanoclay, which may interact chemically with Ca²⁺ available in cement paste thus led to a denser microstructure compare to the control sample. Secondly, the high amount of SiO₂ in halloysite nanoclay and its ultra thin surface might have led to increase the rate of C–S–H due to the consumption of Portlandite in cement matrix. Finally, swelling of nanoscale due to absorption of water within its layers led to expansion of clay and then enhanced filling effect in capillary pores.

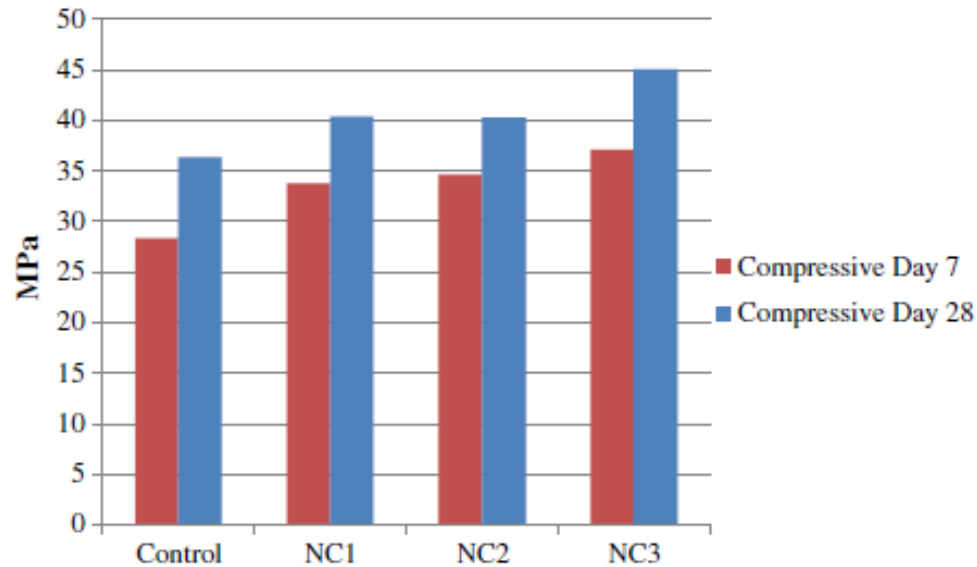


Fig. 3.3 Compressive strength of control, NC1, NC2, and NC3 samples at 7 and 28 days.

Jo et al. (2006)

Observed that the properties of cement mortars with nano-SiO₂ were experimentally studied. The amorphous or glassy silica, which is the major component of a Pozzolana, reacts with calcium hydroxide formed from calcium silicate hydration. The rate of the pozzolonic reaction is proportional to the amount of surface area available for reaction. Therefore, it is plausible to add nano-SiO₂ particles in order to make high-performance concrete.

They studied the compressive strengths of mortars with nano-SiO₂ particles were all higher than those of mortars containing silica fume at 7 and 28 days. It is demonstrated that the nano-particles are more valuable in enhancing strength than silica fume. In addition, the continuous hydration progress was monitored by scanning electron micrograph (SEM) observation, by examining the residual quantity of Ca(OH)₂ and the rate of heat evolution. The results of these examinations indicate that nanoscale SiO₂ behaves not only as a filler to improve microstructure, but also as an activator to promote pozzolonic reaction.

Compressive strengths after 7 and 28 days are shown in Table-3.3. It can be seen that the compressive strength was developed in mortars containing nano-SiO₂ particles in every case higher than that of control cement mortars. The difference in the strength development of the mortars can be attributed to pozzolonic reaction. As mentioned above, nano-particles are thought to be more effective in pozzolonic reaction than silica fume. Also, the nano-SiO₂ would fill pores

to increase the mortar strength, as silica fume does. Therefore, it is confirmed that the addition of nano-SiO₂ to cement mortars improves their strength characteristics. The strength of the mortars was found to increase as the increase as the nano-SiO₂ content increased from 3% to 12%.

The water/cementitious ratio (w/cm) was 0.5, and four contents of nano-SiO₂ particles were 3%, 6%, 10%, and 12% by weight of cement. The compressive strengths of the cement mortars with the addition of silica fume were also evaluated at the w/cm ratio of 0.5 to compare with mortars containing nano-SiO₂ particles. Three contents of silica fume were 5%, 10% and 15% by weight of cement. Result of compressive strength are shown in **Table-3.2**

Table-3.2 compressive strength of cement mortar

S. NO	specimen	Compressive strength(MPa)	
		7 days	28 days
1.	OPC	18.3	25.6
2.	SF	22.5	35.1
3	SF 10	24.7	37.4
4.	SF 15	26.1	38.0
5.	NS3	39.5	54.3
6	NS6	46.1	61.9
7.	NS10	49.2	68.2
8.	NS12	50.7	68.8

3.4.2 COMPRESSIVE STRENGTH OF MORTAR

It can be seen that the compressive strength of cement mortar with NS was higher than that of cement mortar with OPC, and gradually increased with increments of NS content. By using NS content of 6% and a water/binder ratio of 0.65, the compressive strengths of cement mortars with NS particle sizes of 12, 20 and 40 nm were increased, compared with cement mortar with OPC, by about 1.25, 1.52 and 1.65 times, respectively. In the case of cement mortar containing SF, the compressive strength was slightly improved.

Haruehansapong et al. (2013)

Studied the compressive strengths and the microstructure photographs of cement mortars containing nanosilica (NS) with various sizes of 12, 20 and 40 nm and then compared with cement mortar with silica fume (SF). Tested results indicated that NS significantly improved compressive strength of cement mortar and the strength improvement was also dependent on the NS particle size. Cement mortar containing NS 40 nm gave higher compressive strength compared with NS 12 and 20 nm due to their agglomeration and ineffective dispersion. By varying the replacement contents of 3%, 6%, 9% and 12% NS by weight of cement, the optimum replacement content was 9% for all NS particle sizes and SF. These results indicate that the particle size of nanosilica affected only the compressive strength of cement mortar, but it had no effect on the optimum replacement content. The results of microstructure photographs are also supported the compressive strength and optimum replacement content results. NS particles presented high pozzolonic activity and could fill up pores, resulting in homogeneous, dense and compact microstructures.

3.5 EFFECT OF NANOSILICA PARTICLE SIZE ON COMPRESSIVE STRENGTHS

Studied the compressive strength of cement mortar with OPC (without NS), mortar with SF, and mortar with NS at a mortar age of 7 days are observed. It can be seen that the compressive strength of cement mortar with NS was higher than that of cement mortar with OPC, and gradually increased with increments of NS content. By using NS content of 6% and a water/binder ratio of 0.65, the compressive strengths of cement mortars with NS particle sizes of 12, 20 and 40 nm were increased, compared with cement mortar with OPC, by about 1.25, 1.52 and 1.65 times, respectively. However, better strength improvement was obtained with a NS replacement content of 9%, which resulted in strengths of 1.32, 1.67 and 1.74 times that of OPC, respectively. However, the strength improvement obtained in this study cannot be compared with the results presented in the works of Jo et al. (2007) and Sadrmomtazi et al., since the water/binder ratio and the mixture proportions used are different. In the case of cement mortar containing SF, the compressive strength was slightly improved: by 1.03 and 1.06 times for replacement contents of 6% and 9%, respectively. The lower compressive strength improvement of cement mortars with SF compared with cement mortars with NS can be explained by the fact

that SF has lower SiO₂ content, which produces less pozzolonic activity than that of NS. Moreover, SF particle size is larger than that of MH et al. (2006), I Senff et al. (2009) therefore giving it less packing ability than that of NS. In other words, a very small particle of NS can more easily fill in the pores of cement paste, thus increasing the compressive strength of cement mortar compared with SF. Fig. presents the compressive strengths of cement mortar with different NS particle sizes in comparison with the control cement mortar without nanoparticles and cement mortar with SF, at mortar of 7 days. The effect of NS particle size on the compressive strength by varying the nanosilica content is also presented. For all NS contents, higher compressive strength was clearly obtained when larger-sized NS particles were added into the mixtures.

Therefore, the particle size of NS directly affects the compressive strength of cement mortar. Cement mortar with NS particle size of 40 nm gave higher compressive strength than cement mortars with NS particle sizes of 12 and 20 nm. These results indicate that very small NS particle sizes (12 nm and 20 nm) are not beneficial for the packing ability. Instead of the nanoparticles filling in the very small pores of cement paste, they are possibly coated on the surface of cement particles, thereby reducing the hydration reactivity of cement paste. In this case, the strength improvement is less effective in terms of pozzolonic activity and packing ability (filling effect). Another possible reason is that very small particle of NS with size of 12 and 20 nm can be produced agglomeration and poor dispersion behaviors. These behaviors (agglomeration and poor dispersion of 10 and 15 nm-SiO₂) were also found in work of Chaichana et al. who applied nanosilica for LLDPE/SiO₂ nano-composite materials.

F Sanchez et al (2006)

Reported that effective dispersion of nanosilica into cement mortar is the most significantly issue for all nanoparticles applications. Cement mortar with NS particle size of 40 nm gave the highest compressive strength. One reason is that this NS particle is medium-sized, a suitable size which is very effective in terms of pozzolonic activity, packing ability, and particle uniform dispersion. Therefore, the compressive strength improvement arises from all effects. For cement mortar containing SF (average particle size of 100 nm), the compressive strength improvement was lower than for mortar with NS. The reasons are based on the fact that SF particles are of

larger size, and with lower SiO₂ content than that of NS particles. They are thus less effective in terms of pozzolonic activity and packing ability compared with NS particles.

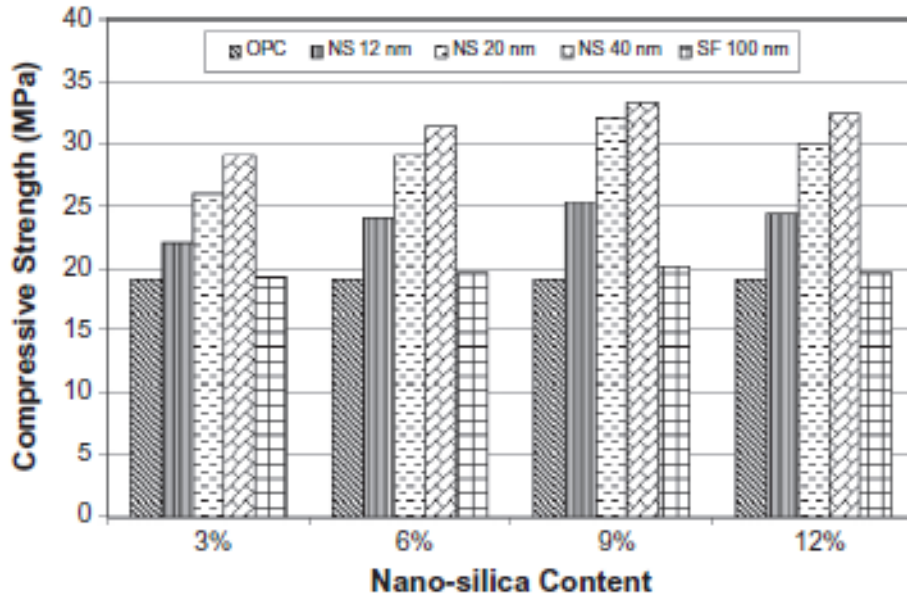


Fig. 3.4 Compressive strength at age of 7 days of cement mortar with OPC, cement mortar with various particle sizes of NS, and cement mortar with SF.

Qing et al. (2006)

Studied the variation of the compressive strength development of hcp with NS or SF added. It is found that all paste strengths of sample A-series were obviously higher than those of control sample CO especially at 3 days. Furthermore, with increasing the NS content, paste strengths increased. For example, compared with sample CO, the strengths of sample A3 increased by 6%, 35%, 23% and 11% at ages of 1 day, 3 days, 28 days and 60 days, respectively. However, with increasing the SF content, all paste strengths of sample B-series were slightly lower than those of sample CO at ages of 1 day and 3 days. But at ages of 28 days and 60 days, strengths with increasing the SF content were obviously higher than those of sample CO, and the strengths were slightly lower than those of sample A-series with the same content of addition. For example, as compared with sample CO, the strengths of sample B3 decreased by 3% and 1% at ages of 1 day and 3 days, and increased by 16% and 10% at ages of 28 days and 60 days, respectively.

