

**EFFECT OF CLOISITE 30B NANOCCLAY ON
MECHANICAL PROPERTIES, THERMAL BEHAVIOUR
AND MICROSTRUCTURE OF CEMENT MORTAR**

*A Dissertation submitted
in partial fulfilment of the requirements for
the award of degree of*

**MASTERS OF ENGINEERING
IN
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Submitted by

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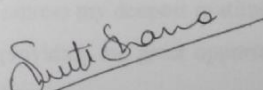
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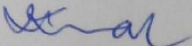

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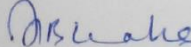
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Kunal Bisht

ABSTRACT

Nanomaterials have great potential in improving properties of the cement mortar and concrete as established by various researchers. Nanomaterials can also improve the mechanical performance, volume stability, durability, and sustainability of cement mortar and concrete. In the construction industry, several types of nanoparticles have been incorporated into cement composite in which nanoclay platelets are an example of such nanoparticles that have recently been widely used in reinforcing cement matrix because of their low cost, wide availability, high aspect ratio, well developed intercalation chemistry (surface modification) and high strength and stiffness.

This thesis presents an initial study on the effect of Cloisite 30B nanoclay on cement mortar. Cloisite 30B nanoclay was added in the varying proportions of 0%, 0.5%, 1%, 2%, 4% and 6% by the weight of cement. Initially the dispersion of nanoclay was carried out by aqueous mixing but due to improper dispersion, powder mixing was adopted. The cement mortar was prepared using the cement-sand ratio 1:3 by weight of cement with water-binder ratio (w/b) as per the consistency of the cement. The fresh mortar paste were first cured at 100% relative humidity for 24 hours and then cured in water for 28 days. The effects of varying percentages of nanoclay in cement mortar or concrete were investigated on mechanical properties which include compressive strength, split-tensile strength and flexural strength. In addition the reaction products were characterized with XRD and TGA/DSC. SEM was employed to investigate the microstructure of final product.

It was investigated that the mechanical and thermal properties of the mortar sample is improved with the addition of 2% and 4% of nanoclay but the addition of nanoclay by 6% leads to significant decrease in properties.

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CHAPTER 1

INTRODUCTION

1.1 General

Cement mortar is a building compound which is the most commonly used material on this planet which is prepared by mixing sand and cement with a specified amount of water. The cement mortar can be used for a number of applications, such as plastering over bricks or other types of masonry. This is referred as sand cement-mortar blends today often incorporate different types of materials to create various types of cement mortars.

The ingredients in cement mortar vary, which depends on the manufacturer specifications. A normal cement mortar will include both sand and cement, with lime added to the mix. Other types of aggregates may be added which depends on the texture that is preferred for the mortar. In recent years, the addition of nano- materials such as clay have helped to create cement mortar products that provide additional strength without negatively impacting the binding powers of the cement mortar.

In the last decade the performance of cement mortar has been significantly improved by applying different kinds of micro and nano-particles from fundamental research disciplines that has not been used for construction materials before. Nanotechnology seems to hold the key that allows construction and building material to replicate the features of natural systems improved until perfection during millions of years. Until today concrete has been seen as a structural material but nanotechnology can help to make it a multi-purpose smart material.

Processes occurring at the nano-scale ultimately affect the engineering properties and the performance of the bulk material. By the use of nanotechnology the structure of the fundamental calcium-silicate-hydrate (CSH) gel which is responsible for the mechanical and the physical properties of the cement pastes, including shrinkage, creep, porosity, permeability and elasticity, can be modified to obtain better durability.

“Nanotechnology is commonly defined as the understanding, control and restricting of matter on the order of nanometers (i.e., less than 100nm) to create materials with fundamentally new properties and functions”.

There are two ways to approach the nano-scale: Shrinking from the top down, or growing from the bottom up.

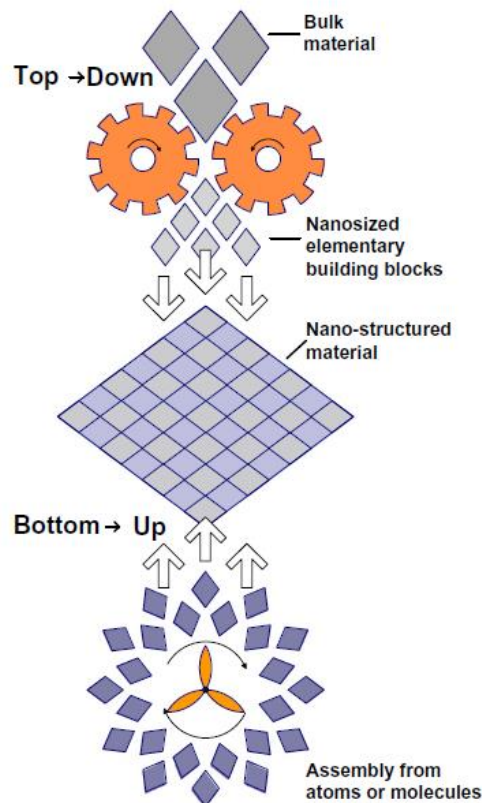


Fig. 1.1: Illustration of top-down and bottom –up approaches
(Sobolev and Ferrada, 2005)