The influence of nano-SiO₂ and silica fume on consistency and setting time are different. Nano-SiO₂ makes cement paste thicker and accelerates the cement hydration process. Compressive strengths of (HCP) increase with increasing the nano-SiO₂ content, especially at early ages. However the strengths of (HCP) decrease slightly with increasing the silica fume content at early ages, but increase at later ages.

M. et al. (2013)

This paper presented an outline of the previous works carried out on using NS into the traditional cementitious materials based on PC and AAFA (alkali active fly ash). Heat of hydration, workability, setting time, strength, abrasion resistance, freeze–thaw resistance, fire resistance, drying shrinkage, resistance to aggressive environmental, leaching, water absorption, chloride penetration and permeability of PC-based materials modified with NS as well as comparison between NS and other nano types have been reviewed.

Li et al. (2004)

Studied the compressive strength of plane cement mortars modified with NS. Cement was partially replaced with NS at levels of 0%, 3%, 5%, 10% and 20%, by weight. Fixed w/b ratio of 0.5 and various dosages of water reducing agents were employed. The results showed an increase in the compressive strength with the addition of NS, at ages of 7 and 28 days. The enhancement in the 28 days compressive strength was 13.8%, 17%, 26% and 22% with the inclusion of 3%, 5%, 10% and 20% NS, respectively. The replacement level of 10% gave the highest compressive strength. The compressive strength, at ages of 7 and 28 days, of mortars modified with NS. Cement was partially replaced with NS at levels of 0%, 3%, 5% and 10%, by weight. Fixed w/b ratio of 0.5 and various dosages of water reducing agents were employed. The results showed an increase in the compressive strength with the addition of NS. The enhancement in the 7 days compressive strength was 5.7%, 20.1% and 20.1% with the addition of 3%, 5% and 10% NS, respectively, whilst the enhancement in the 28 days compressive strength was 13.8%, 17% and 26%, respectively. The addition of 10% NS showed the optimum content which gave the highest compressive strength followed by 5% and 3%, respectively.

Jo et al. (2007)

Studied the partially replaced cement, in mortars, with NS at levels of 0%, 3%, 6%, 10% and 12%, by weight. They reported that the compressive strength increased with the addition of NS. As NS content increased, as the compressive strength also increased at ages of 7 and 28 days. The enhancement in the 28 days compressive strength was 112.11%, 141.79%, 166.41% and 168.75% at replacement levels of 3%, 6%, 10% and 12%, respectively.

In another investigated the compressive strength, at ages of 7 and 28 days, of mortars modified with NS. Cement was partially replaced with NS at levels of 0%, 3%, 6%, 9% and 12%, by weight. Different w/b ratios of 0.23, 0.25, 0.32, 0.35 and 0.48 and various dosages of high-range water reducing were employed. The results showed that at w/b ratio of 0.23, the addition of 6% NS gave the highest compressive strength, followed by 9%, 12% and 3%, respectively. At w/b ratio of 0.25, the addition of 9% NS gave the highest compressive strength, followed by 12%, 6% and 3%, respectively. At the remaining w/b ratios, the addition of 12% NS gave the highest compressive strength, followed by 9%, 6% and 3%, respectively. They also reported that the NS behaved not only as a filler to improve cement mortar microstructure, but also as a promoter of pozzolonic reaction.

Lin et al. (2008)

Studied the compressive strength, at ages of 3, 7 and 28 days, of mortars modified with NS. 0%, 1%, 2% and 3% of NS was added. Fixed w/b ratio of 0.7 was used. The results showed an increase in the compressive strength with increasing NS content, at all ages.

International Journal of Applied Engineering Research. (2014)

They studied to investigate the influence partial replacement of cement with colloidal Nano-silica on the compressive strength of cement mortar. This paper was reported the results of compressive strength test undertaken on 70.6 mm cube samples of the cement mortar prepared with three different water cement ratio along with varying percentage of Nano-silica. The compressive strength is determined after 7 and 28 days of curing, and water absorption after 28 days. The results of this experimental study reveal that the incorporation of Nano-silica enhances the early strength of cement mortar along with improvement of strength at 28 days. Moreover,

the study reveals that water absorption of cement mortar reduces with addition of Nano-Silica due to reduction of minute pores present in cement mortar.

They studied that variation of 7 days Compressive strength of mortar specimens containing different percentages of Nano-Silica. It can be observed that 7 days compressive strength of mortar increases with addition of NS and this enhancement of strength augmented with increasing percentages of NS. The improvement of 7 days compressive strength is around 13% to 17% with the addition of 3% NS in mortar mixes.

Moreover, the reduction of strength with the increase in water cement ratio. The 28 days CS of mortar for different water cement ratio with variation of percentage of NS, which shown that 13 % to 18% improvement in CS due addition of NS. The behavior of 28 days compressive strength with respect to variation of w/c for particular NS content is similar to 7 days compressive strength.

- The 7 days Compressive strength of cement mortar containing colloidal NS was more than that of reference for every water cement ratio because silica Nano-particles acted as nucleation centers, contributing to the acceleration of the hydration of Portland cement.
- The increase of 28 days CS of cement mortar containing NS compared to control mortar was owing to the fact that Nano-particles can fill the voids of the C-H-S structure leading to a dense microstructure.
- The reduction in 7 and 28 days Compressive strength of mortar with increase in water cement ratio could be due to the development a weaker mortar matrix.

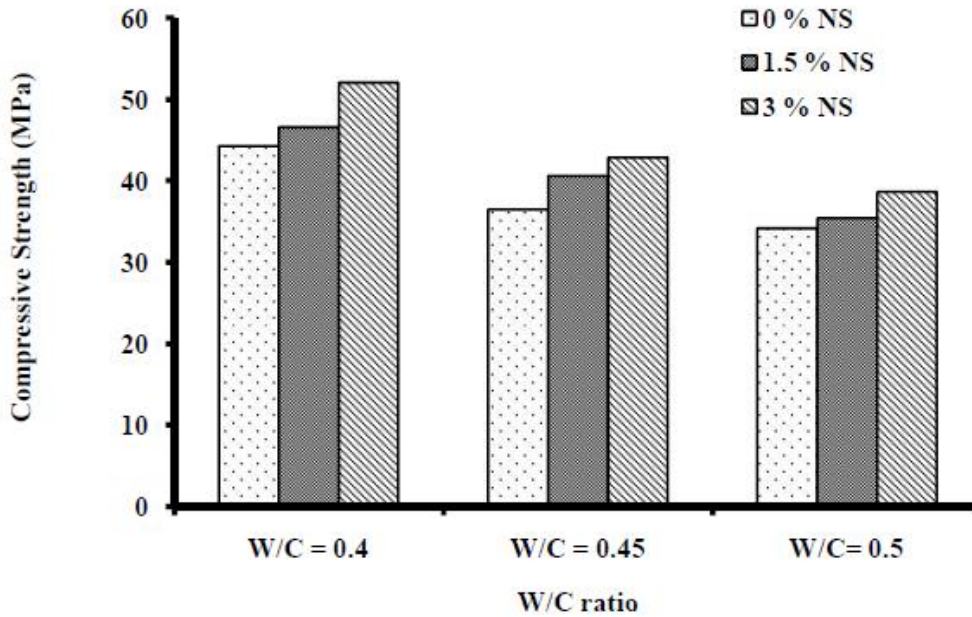


Fig. 3.5 Variation of 28 days compressive strength.

Li at el. (2003)

Observed the mechanical properties of Nano-Fe₂O₂ and Nano-SiO₂ cement mortars were experimentally studied. The experimental results showed that the compressive and flexural strengths measured at the 7th day and 28th day of the cement mortars mixed with the nano-particles were higher than that of a plain cement mortar.

3.6 LITERATURE REVIEW ON XRD

Qing at el. (2003)

Observed at the given age, when glass plate was split apart between HCP and glass, the fracture surface (interface) on hardened cement paste was analyzed by XRD immediately, in order to determine the degree of interaction between CH and NS or SF, and to observed the orientation, size and morphology of CH crystals or other hydration products at the interface. **Fig. 3.4** shows XRD powder patterns of NS and SF. Strong broad peaks of NS and SF were centered on 23_ and 22 (2θ), respectively, which was in keeping with the strong broad peak of a characteristic of amorphous SiO₂. The results shown that both NS and SF are in an amorphous state.

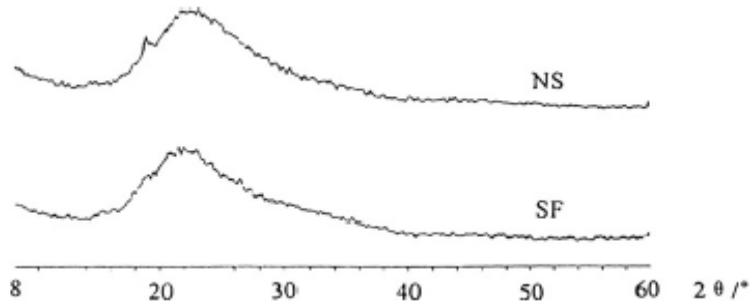


Figure-3.4 XRD of cement paste compare with nano silica and silica fume.

3.7 CONCLUDING REMARKS

Following chapter represent literature review on rheological properties of cement pastes and mortar. The incorporation of various percentage of nano silica by mass of cementitious material reduced initial setting time and final setting time of cementitious material and strength gain in early age.

CHAPTER 4

EXPERIMENTAL PROGRAM

4.1 GENERAL

The following chapter represents the experimental setup and evaluates the effect of nanosilica on rheological properties and compressive strength of cementitious paste. The effect of addition of nano silica was studied on paste prepared with three types of cement OPC, PPC and slag cement. The superplasticizer dosage in each case was first decided then specimens were casted to determine the compressive strength of pastes. Detail experimental program is discussed in the following section.

4.2 MATERIAL SYSTEM

The basic material was used in the specimen preparation such as Pozzolana Portland cement, ordinary Portland cement, slag cement, water, superplasticizer, and nano silica. The properties of these basic materials are as follows.

4.2.1 Ordinary Portland Cement (OPC)

Ordinary Portland cement (grade-43) was used in the investigation. The physical properties of the cement were tested in laboratory as per the IS Standard specification and results are presented in Table 4.1. Chemical composition of the cement was supplied by the manufacturer and is presented in the Table 4.2. Compressive strength of OPC at 3 days, 7 days and 28 days of curing are represented in Table 4.3

Table-4.1 Physical Properties of OPC

S.NO	Characteristics	Result	Requirement as per IS:8112-1989
1	Normal consistency	30%	-
2	Initial setting time	148 min	Min 30
3	Final setting time	263 min	Max 600
4	Specific gravity	3.15	-
5	Blain's fineness	287	-

		m ² /Kg	
6	Soundness	1	Max 10

Table 4.2 Chemical properties of ordinary Portland cement

S.NO	Oxide composition	Values
1.	CaO	60-65%
2	SiO ₂	22%
3	Al ₂ O ₃	5.93%
4	Fe ₂ O ₃	0.5 to 6%
5	SO ₃	1.3 to 3%
6	MgO	0.1 to 4%
7	K ₂ O	0.4 to 1.3
8	Na ₂ O	-

Table 4.3 Compressive Strength of OPC (Grade-43)

S.NO	Day of curing	Compressive Strength(MPa)
1	3 days	26.5
2	7 Days	38.2
3	28 days	53.6

4.2.2 Portland Pozzolonic cement (PPC)

Portland Pozzolana cement (PPC) is used for the present investigation. The cement is of uniform color i.e. grey with a light greenish shade and is free from any hard lumps. There are four major compounds present in all the cement. The variation in percentage composition of compounds influences the properties of cement. Portland Pozzolana Cement is kind of blended cement which is produced by intergrading of OPC clinker along with gypsum and pozzolonic materials in certain proportions. Pozzolana is a natural or artificial material containing silica in a reactive form. The chemical properties of cement are given in Table 4.4 and the physical properties of the cement are shown in Table 4.5. All the tests are carried out in accordance with procedure laid

down in IS: 1489(part-1)1991. Table 4.6 shows the compressive strength of cubes at 3 days, 7 days and 28 days after curing.

Table 4.4 Chemical composition of PPC

S.NO	Particulars	Typical range (%)
1	Insoluble residual	24 to 27%
2	Magnesia	2 to 3 %
3	Sulphuric anhydride	1.5 to 1.8%
4	Total lose on Ignition	2 to 3%
5	Chloride	0.015 to 0.017

Table 4.5 Physical properties of PPC

S.NO	Characteristic	result	Standard values
1	Normal consistency	29%	-
2	Initial setting time	70 min	Should not be less than 30 minutes
3	Final setting time	300 min	Should not be more than 600 minutes
4	Fineness	6%	<10
5	Specific gravity	3.148	-

Table 4.6 Compressive strength of PPC (cement sand ratio is 1:3)

S.NO	Day of curing	Compressive strength(MPa)
1	3 Days	16.2
2	7 Days	25.6
3	28 Days	36.5

4.2.3 Slag Cement

The term "slag cement" is a very general term that can be used to include many types of materials and combinations. In recent years, "slag cement" has been commonly used to refer to either combinations of Portland cement and ground slag or to the ground slag alone. In the present investigation slag cement was used. It is also known as ground granulated blast-furnace slag (GGBFS). GGBFS has been often used for civil engineering structure, but it has rarely been used for reinforced concrete because of slow strength growth.

The slag cement used in the present study has the chemical composition provided by the manufacturer as listed in Table 4.7. The physical properties of the cement are presented in Table 4.8 and compressive strength of the 70.4 mm cubes at 3 days 7 days and 28 days are presented in Table 4.9.

Table-4.7 Chemical composition of Slag Cement

Contents	Oxide compound
SiO ₂	33.64 %
Al ₂ O ₃	14.33 %
Fe ₂ O ₃	0.16 %
CaO	42.93 %
MgO	6.38 %
Na ₂ O	0.20 %
K ₂ O	0.34 %
TiO ₂	0.61 %
P ₂ O ₅	0.01 %
MnO	0.36 %

Table 4.8: Physical properties of Slag cement

Properties	Observed value
Specific surface area	350 to 500 m ² /Kg.
Initial setting time	500 minutes.
Final setting time	1000 minutes.

Soundness	< 1
Specific gravity	2.85 to 2.95

Table-4.9 Compressive strength of slag cement

S.NO	Days of curing	Compressive strength (MPa)
1	3 days	15
2	7 days	25.2
3	28 days	34.6

4.2.4 Nano Silica

Cemsyn (XTX) nano silica was used throughout the investigated, which is in the colloidal form (Fig. 4.1). The basic properties of nano silica were taken from the manufacturer are represented in Table-4.10.



Figure 4.1 colloidal nano silica used in the study

Table 4.10 Properties of Colloidal nano silica

S.NO	Cemsyn (XTX) Nano silica	
	Properties	Result
1	active nano content	30-32
2	pH(20 ⁰)	9.9-10
3	specific gravities	1.20-1.22
4	Particle size	8-20 nm

4.2.5 Superplasticizer

To improve the workability of the mix in fresh state, superplasticiser are most widely used. Throughout the investigation, complast SP430 (Fig. 4.2) was used as superplasticizer. Complast SP430 is based on Sulphonated Naphthalene Polymers and supplied as a brown liquid instantly dispersible in water. Physical properties of superplasticizer represent in Table 4.11. Dosage of superplasticiser was determined by marsh cone test.



Fig. 4.2 superplasticizer SP430 observed in the laboratory.

Table 4.11 Physical Properties of superplasticizer

Properties	Observed value
Specific gravities	1.220 to 1.225.
Chloride content	Nil
Air entrainment	Approx. 1% additional air is entrained.
Temperature	30°C

4.2.6 Water

Fresh and clean tap water is used for casting the specimens in the present study. The water is relatively free from organic matter, silt, oil, sugar, chloride and acidic material as per Indian standard.

4.3 MARSH CONE TEST

The marsh cone test is a simple approach to get an idea about the rheological behavior of the cement pastes. It is also a workability test used for specification and quality control of cement paste. The marsh cone test standard varies from country to country but the procedure remains same. The time needed for the certain amount of material to flow out of a cone is recorded. This measured flow time is called fluidity of tested material. The detailed procedure of the marsh cone test is discussed in the following sections:

4.3.1 Introduction to marsh cone apparatus

Marsh cone have been used in industrial sectors to appreciate the fluidity of different types of grout or mud, such as drilling mud in the petroleum industry. Marsh cone is a conical brass vessel, (Funnel shaped) with a smooth aperture. The capacity of marsh cone used in the present investigation is 1.2 liters (Fig. 4.3). There is an opening of 5 mm at the bottom of the cone from where the cement paste is allowed to pass through. The time taken by a fixed amount of cement paste to pass through this orifice is recorded as the flow time of the paste.



Fig. 4.3: Marsh cone apparatus used in the laboratory.

4.3.2 Test Procedure of marsh cone test

In the present work, a smooth paste mix is obtained by taking 1 kg of cement. To this cement, the required amount of water was added, depending upon the w/c ratio of the paste mix. Both the materials were mixed in the DIGI mortar mixer. Hand mixing is not recommended in this because it may not give consistent results because of unavoidable lump formation which block the aperture. Dry cement is first taken into the container. It is mixed for 1 minute with mixer operating at slow speed of 140 ± 5 revolution per minute. Then water was added during the next 1 min of mixing. After 1 minute of slow mixing, remaining water along with the superplasticizer and nano silica was added and mixed for 1.5 min at slow speed. The mixer is stopped and the paste is scraped from the sides of the bowl and hand mixed and further mixing was continued for 2 min at the high speed of 285 ± 10 revolution per minutes. The prepared mix is filled in the marsh cone and allowed to flow through the orifice of the marsh cone (Fig. 4.4). The time taken by the slurry to pass through the orifice was obtained with the help of stop watch. The time in seconds is called the "Marsh Cone Time.

The procedure is repeated by adding the required percentage of superplasticizer into the mix. The dosage of superplasticizer was gradually increased to 0.5%, 1%, 1.5%, 2% and 2.5%. The graph is then prepared between the flow time and the superplasticizer dosage. The dose at which the Marsh cone time is lowest is called the saturation point. Any further increase in the superplasticizer dosage either increased the flow time or had no effect on the flow time.

The flow time for each mix was noted at three time intervals: immediately after mixing of ingredients (initial reading), 5 minutes after mixing of the ingredients and 60 minutes after mixing of the ingredients.



Fig. 4.4 Marsh cone test procedure

4.4 PREPARATION OF PASTE MIXES

Once the superplasticizer dosage is selected for each mix, the paste mix was prepared for each mix by mixing cement, nanosilica and superplasticizer. Mixing was done DIGI mortar mixer (Fig. 4.5) using optimum dosages of superplasticiser. A total of 27 paste mixes were prepared for three types of cement and by using three dosages of nanosilica in each case. Further, the mixes were prepared at three w/c ratios.



Fig. 4.5 DIGI Mortar Mixer used for preparation of cement pastes

4.5 CASTING AND CURING OF THE SPECIMENS

The cube specimens of (50×50×50) mm were prepared by using the pastes prepared earlier. These cubes were cured for 3 days, 7 days and 28 days. Three cubes were used for each testing and the average value was taken as the mean compressive strength of the paste. Therefore, for 27 pastes, $27 \times 3 \times 3 = 243$ cubes were cast for compressive strength measurement.

4.6 CUBE COMPRESSIVE STRENGTH

This test was performed as per IS:1727,1969. After curing, the cubes were taken out from water tank and cleaned with cloth to wipe out excess water on the surface of cube and bring them to dry condition for 1 hour. The cube was tested at age of 3 days, 7 days and 28 days. They were tested in universal testing machine. Ensure that cast surface of the cubes should be kept at 90 degree to the platens. The compressive load was applied through hydraulic jack at a constant rate of 140 kg/cm²/minute as per IS 1717(1967) till failure (Fig. 4.6). The average of failure compressive strength of three cubes was considered as the representative compressive strength of the paste mixes.



Fig. 4.6: Marsh cone test procedure

4.7 CONCLUDING REMARKS

Nano silica is used with different types of cement to modify the rheological properties of cement pastes. It also modifies the properties of hardened pastes. An experimental programme is used to study the properties of cement pastes made with nano silica.

CHAPTER-5

RESULTS AND DISCUSSIONS

5.1 GENERAL

In this chapter, the findings of the experimental investigation are presented, where in various tests have been conducted to evaluate the effect of nano silica on rheological properties of cement pastes, and on hardened paste properties. Rheological properties of the mixes include the variation of flow rate at different superplasticizer dosages and values of initial setting time and final setting time of mixes at the decided superplasticizer dosage. Properties of hardened cement pastes include compressive strength test on all mixes made with different types of cement and different nano silica replacement levels.

5.2 OPTIMUM DOSAGES OF SUPERPLASTICISER

In order to find the optimum dosages of superplasticizer and to get an idea of fluidity of grout, marsh cone test (Fig 5.1) was conducted for each mixes,. The test was conducted at three interval of mixing, immediately after mixing of ingredients (initial), 5 minutes after mixing and 60 minutes after mixing. The flow rates at three intervals help us to get an idea about fluidity loss in each mix. The value of flow time of 0 min was used to determine the saturation dosages of superplasticizer. Difference between the flow rate values at 60 min and 5 min expresses the fluidity loss of each mixes. The results of various cement paste are presented in using Fig 5.2 to 5.10.

From all the figures, it is clear that with the addition of superplasticizer, flow rate decreases. However, there is an optimum dosage of superplasticizer in each case, after which further addition of superplasticizer does not affect the flow rate. This dosage is defined as the saturation dose of superplasticizer. In some of the mixes, with further addition of superplasticizer, flow rate starts increasing. This indicates the negative effect of increased use of superplasticizer. It is confirmed by other researchers also in their work.

5.2.1 Effect of water cement ratio

As the water cement ratio decreases, the flow rate increases significantly, however, as superplasticizer is added, even a small dosages of superplasticizer decreases the flow rate

drastically. Once the flow rate is reduced there is a small variation in flow rate with further addition of superplasticizer.

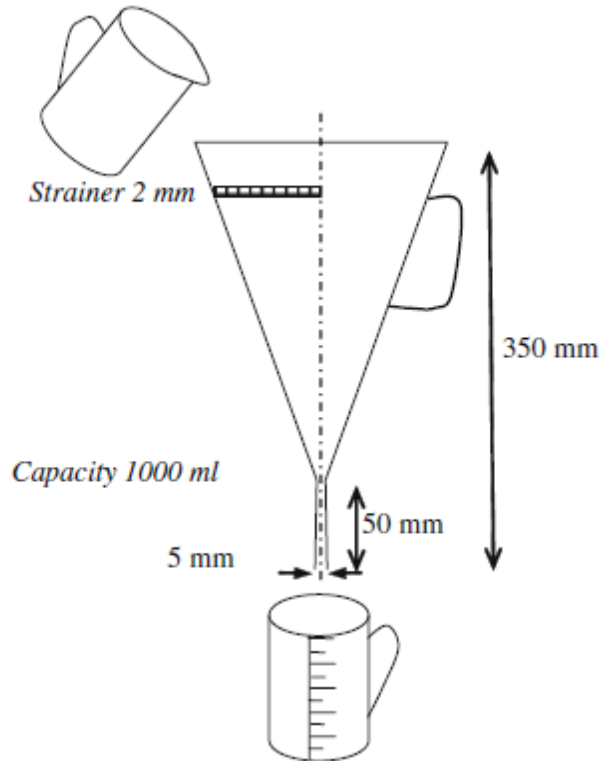


Fig .5.1 Marsh cone Apparatus

5.2.2 Effect of cement type

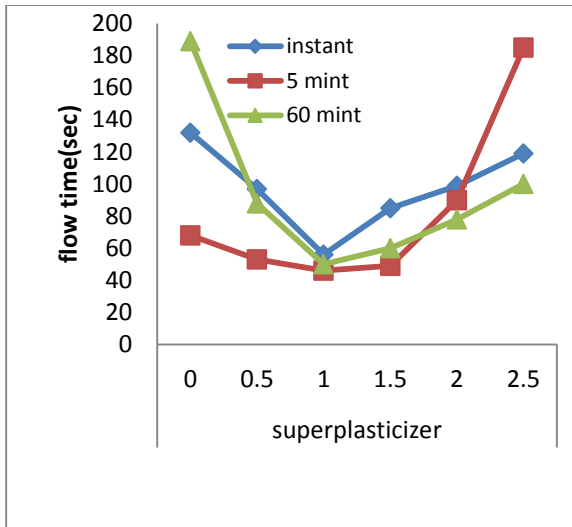
In the case of OPC cement mixes (Fig. 5.2 to 5.4), the saturation dose varies from 0.5% to 1% in most of the mixes made at different w/c ratios and with addition of nano silica. Other blended cements (PPC and slag cement) have the saturation dosage varying in the range of 0.5% to 1.5%. However, in all cases, the fluidity performance is similar to OPC cement.