Nanotechnology encompasses two main approaches: the “top-down” approach, in which larger structures are reduced in size to the nanoscale while maintaining their original properties without atomic-level control or deconstructed from the larger structures into their smaller composite parts. The “bottom-up” approach is also called as the “molecular manufacturing” or “molecular nanotechnology”. In this approach materials are engineered from atoms or molecular components through a process of assembly or self assembly. While most contemporary technologies rely on the “top-down” approach, molecular nanotechnology holds the great promise for breakthroughs in materials and manufacturing electronics, medicine and health care, energy, biotechnology, information technology, and national security.

The nano-particles have high surface area to volume ratio which has the potential for high chemical reactivity. The nano-particles act as a nucleus for cement which promotes the cement hydration due to its high chemical reactivity. Nano-

particle also act as nano-reinforcement and filler due to which micro-structure becomes denser and hence increases the pozzolanic activity of the cement matrix.

The potential of nanotechnology to improve the performance of cementitious material and to lead to the development of novel, sustainable, advanced cement-based composites with unique mechanical, thermal, and electrical properties is promising and many new opportunities are expected to arise in coming years.

1.2 Nanotechnology in Construction

Nanotechnology makes construction faster, cheaper, safer, and more varied. The automation of nanotechnology construction can allow for the creation of structures from advanced homes to massive skyscrapers much more quickly at much lower cost. In the coming future, Nanotechnology can be used to sense cracks in foundations of architecture and can send nanobots to repair them.

Nanotechnology is the most prominent research area that encompasses a number of disciplines such as electronics, bio-mechanics and coatings. These disciplines guide in the areas of civil engineering and construction materials. When nanotechnology is implemented in the construction of homes and infrastructure, such structures will be stronger. If buildings are stronger, then less of them will require reconstruction and less waste will be produced.

Nanotechnology in construction involves the use of nano-particles such as alumina and silica. The manufacturers are also investigating the methods of producing nano-cement. If cement with nano-size particles can be manufactured and processed, it will open up a large number of opportunities in the fields of ceramics, high strength composites and electronic applications.

Nanomaterials have a high cost as compared with conventional materials, which means that they are not likely to feature in high-volume building materials.

1.3 Nanomaterials Used for Civil Engineering Applications

1.3.1 Titanium dioxide nanoparticles (TiO₂)

The titanium dioxide nano-particles 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.

1.3.2 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 reduces bleeding water and segregation by the improvement of the cohesiveness.

1.3.3 Zinc oxide nanoparticles (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.

1.3.4 Silver nanoparticles

Silver is an especially attractive metal due to its remarkable size and shape dependent optical properties, highest efficiency of Plasmon excitation, and highest electrical and thermal conductivity in the bulk among all metals. These special properties have led to promising applications of silver nanoparticles catalysis for the selective oxidation of styrene, environmentally friendly antimicrobial coatings, real-time optical sensors, printed electronics and photonics. Silver nanoparticles are nanoparticles of silver i.e. silver particles of between 1 nm and 100 nm in size. While frequently described as being silver some are composed of a large percentage of silver oxide due to their large ratio of surface to bulk silver atoms.

Over the last decade silver nanoparticles have found applications in catalysis, optics, electronics and other areas due to unique size-dependent optical, electrical and magnetic properties. Currently most of the applications of silver nanoparticles are in antibacterial/antifungal agents in biotechnology and bioengineering, textile engineering, water treatment, and silver-based consumer products.

1.4 Types of Nanoclay

The extraordinary chemical and physical properties of materials at the nanometer scale enable novel applications ranging from structural strength enhancement to self-cleaning properties. Consequently, various nanoclay has been used in the cement mortar to make it a real “smart” material.

The nanoclays are nanoparticles of layered mineral silicates. Nanoclays are organized into several parts which depend upon its chemical composition and nanoparticle morphology, such as montmorillonite, cloisite, bentonite, kaolinite, hectorite, and halloysite.

1.4.1 Montmorillonite

Nano-montmorillonite (NM) belongs to general mineral group of clays. The particle shape of montmorillonite is sheet like structure, whose dimensions in two directions far exceed its thickness. It consists of a three layered structure of aluminium which is sandwiched between two layers of silicon. Montmorillonite is the major ingredient of the volcanic ash called bentonite. It has an ability to swell to many times its original weight and volume when it absorbs water.