5.2.3 Effect of percentage of nano silica

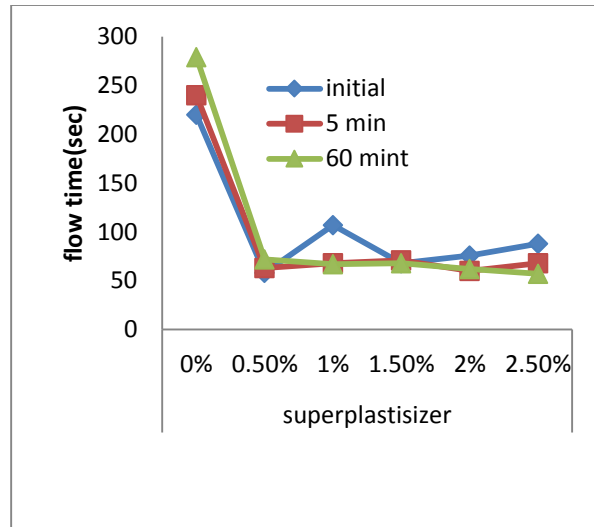
There is no different trend in flow rate as the nano silica content is increased. In some cases addition of nano silica increased the initial flow rate while in others, it actually decreased the initial flow rate. One general trend with the addition of nano silica is that its addition increased the saturation dosages by a small amount.

5.3 FLUIDITY LOSS

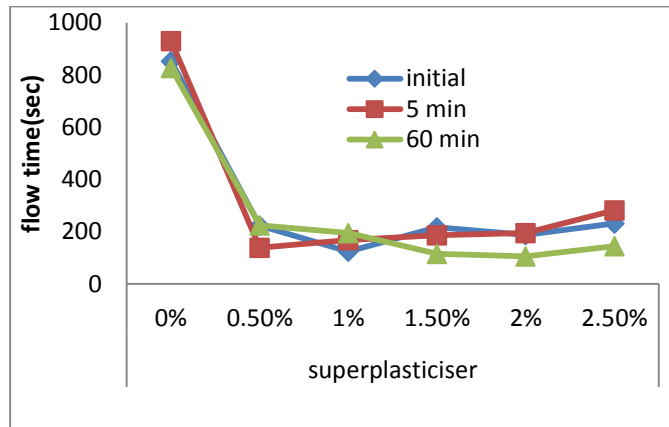
The difference in the values of 60 min and 5 min was used to calculate fluidity loss of all the mixes. It is clear from all the figures that the fluidity loss is high when no superplasticizer is added. Once superplasticizer is added in the grout, the fluidity loss is less. At the saturation dosages, in nearly all the mixes irrespective of water cement ratio, the fluidity loss is very small. However, as the superplasticizer dosages is increased beyond saturation point the fluidity loss start increasing. It indicates that large additions of superplasticizer are not only inefficient in improving fluidity, but also have detrimental effect on the fluidity loss of the mixes with time. Out of the three cement types used in the study, OPC has maximum fluidity loss; with the slag cement has been minimum fluidity loss.



(a) w/c=0.45

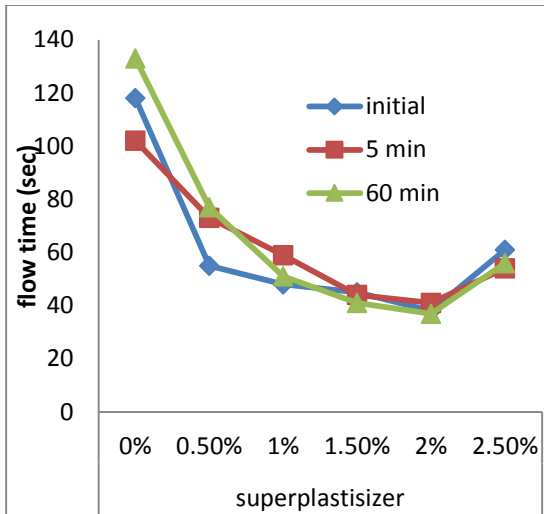


(b) w/c=0.45

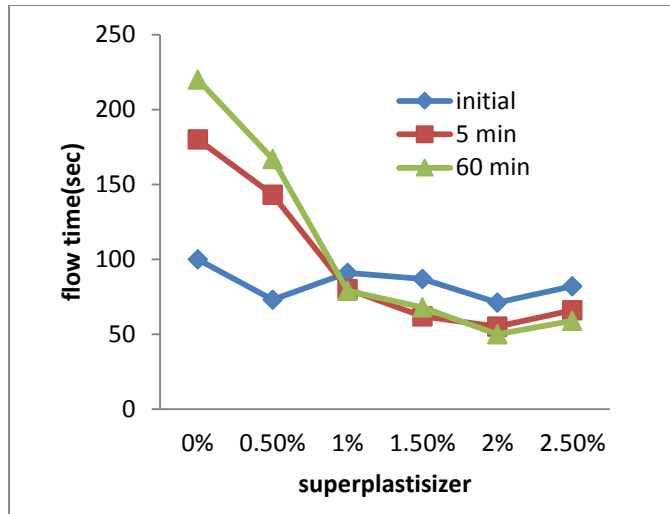


(c) w/c=0.35

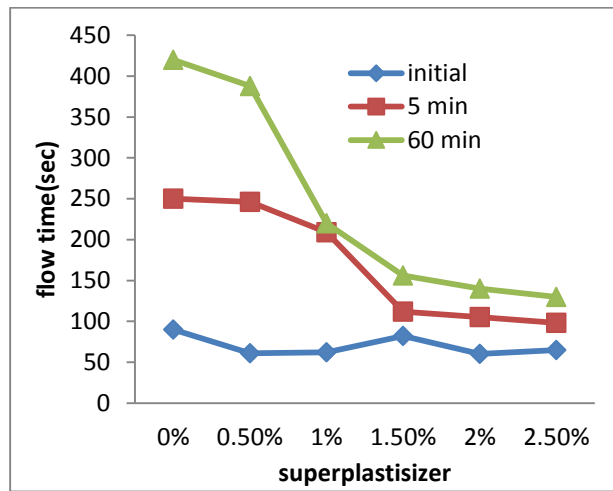
Fig 5.2 Flow time at different w/c ratios of cement pastes made using OPC at 0% NS



(a) w/c ratio=0.45

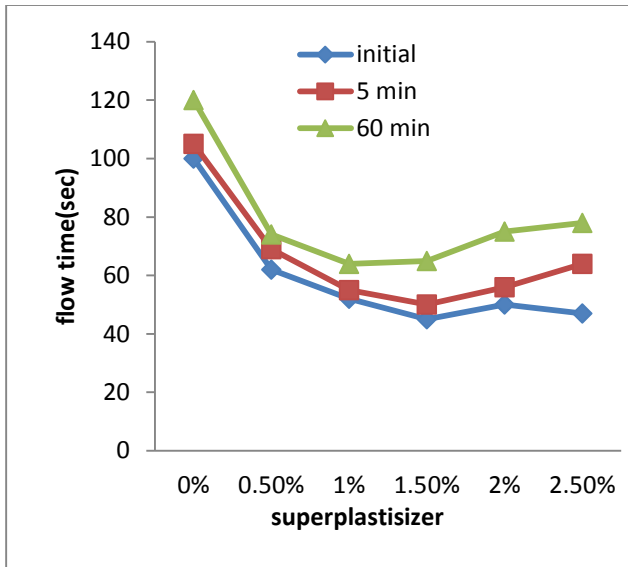


(b) w/c ratio = 0.40

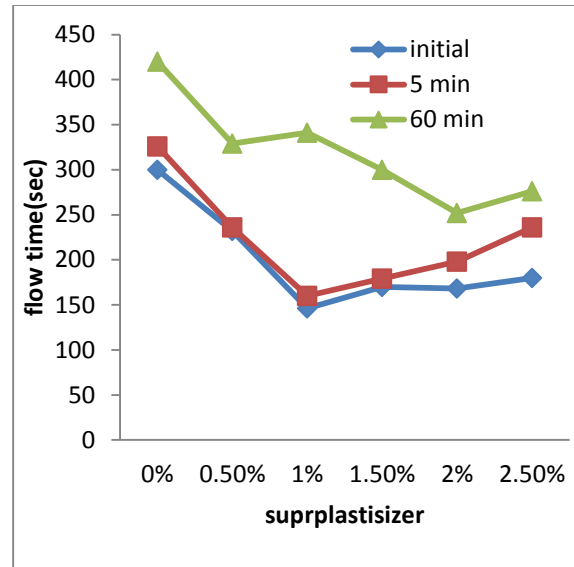


(c) w/c ratio = 0.35

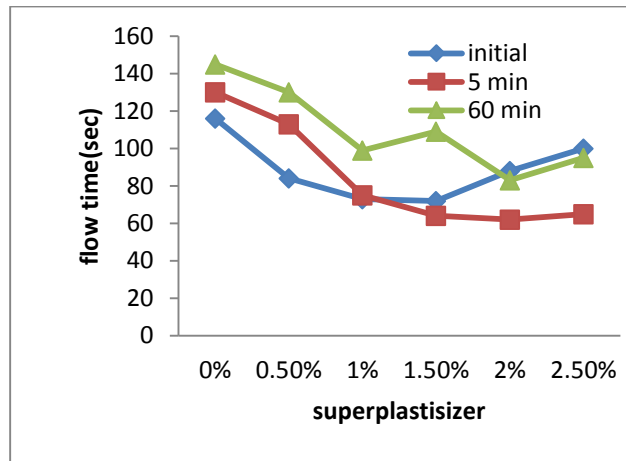
Fig. 5.3 Flow time at different w/c ratios of cement pastes made using OPC at 1% NS



(a) w/c=0.45

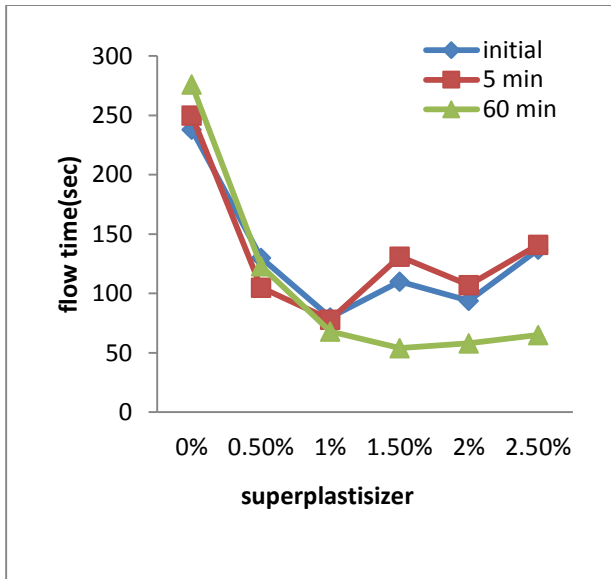


(b) w/c=0.40

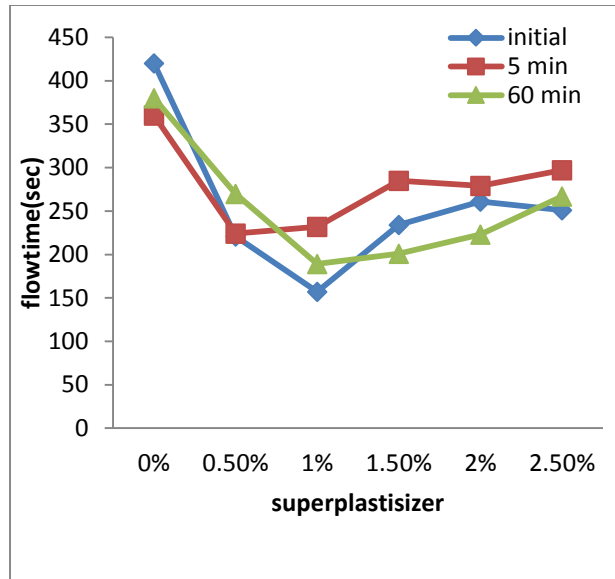


(c) w/c=0.35

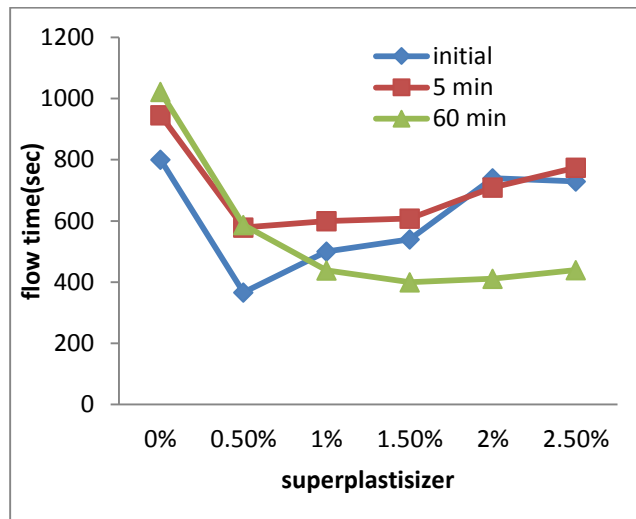
Fig. 5.4 Flow time at different w/c ratios of cement pastes made using OPC at 2% NS.



(a) w/c=0.45

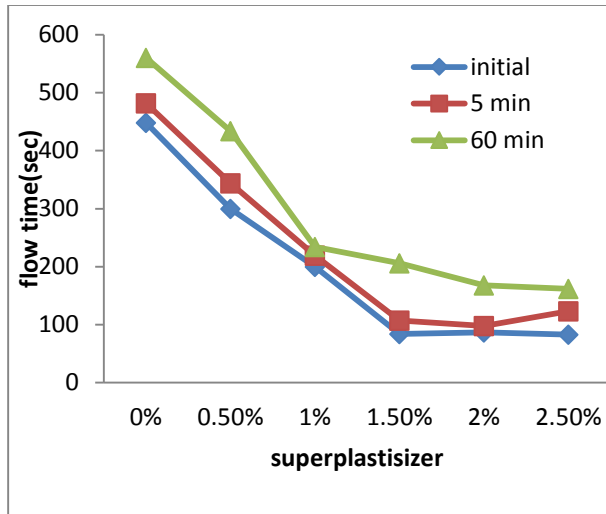


(b) w/c=0.40

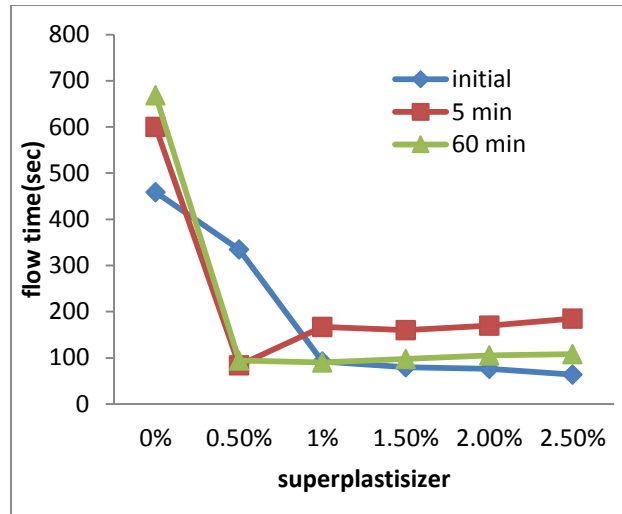


(b) w/c=0.35

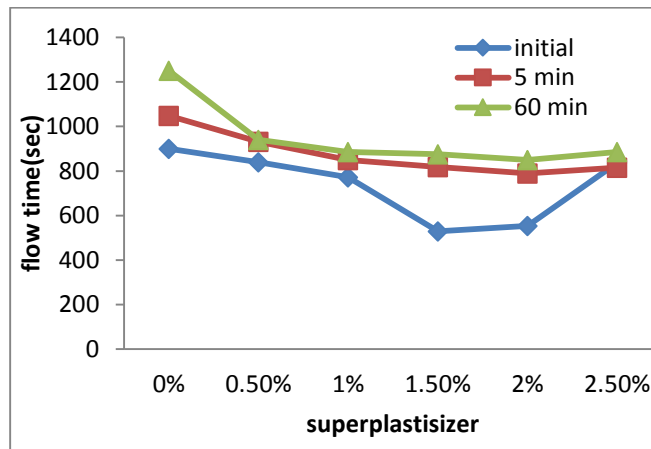
Fig. 5.5 Flow time at different w/c ratios of cement pastes using PPC made at 0% NS.



(a) w/c=0.45

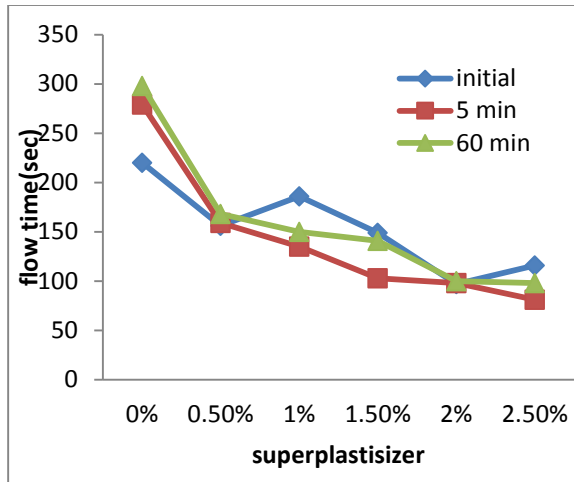


(b) w/c=0.40

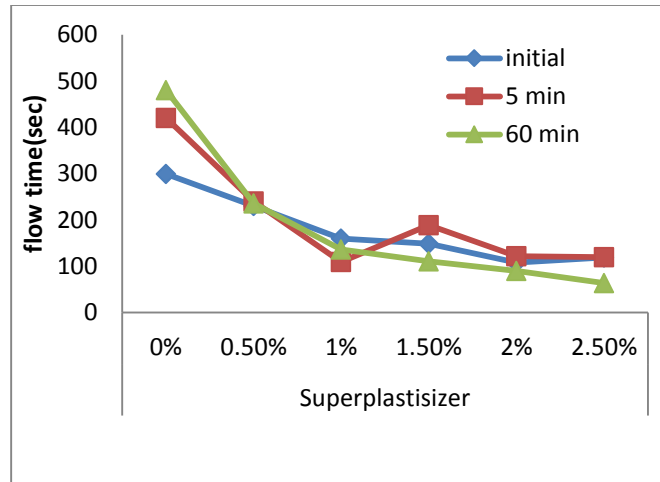


(c) w/c=0.35

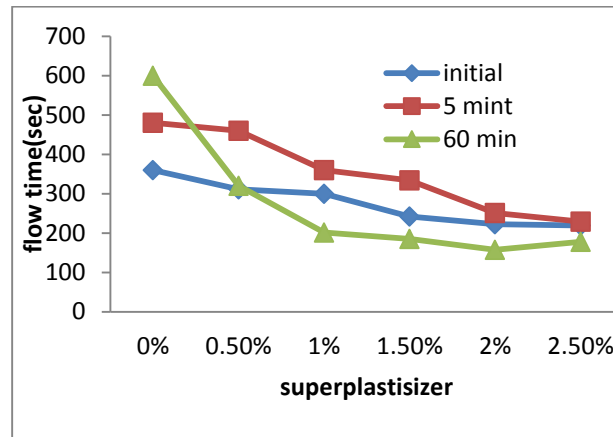
Fig. 5.6 Flow time at different w/c ratios of cement pastes using PPC made at 1% NS.



(a) w/c=0.45

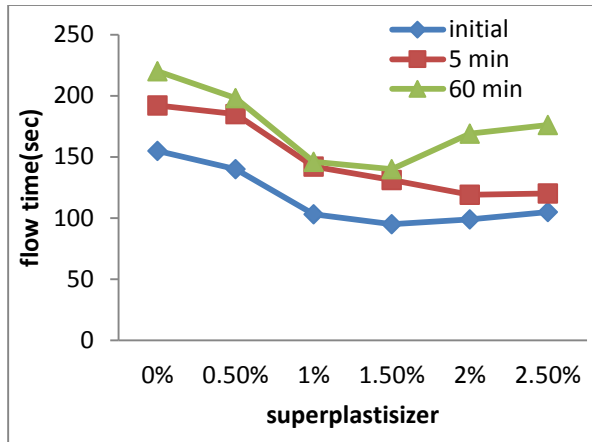


(b) =0.40

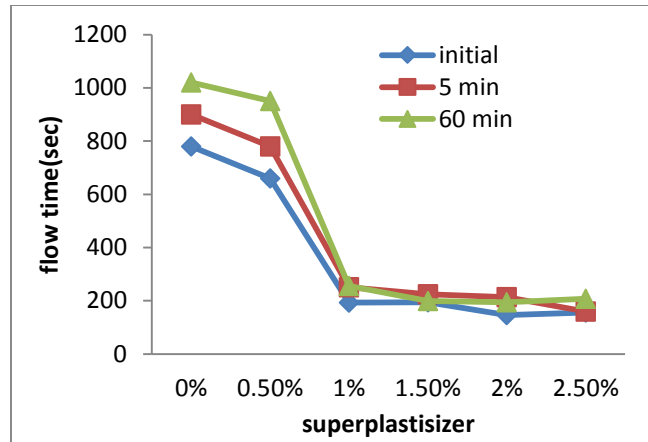


(c) w/c=0.35

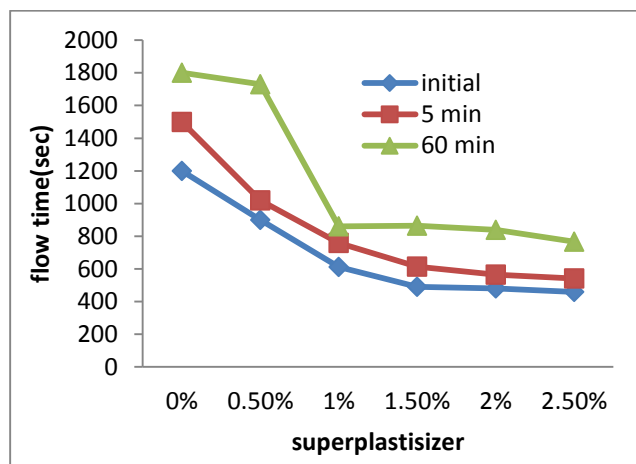
Fig. 5.7 Flow time at different w/c ratios of cement pastes using PPC made at 2% NS.