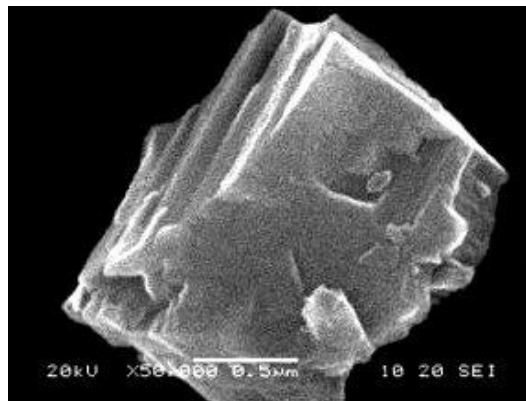


Fig. 1.2: SEM of montmorillonite (www.googleimages.com)

1.4.2 Kaolinite

Kaolinite is a clay mineral and also a part of the group of industrial minerals. The chemical composition of Kaolinite is $Al_2Si_2O_5(OH)_4$. It is having a layer of silicate. In Kaolinite one part of the tetrahedral structure connected to the oxygen atoms to one octahedral sheet of alumina octahedral. The rocks that are rich in kaolinite are also known as kaolin or china clay. Kaolinite is a soft, earthy, usually off-white mineral

which is produced by the chemical weathering of aluminium silicate minerals like feldspar.

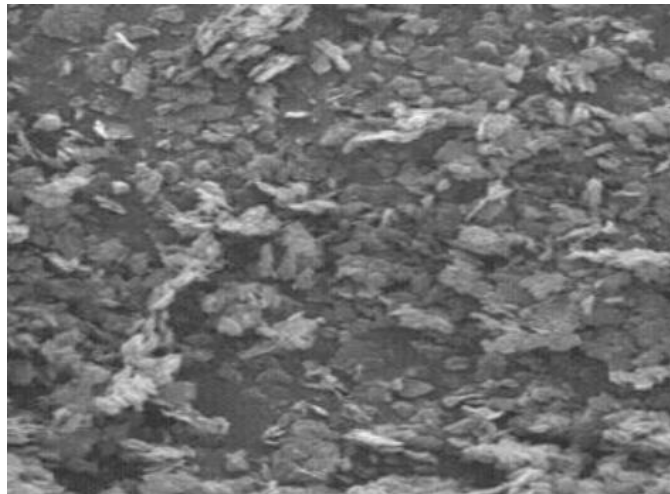


Fig. 1.3: SEM image of Kaolinite (www.googleimages.com)

1.3.3 Halloysite nanoclay

Halloysite nanoclay is one the subcategory of the nanoclay. It is a two-layered aluminosilicate with a hollow nano-tubular structure which is composed of hydrated aluminum oxide and silicon oxide that can be used as a component in coatings and nano-composites. Halloysite nanoclay is usually immediately available in most volumes, including bulk orders. The nanoscale elemental powders and suspensions, as alternative high surface area forms, may be considered.

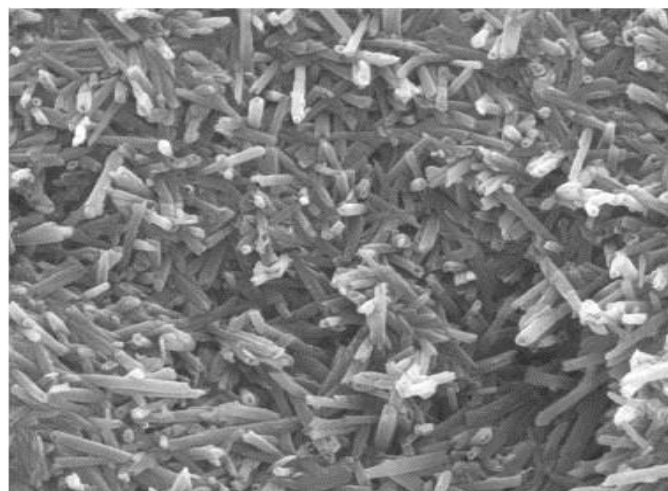
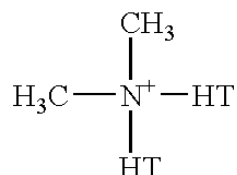


Fig. 1.4: SEM image of Halloysite nanoclay (www.googleimages.com)

1.3.4 Cloisite

Cloisite is an organically modified montmorillonite with quaternary ammonium salt. The chemical formula of montmorillonite is $(\text{Na}, \text{Ca})_{0.33} (\text{Al}, \text{Mg})_2 \text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot n\text{H}_2\text{O}$ having a molecular weight of 540.46. The chemical structure of organic modifier which dimethyl dehydrogenated tallow and the chemical structure is explained below.