(a) w/c= 0.45

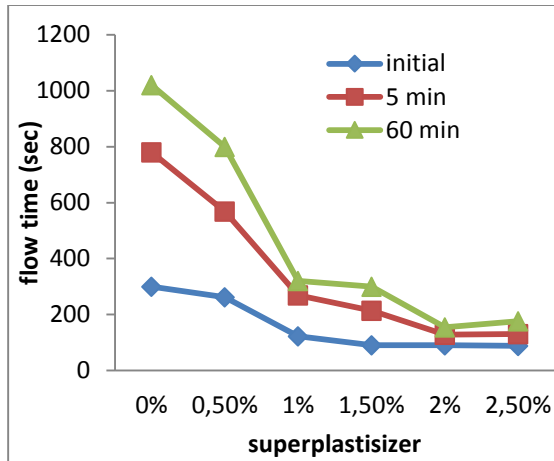


(b) w/c=0.40

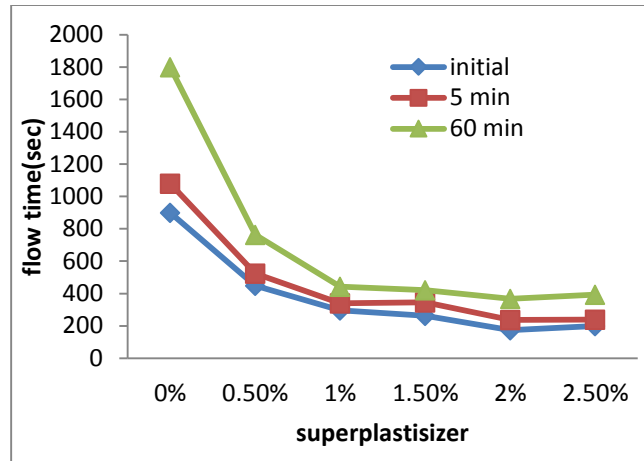


(c) w/c =0.35

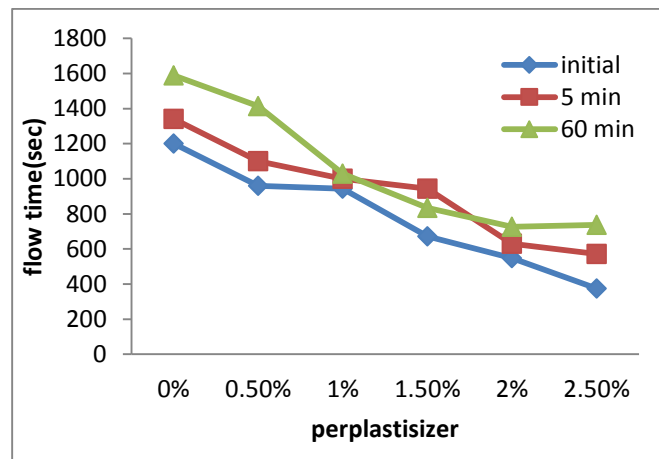
Fig. 5.8 Flow time at different w/c ratios of cement pastes using slag cement made at 0% NS.



(a) w/c=0.45

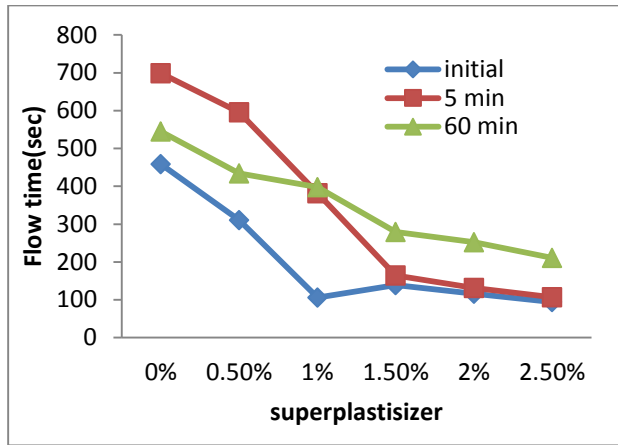


(b) w/c =0.40

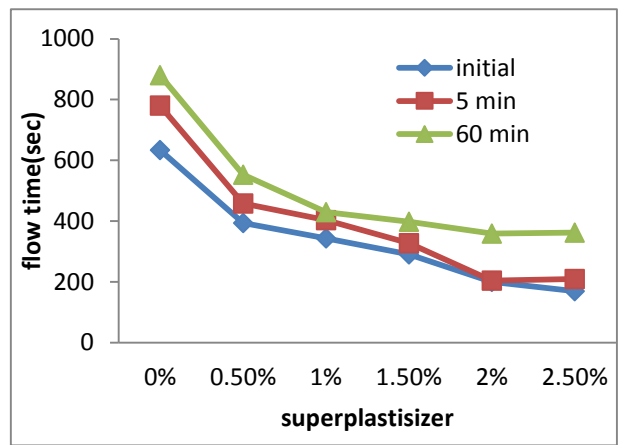


(c) w/c =0.35

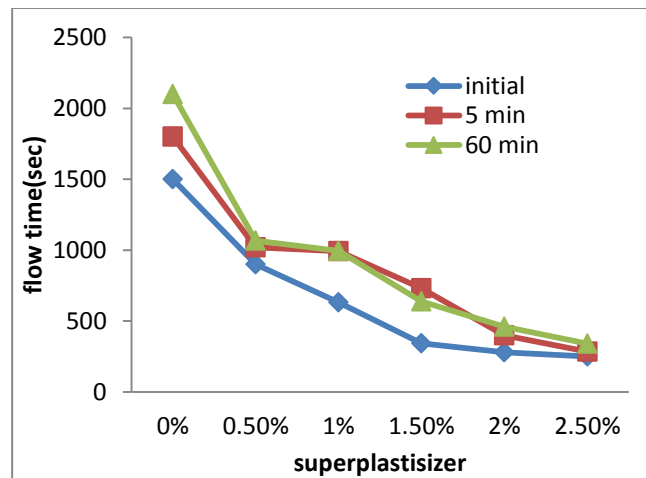
Fig. 5.9 Flow time at different w/c ratios of cement pastes using slag cement made at 1% NS.



(a) w/c = 0.45



(b) w/c = 0.40



(c) w/c = 0.35

Fig. 5.10 Flow time at different w/c ratios of cement pastes using slag cement made at 2% NS.

5.4 EFFECT OF NANO SILICA ON SETTING TIME OF DIFFERENT MIXES

The consistency and the setting time of fresh pastes were tested according to IS 9597:1989. The consistency was ascertained by putting the paste in a mould consisting of a steel ring (40 mm in height) on a sheet of glass and by determining the penetration depth of a plunger applied to the top surface of the paste specimen. The initial and the final setting time were determined with the needle of the vicat apparatus.

The value of initial setting time and final setting time for all the mixes, made by addition of different types of cement at the various percentages of NS are presented in Table 5.1.

From the table it is clear that the addition of NS accelerate the setting process in all the type of cements. Both initial and final setting time decreases with increases in NS. Along with that, the difference between initial setting time and final setting time (value of Δt in Table 5.1) also decreased with the addition of NS in all the cement types. It indicates that the NS accelerate the setting processes. This can be due to very fine particle size of NS that's start the hydration processes very quickly in all the cement types. PPC is observed to have more initial setting time and Δt , while slag cement has minimum initial setting time and Δt . The initial setting time of slag cement is very near to the minimum allowable value prescribed by IS 9597:1989.

Table-5.1 Initial setting time and final setting time of different types of cement Pastes

Mixes	NS (%)	consistency	Setting time of cement paste		Δt
			Initial setting time	Final setting time	
OPC1	0 %	29	134 min	254 min	120
OPC2	1%	29	120 min	208 min	88
OPC3	2%	29	112 min	168 min	56
PPC1	0%	33	158 min	300 min	141
PPC2	1%	33	135 min	265 min	130
PPC3	2%	33	120 min	200 min	80
SC1	0%	34	75 min	130 min	55
SC2	1%	34	56 min	124 min	68
SC3	2%	34	45 min	112 min	50

5.5 COMPRESSIVE STRENGTH OF CEMENT MIXES

For getting compressive strength of pastes, the ingredients were mixed in the DIGI mortar mixer and the cubes of dimension of 50 mm×50 mm×50 mm were cast. The cube were cured in the curing tank are at the end of required days of curing such as 3 days, 7 days and 28 days. The cubes were tested where compression testing machine, the rate of loading was kept at 140 kg/cm²/minute as per IS 1717(1967) till failure. The result observed for all the mixes are presented in Table 5.2 to 5.4 for OPC, PPC and Slag cements respectively.

5.5.1 Effect of NS addition on compressive strength

In the order to study the effect of NS on compressive strength of cement pastes, the bar graphs are made for each w/b ratio for different types of cements. They are represented from Figure 5.11 to 5.19. As can be seen from all the graphs, the addition of NS leads to increase in compressive strength of cement pastes. However, the rate of increase is high when 1% of NS is added and

the rate of increase slows down as the percentage of NS is increased from 1% to 2%. It indicates 1% of NS is sufficient to give the positive effect and any further increase in NS content does not contribute much to the strength of the mix.

On comparing the relative effect of addition of NS at different days of curing, it is observed that the effect is maximum at 3 days of curing with the percentage increase in strength is as high as 50% in some cases. As the days of curing increases, the percentage increase in strength lowers down. It is nearly 10% at the 28 days of curing with some mixes recording an increase as small as 5%. It can, therefore, be concluded that the addition of NS helps in early age development of compressive strength. It can be due to very small particle size of NS, which increases its reactivity and hence hydration at early ages. The similar conclusions are observed by **Qing et al. (2007)**, **Stefanidou et al. (20012)**.

5.4.2 Effect of cement type on compressive strength

For comparing the effect of cement type on compressive strength, Figure 5.20 to fig. 5.22 are made. From the figures, it can be seen that the addition of NS is more beneficial in the case of blended cements, as compared to OPC. The addition of NS in slag cement lead to maximum increase in strength. The percentage increase in strength at three days of testing with 1% addition of NS in slag cement is 41%, 34% and 40% for w/c ratio of 0.45, 0.40 and 0.35 as compared to the corresponding value for OPC, that are 31%, 29% and 20% respectively. Even at 28 days of curing, the maximum increase in strength is observed in slag cement only. The 28 days compressive strength of slag cements at all w/c ratios is nearly equal to the corresponding strength of OPC pastes. It indicates that negative effects of blended cements on compressive strength can be compensated by the addition of small amount of NS.

Table-5.2 Compressive strength of OPC with 0.45, 0.40 and 0.35 water cement ratio.

Day of curing	w/c ratio	Compressive strength(MPa)			% age rate increase	
3 days	0.45	24.0	16.54	18.32	-0.31	18.92
7 days		28.28	23.15	27.49	-0.18	27.49
28 days		31.56	34.9	40..49	0.10	40.49
3 days	0.40	24.96	24.22	22.22	-0.029	-0.10
7 days		27.85	32.98	29.94	0.184	0.75
28 days		56.68	42.56	47.92	-0.24	-0.154
3 days	0.35	29.22	36.47	37.22	0.24	0.27
7 days		537.05	59.44	35.29	0.60	0.04
28 days		57.62	45.7	56.89	-0.20	0.01

Table-5.3 Compressive strength of PPC with 0.45, 0.40 and 0.35water cement ratio.

Day of curing	w/c ratio	Compressive strength (MPa)			% age rate increase	
3 days	0.45	17	21.32	19.32	0.25	0.15
7 days		21.09	28.27	26.32	0.34	0.26
28 days		37.88	28.27	26.73	0.34	0.26
3 days	0.40	21.02	28.03	28.01	0.33	0.33
7 days		41.21	31.86	30.27	-0.33	-0.26
28 days		46.57	44.22	44.73	-0.05	-0.03
3 days	0.35	17.68	21	24.46	0.18	0.03
7 days		42.72	25.88	30.45	-0.29	0.28
28 days		50.41	35.6	42.39	-0.29	0.15

Table-5.4 Compressive strength of slag cement with 0.45, 0.40 and 0.35 water cement ratio.