Cloisite is of different types such as Cloisite 10A, Cloisite 20A, Cloisite 30B, Cloisite Na+.

Table 1.1: Physical and chemical properties of different types of Cloisite Nanoclay

S.No	Density g/cc	Moisture Content	Average Size	Basal Spacing, d_{001}	Colour	Modifier Concentration
Cloisite 10A	1.90	<2%	6 μm	19.2 Å	Off- white	125meq ^a /100g clay
Cloisite 20A	1.77	<2%	6 μm	19.2Å	Off- white	95meq ^a /100g clay
Cloisite 30B	1.98	<2%	6 μm	18.5 Å	Off- white	90 meq ^a /100g clay
Cloisite Na+	2.86	<2%	6 μm	11.7Å	Off- white	92.6meq ^a /100g clay

The type of nanoclay used in the present investigation is Cloisite 30B. The choice of the type of the nanoclay was done on the basis of past published research whereby very little focus has been on this type of nanoclay and also dependent on the availability of the nanoclay.

1.5 Details of Cloisite 30B

1.5.1 Cloisite 30B

Cloisite 30B nanoclay is a siliceous and aluminous material. Cloisite 30B nanoclay belongs to a mineral admixture which improves the properties of the blended cement. Cloisite 30B is off-white in colour as shown in **Fig. 1.3**.



Fig. 1.3 Cloisite 30B sample

Fig. 1.4 represents the SEM image of the Cloisite 30B nanoclay shows the presence of layered aluminium silicate.

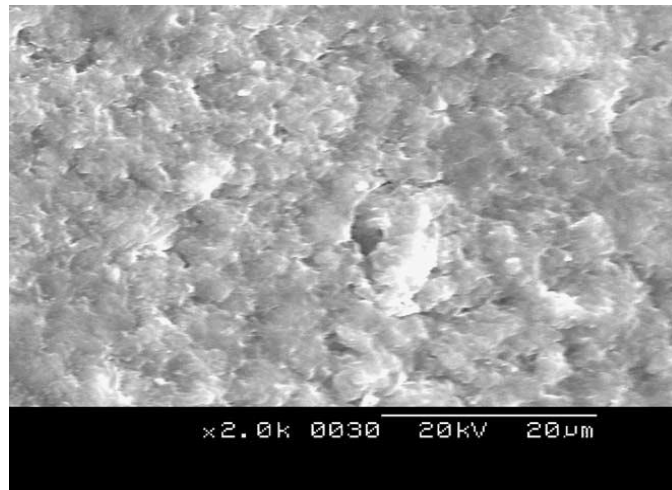


Fig. 1.4: SEM image of Cloisite 30B (www.googleimages.com)

1.5.2 Effect of Cloisite 30B nanoclay on cement mortar

Cloisite 30B nanoclay has extreme fineness of the nanoclay and very high amorphous silicon dioxide content makes Cloisite 30B nanoclay extremely reactive pozzolanic

material. As the Portland cement in mortar begins to react chemically, it releases calcium hydroxide. The Cloisite 30B nanoclay reacts with this calcium hydroxide to form additional binder material called calcium silicate hydrate (CSH), which is very similar to the calcium silicate hydrate formed from Portland cement. It is an additional binder that gives improved properties to the cement mortar.

1.6 Advantages of Nanoclay

Cement mortar is the most commonly used construction material on planet. It presents a higher permeability that allows water and other aggressive elements to enter which leads to carbonation and chloride ion attack, resulting in corrosion problems. Use of nanoclay in this field proves to be a great enrichment to the cement mortar to improve its properties. Following are some of the advantages of the using nanotechnology in cement mortar:

- Nanoclay helps to make mortar a multipurpose smart functional material.
- The use of nanoclay is used to increase the strength and durability of cementitious composites as well as for pollution reduction.
- Production of thermal insulation materials with a performance ten times commercial current options.
- Production of coats and thin films self-cleansing ability and self colour change to minimize energy consumption.
- Production of cheap corrosion free steel.
- Production of nano-sensors and materials with sensing ability and self-repairing ability.

To date nanoclay applications and advances in the construction and building materials fields have been uneven. Exploitation of nanoclay in cement mortar on a commercial scale remains limited with few results successfully converted into marketable products. Although nanoclay has potential to be the key to a brand new world in the field of construction but scientists are still trying to grasp their astonishing complexities.

1.7 Closing Remarks

This chapter deals with various types of material in civil engineering applications with main focus on nanoclay. Undoubtedly, nanoclay has the potential to be a key to the

brand new world in the field of construction and building materials. Until today cement mortar has primarily been seen as a structural material but nanoclay helps to make it as a multi-purpose “smart material”. Since the present study deals with the effect of nanoclay addition to cement mortar paste, the next chapter presents a review of the work done so far in the use of nanoclay in the cementitious material.

2.1 General

This chapter presents an exhaustive review of the latest works done using nanoclay as filler in cement mortar. The important contributions of the researchers are discussed and how nanoclay has affected the cementitious material properties. The works which have contributed deeply for understanding the effect of nanoclay (NC) in cement mortar are also included in this chapter.

Main focus is to discuss the effect of nanoclay on mechanical, thermal, chemical and micro-structure properties in cementitious materials.

2.2 Effect of NC on Compressive Strength

Chang et al., 2007 studied the material properties of Portland cement paste with the addition of montmorillonite nanoclay. In this case montmorillonite nanoclay was added at four different proportions i.e. 2%, 4%, 6% and 8% as shown in **Fig. 2.1**.

From **Fig. 2.1** it is clear that compressive strength of cement paste composite with the addition of montmorillonite nanoclay at different proportions was checked at four ages i.e. 7 days, 14 days, 28 days and 56 days. It is clear from the **Fig. 2.1** that the optimum value of the compressive strength was obtained at the addition of 0.6% of montmorillonite nanoclay. It is observed from the figure that the maximum percentage of strength increase is about 13.24% which occurs at the age of 56 days.

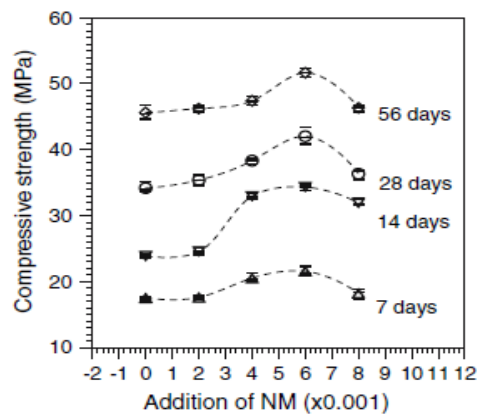


Fig. 2.1: Compressive strength of cement paste at various additions of NM and ages (Chang et al., 2007)

In this case there is small increase in the compressive strength which indicates that some additional strong bonds may be formed due to the addition of montmorillonite nanoclay from which latter effect can be expected.

Morsy et al., 2010 presented the effect of nanoclay on mechanical properties and microstructure of Ordinary Portland cement mortar. In this case nano-metakaolin was added at four different proportions i.e. 2%, 4%, 6% and 8% as shown in **Fig. 2.2**.

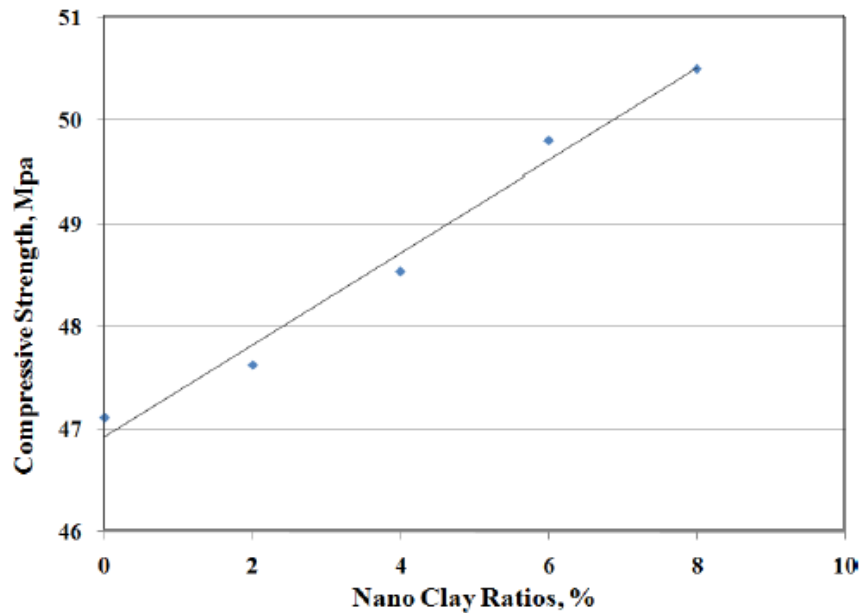


Fig. 2.2: Compressive strength of NMK mortar hydrated for 28 days (Morsy et al., 2010)

From **Fig. 2.2** it is clear that compressive strength of cement paste composite with the addition of nano-metakaolin at different proportions was checked at 28 days. It is clear from the figure that optimum value of strength obtained at the addition of 8% of nano-metakaolin with the replacement of 8% of Ordinary Portland cement.