Day of curing	w/c ratio	compressive strength (MPa)			% rate increase	
		0%	1%	2%	1%	2%
3 days	0.45	15.28	13.94	18.75	-0.08	0.22
7 days		30.61	29.95	18.65	-0.02	-0.39
28 days		37.13	34.46	47.64	-0.07	0.28
3 days	0.40	18.02	19.19	27.71	0.06	0.53
7 days		35.29	34.29	23.91	-0.29	-0.32
28 days		47.42	46.05	35.34	-0.02	-0.25
3 days	0.35	23.00	27.09	39.08	0.17	0.69
7 days		29.20	41.08	38.09	0.40	0.30
28 days		34.26	41.25	56.65	0.20	0.65

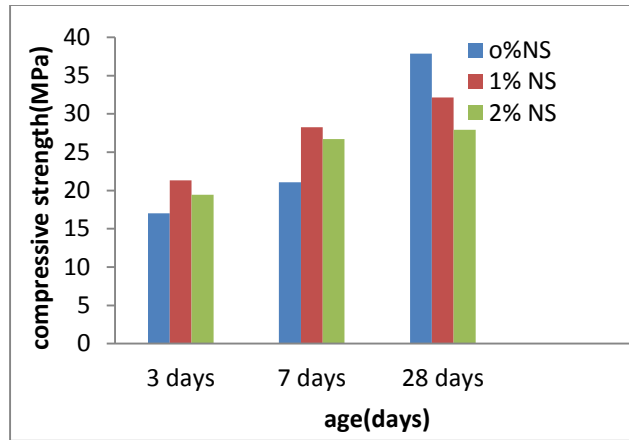


Fig 5.11 Development of Compressive strength of cement paste made by OPC at w/c ratio of 0.45

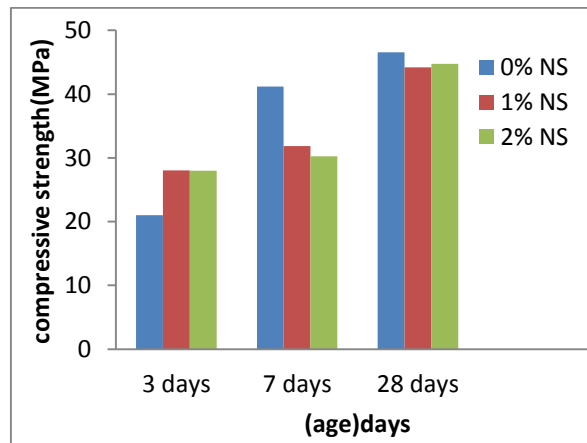


Fig 5.12 Development of Compressive strength of cement paste made by OPC at w/c ratio of 0.40

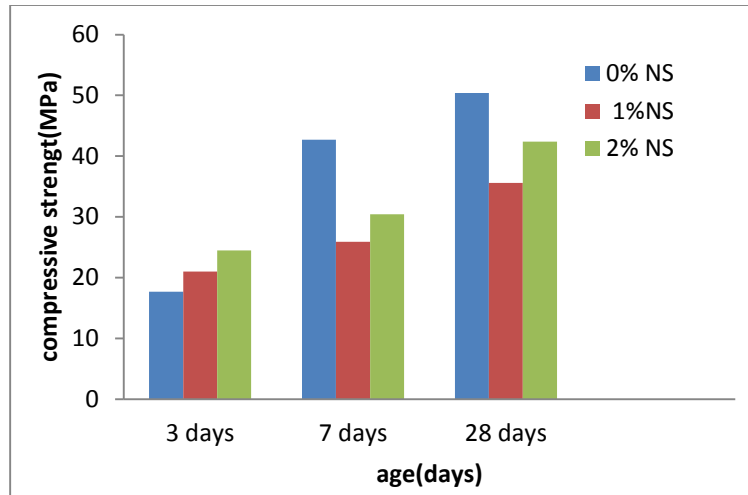


Fig 5.13 Development of Compressive strength of cement paste made by OPC at w/c ratio of 0.35

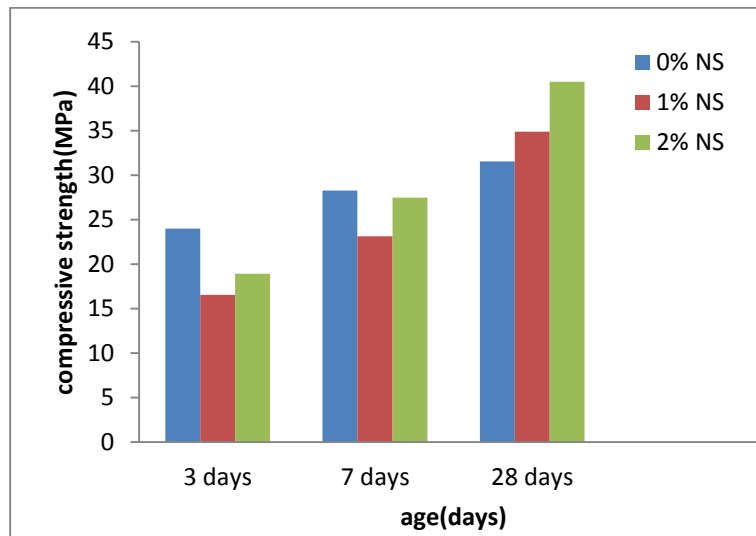


Fig 5.14 Development of Compressive strength of cement paste made by ppc at w/c ratio of 0.45

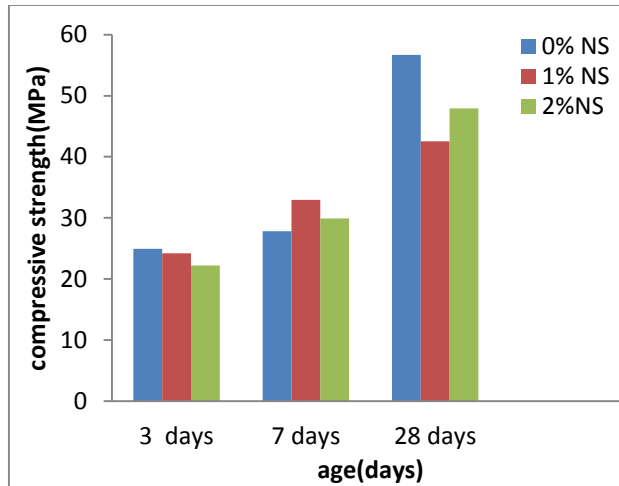


Fig 5.15 Development of Compressive strength of cement paste made by PPC at w/c ratio of 0.40

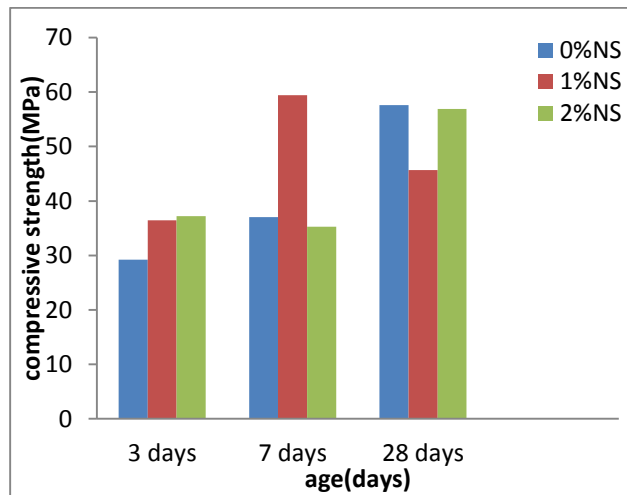


Fig 5.16 Development of Compressive strength of cement paste made by PPC at w/c ratio of 0.35

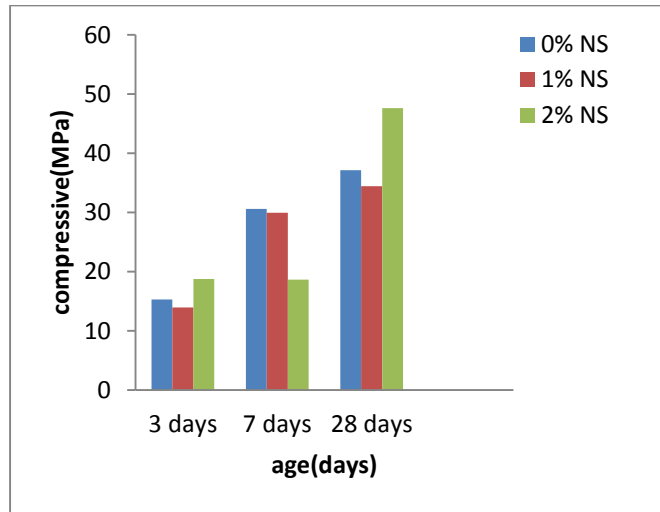


Fig 5.17 Development of Compressive strength of cement paste made by slag cement at w/c ratio of 0.45

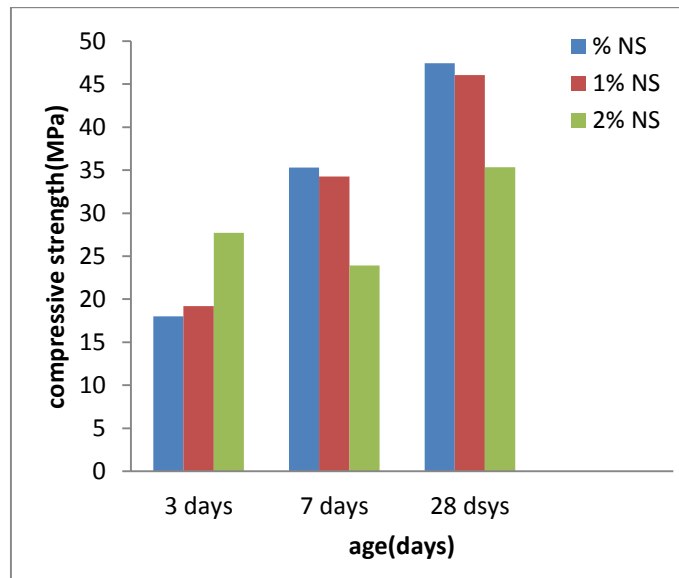


Fig 5.18 Development of Compressive strength of cement paste made by slag cement at w/c ratio of 0.40

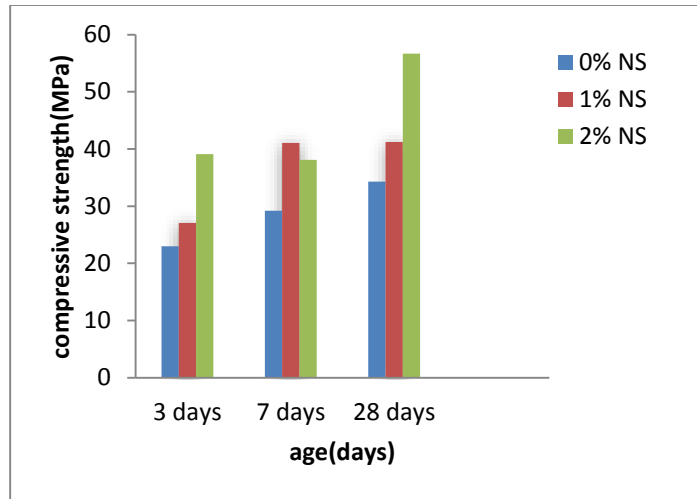


Fig 5.19 Development of Compressive strength of cement paste made by slag cement at w/c ratio of 0.35

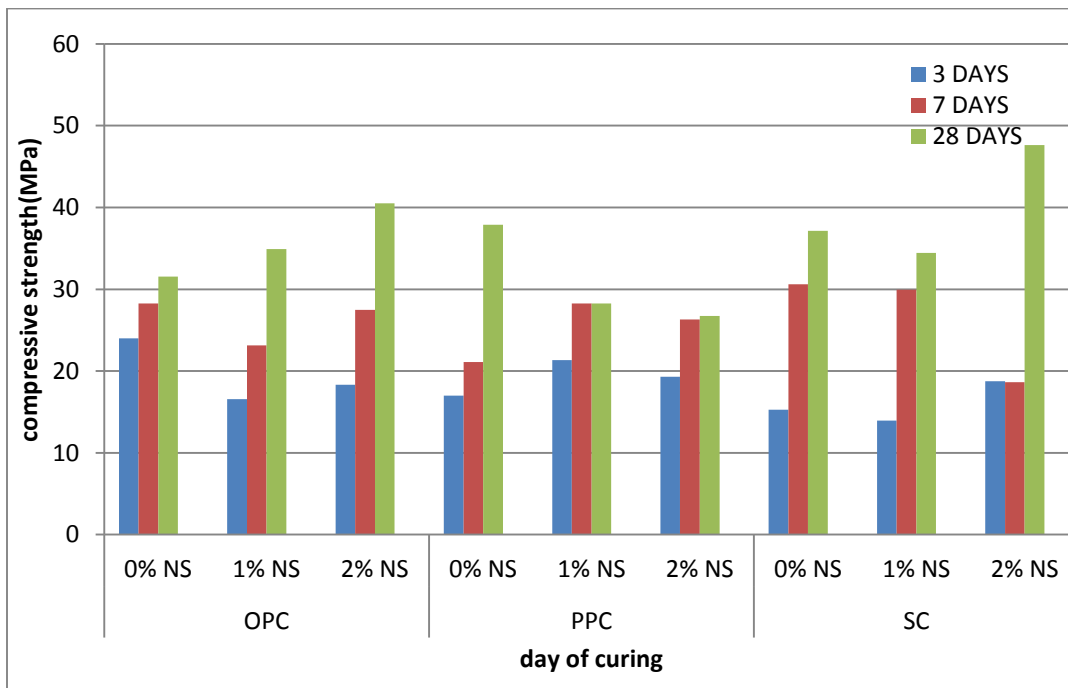


Fig 5.20 Development of compressive strength of cement paste made by OPC, PPC & slag cement at w/c=0.45