It is observed from the figure that there is 7% increase in the compressive strength with addition of 8% nano-metakaolin as compared to mortar mix. The nano-metakaolin belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of nano-metakaolin fills the voids of the cement mortar and make the mixture denser and the mechanical property is improved due to pozzolanic reaction of nano-metakaolin with free lime.

In this case there is small increase in compressive strength due to agglomeration of nano-metakaolin particles around cement grains which decreases the cement hydration.

Morsy et al., 2010 presented the hybrid effect of carbon nanotube and nanoclay on physico-mechanical properties of cement mortar. In this case CNT is added at different proportions i.e. 0.005%, 0.02%, 0.05% and 0.1% and the proportion of nano-metakaolin in each case remain same i.e. 6%.

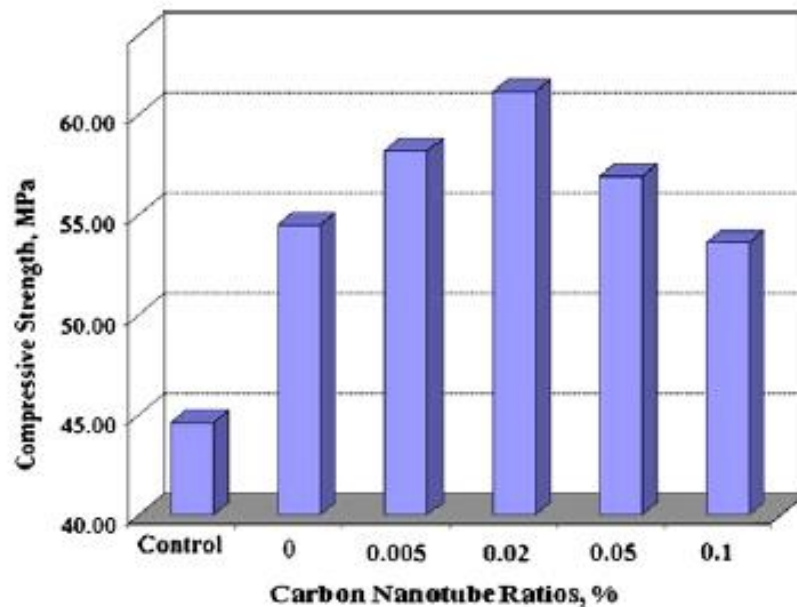


Fig. 2.3: Compressive strength of blended cement mortar containing exfoliated 6%NMK versus CNT's ratio's at 28 days of hydration (Morsy et al., 2010)

From **Fig. 2.3** it is clear that compressive strength of cement paste composite with the addition of CNT at different proportions and nano-metakaolin at same proportions was checked at 28 days. It is clear from the figure that optimum value of strength obtained at the addition of 0.02% CNT and 6% nano-metakaolin with the replacement of 6% of Ordinary Portland cement.

It is observed from the figure that there is 18% increase in the compressive strength with addition of 0.02% CNT and 6% nano-metakaolin as compared to mortar mix. The nano-metakaolin belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of nano-metakaolin acts as a filler and fills the voids of the cement mortar and make the

mixture denser and the mechanical property is improved due to pozzolanic reaction of nano-metakaolin with free lime which adds the bonding strength and solid volume which results into higher compressive strength.

Aly et al., 2011 presented the effect of nanoclay particles on mechanical, thermal and physical behaviour of waste-glass cement mortar. In this case waste-glass is added at different proportions i.e. 5%, 20%, 30% and 50% and the proportion of Cloisite 30B nanoclay in each case remain same i.e. 2.5% with the replacement of equal proportion of the Ordinary Portland cement.

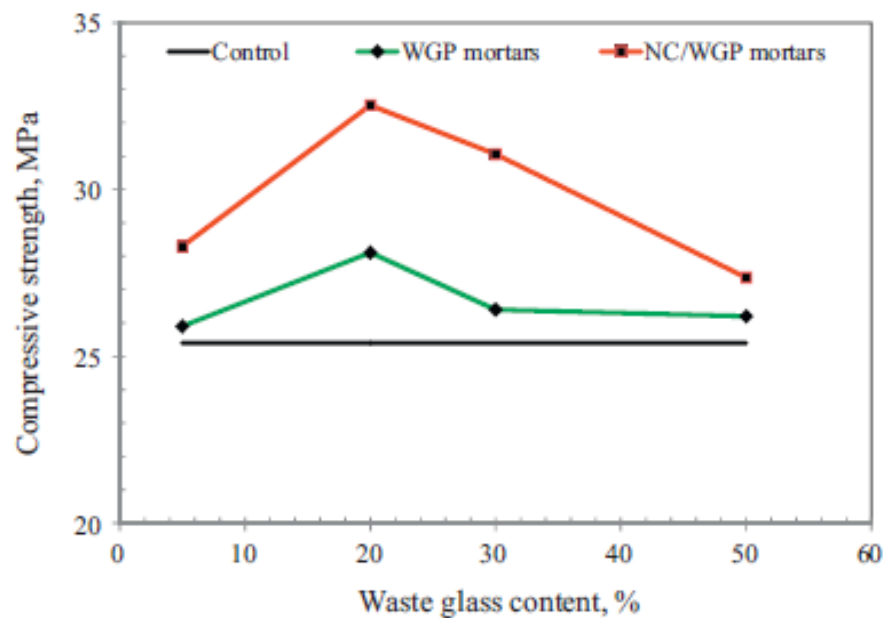


Fig. 2.4: 28-Day compressive strength of target mortars (Aly et al. 2011)

From Fig. 2.4 it is clear that compressive strength of cement paste composite with the addition of WGP at different proportions and Cloisite 30B nanoclay at same proportions was checked at 28 days. It is clear from the figure that optimum value of strength obtained at 20% with the addition of only WGP and after 20% the strength starts decreasing.

By adding Cloisite 30B particles in WGP there is 28% increase in the compressive strength as compared to the control specimen.

The increase in compressive strength shows that Cloisite 30B particles and finely ground WGP improves the mechanical properties of the cement paste.

Salami et al., 2013 presented the physico-mechanical characteristics of blended white cement pastes containing thermally activated ultrafine nanoclays. In this case nano-metakaolin was added in different proportions i.e. 2%, 4%, 6%, 8%, 10%, 12% and 14% by the weight of cement. In this case there is replacement of cement to the proportion of nano-metakaolin added.

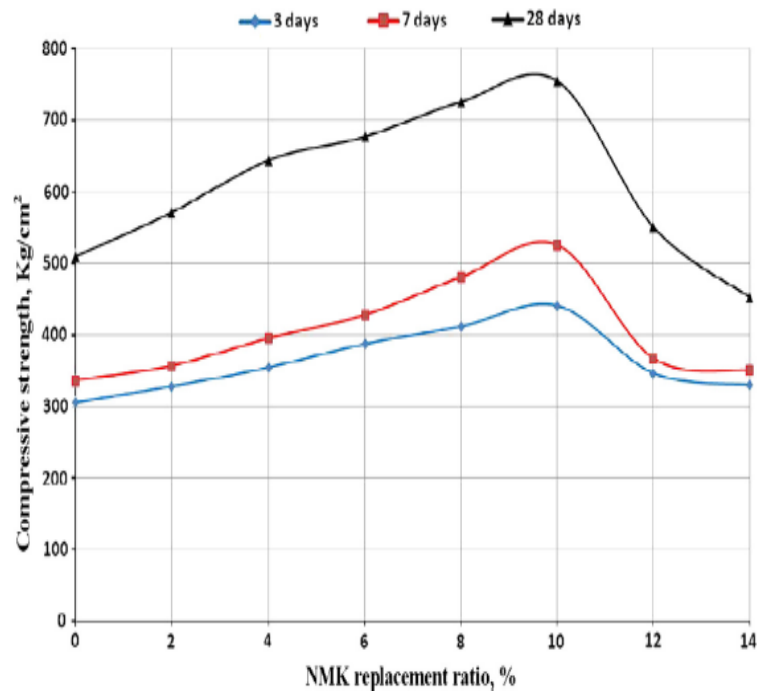


Fig. 2.5: Variation of compressive strength of NMK-modified cement pastes with NMK ratios at different curing ages (Salami et al., 2013)

From **Fig. 2.5** it is clear that compressive strength of cement paste composite with the addition of nano-metakaolin at different proportions was checked at 28 days. It is clear from the figure that optimum value of strength obtained at 10% with the addition of nano-metakaolin. Figure represents that at 28 days there is 48% increase in compressive strength.

The presence of high silica content, ultra fineness and specific surface area are the main reason for increase in the compressive strength.

Farzadnia et al., 2013 presented the effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars. In this

case halloysite nanoclay was added in different proportions i.e. 1%, 2% and 3% by the weight of cement.