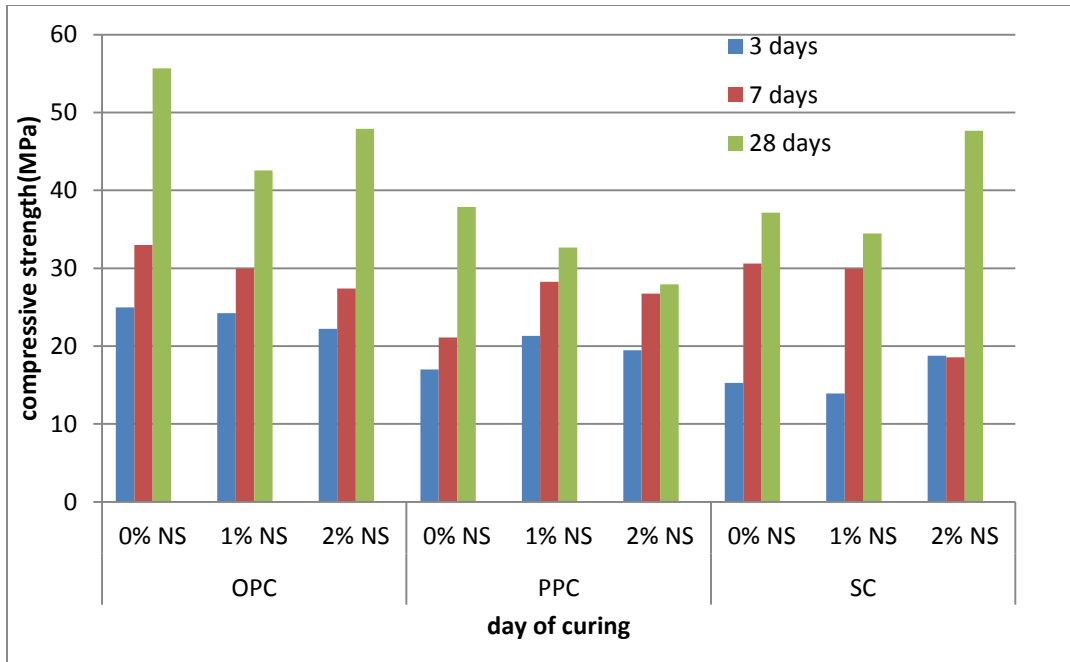


Fig 5.21 Development of compressive strength of cement paste made by OPC, PPC& slag cement at w/c=0.45

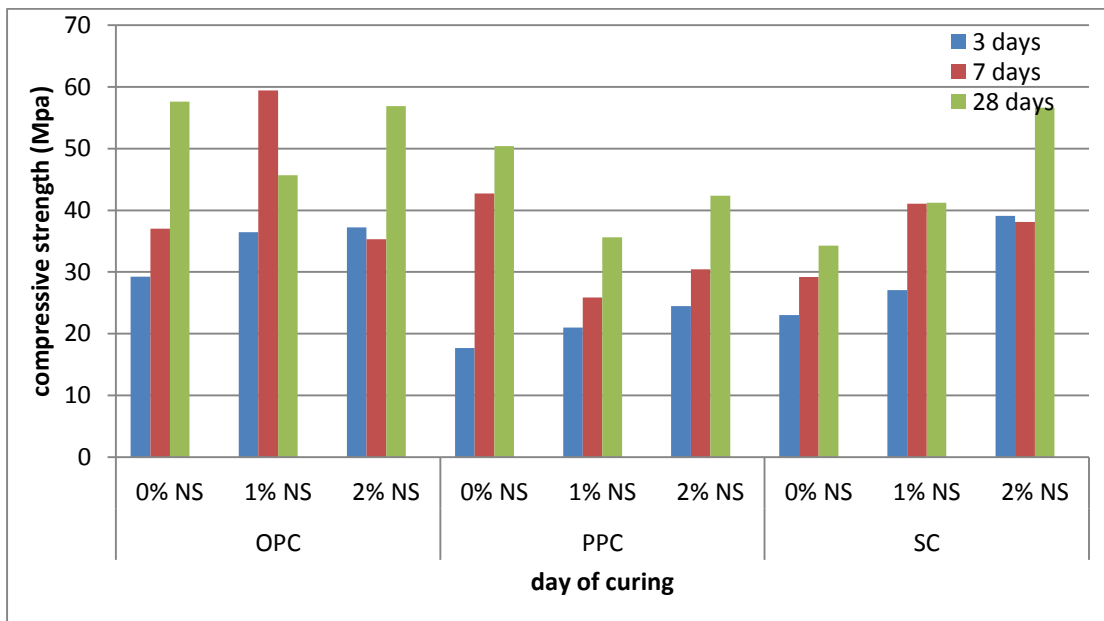


Fig 5.22 Development of compressive strength of cement paste made by OPC, PPC& slag cement at w/c=0.45

CHAPTER 6

CONCLUSIONS

6.1 MAIN CONCLUSION

The results obtained from the tests, carried out in the present research work for evaluating the effect of colloidal NS on the mechanical and rheological behavior of cement pastes, leads to the following conclusions:.

- Marsh cone Test was more reliable technique to define the dosages of superplasticizer of cement mixes. The flow time of the mix helps in finalizing the saturation dosage of superplasticiser, while the difference in flow time at 60 minutes and 5 minutes tells about the fluidity loss of the mix. For selected water cement ratio was 0.45, 0.40 and 0.35. The superplasticizer dosage of the mixes varies from 0.5% to 1.5% for all the mixes. Addition of nano silica leads to increase in dose of superplasticizer. The fluidity loss is maximum in the case of slag cements.
- Nano silica reduces the initial setting time and final setting time of all the mixes. The initial setting time of slag cement is very near to the minimum value recommended by IS code. Therefore, care must be taken while using slag cement with nano silica.
- The pozzolonic activity of nano silica is very good. It is very less particle size than cement and fills the pores of cementitious materials, thus improving the compressive strength of the mixes. The maximum increase in compressive strength is achieved at 3 days of testing, indicating its effect on early compressive strength. Nano silica actually affects the hydration process at early ages.
- 1% of nano silica is the optimum dosage of for maximum increase in compressive strength.

6.2 SCOPE FOR FURTHER WORK

In order to completely understand the phenomenon of working of nano silica, it is important to study the mineralogical characteristics of the cement paste matrices, along with the mechanical properties of the pastes.

REFERENCES

- Berra, M., Carassiti, F., Mangialardi, T., Paolini, A. E., & Sebastiani, M. (2012).** “Effects of nanosilica addition on workability and compressive strength of Portland cement pastes”. *Construction and Building Materials*, 35, 666-675.
- Colleparidi, M., Colleparidi, S., Skarp, U., & Troli, R. (2004).** “Optimization of silica fume, fly ash and amorphous nano-silica in superplasticized high-performance concrete”. *ACI Special Publication*, 221.
- Farzadnia, N., Abang Ali, A. A., Demirboga, R., & Anwar, M. P. (2013).** “Effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars”. *Cement and Concrete Research*, 48, 97-104.
- Hallal, A., Kadri, E. H., Ezziane, K., Kadri, A., & Khelafi, H. (2010).** “Combined effect of mineral admixtures with superplasticizers on the fluidity of the blended cement paste”. *Construction and Building Materials*, 24(8), 1418-1423.
- Hou, P. K., Kawashima, S., Wang, K. J., Corr, D. J., Qian, J. S., & Shah, S. P. (2013).** “Effects of colloidal nanosilica on rheological and mechanical properties of fly ash–cement mortar”. *Cement and Concrete Composites*, 35(1), 12-22.
- Haruehansapong, S., Pulngern, T., & Chuchepsakul, S. (2014).** “Effect of the particle size of nanosilica on the compressive strength and the optimum replacement content of cement mortar containing nano-Silica”. *Construction and Building Materials*, 50, 471-477.
- Jo, B. W., Kim, C. H., Tae, G. H., & Park, J. B. (2007).** Characteristics of cement mortar with nano-silica particles. *construction and building Materials*, 21(6), 1351-1355.
- Li, H., Xiao, H. G., Yuan, J., & Ou, J. (2004).** Microstructure of cement mortar with nano-particles. *Composites Part B: Engineering*, 35(2), 185-189.

Ltifi, M., Guefrech, A., Mounanga, P., & Khelidj, A. (2011). “Experimental study of the effect of addition of nano-silica on the behaviour of cement mortars”.*Procedia Engineering*, 10, 900-905.

Liu, X., Chen, L., Liu, A., & Wang, X. (2012). “Effect of nano-CaCO₃ on properties of cement paste”. *Energy Procedia*, 16, 991-996.

Lin, D. F., Luo, H. L., & Zhang, S. W. (2007). “Effects of nano-SiO₂ on tiles manufactured with clay and incinerated sewage sludge ash”. *Journal of Materials in Civil Engineering*, 19(10), 801-808.

Mukharjee, B. B., & Barai, S. V. (2014). “Characteristics of Mortars Containing Colloidal Nano-Silica”. *International Journal of Applied Engineering Research*,9(1), 17-22.

Pamnani, N. J., Patel, P. D., Verma, D. A., & Pitroda, J. (2013). “Comparison and Optimization of Dosage of Different Super-Plasticizers for Self Compacted Concrete Using Marsh Cone”.*International Journal of Engineering and Innovative Technology (IJEIT)* Volume, 2.

Qing, Y., Zenan, Z., Deyu, K., & Rongshen, C. (2007). “Influence of nano-SiO₂ addition on properties of hardened cement paste as compared with silica fume”. *Construction and Building Materials*, 21(3), 539-545.

Olar, R. (2011). “Nanomaterials and Nanotechnologies for Civil Engineering”.*Institutul Politehnic din Iasi. Buletinul. Sectia Constructii. Arhitectura*, 57(4).

Roussel, N., & Le Roy, R. (2005). “The Marsh cone: a test or a rheological apparatus?” *Cement and Concrete Research*, 35(5), 823-830.

Senff, L., Labrincha, J. A., Ferreira, V. M., Hotza, D., & Repette, W. L. (2009). “Effect of nano-silica on rheology and fresh properties of cement pastes and mortars”. *Construction and Building Materials*, 23(7), 2487-2491.

Shaikh, F. U. A., Supit, S. W. M., & Sarker, P. K. (2014). “A study on the effect of nano silica on compressive strength of high volume fly ash mortars and concretes”. *Materials & Design*, 60, 433-442.

Stefanidou, M., & Papayianni, I. (2012). “Influence of nano-SiO₂ on the Portland cement pastes”. *Composites Part B: Engineering*, 43(6), 2706-2710.

Zhang, M. H., & Islam, J. (2012). “Use of nano-silica to reduce setting time and increase early strength of concretes with high volumes of fly ash or slag”. *Construction and Building Materials*, 29, 573-580.

Zhu, W., Bartos, P. J. M., & Porro, A. (2004). “Application of nanotechnology in construction”. *Materials and Structures*, 37(9), 649-658.