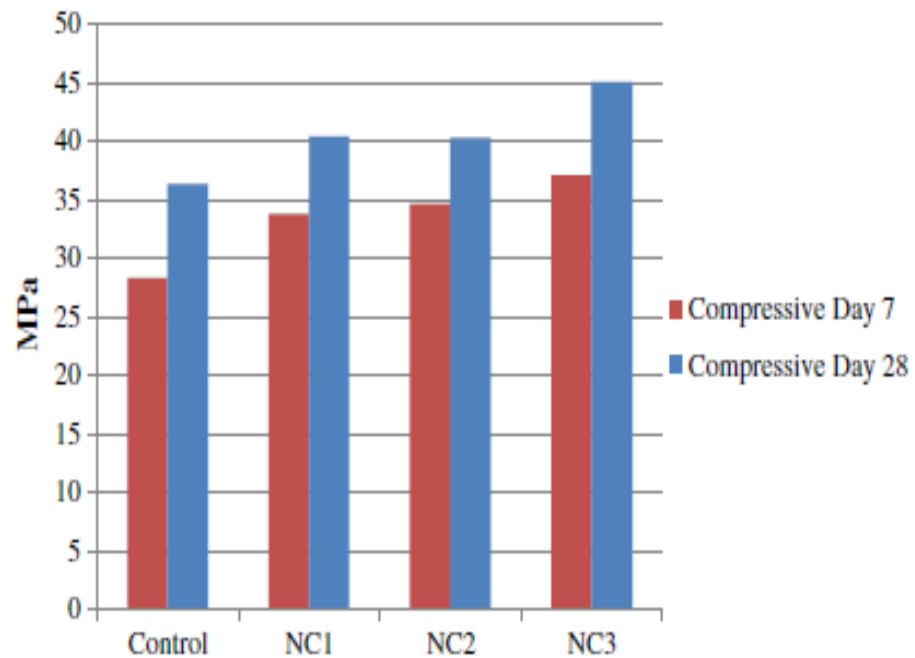


Fig. 2.6: Compressive strength of control, NC1, NC2, NC3 samples at 7 and 28 days (Farzadnia et al., 2013)

From **Fig. 2.6** it is clear that compressive strength of cement paste composite with the addition of halloysite nanoclay at different proportions was checked at 7 and 28 days. It is clear from the figure that optimum value of strength obtained at 3% with the addition of halloysite nanoclay. Figure represents that with addition of 3% halloysite nanoclay at 28 days there is 24% increase in compressive strength as compared to control samples.

The presence of high silica content, ultra fineness and specific surface area are the main reason for increase in the compressive strength.

2.3 Effect of NC on Flexural Strength

Aly M. et al., 2011 presented the effect of nanoclay particles on mechanical, thermal and physical behaviours of waste-glass cement mortar. In this case waste-glass is added at different proportions i.e. 5%, 20%, 30% and 50% and the proportion of Cloisite 30B nano-clay in each case remain same i.e. 2.5% with the replacement of equal proportion of the Ordinary Portland cement.

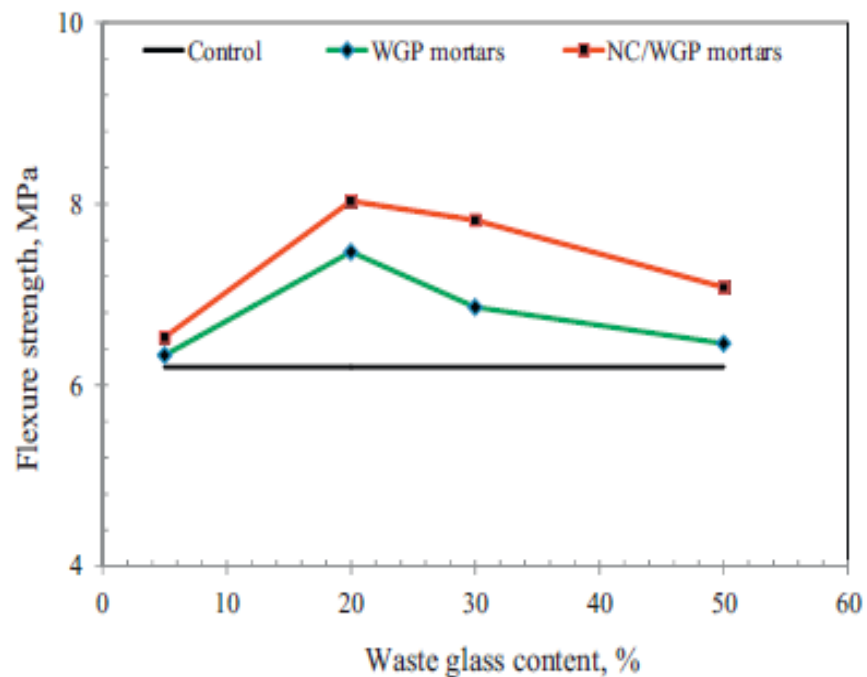


Fig. 2.7: 28-Day flexural strength of target mortars (Aly et al., 2011)

From **Fig. 2.7** it is clear that flexural strength of cement paste composite with the addition of WGP at different proportions and Cloisite 30B nanoclay at same proportions was checked at 28 days. It is clear from the figure that optimum value of strength obtained at 20% with the addition of only WGP and after 20% the strength starts decreasing.

By adding Cloisite30B particles in WGP there is 29% increase in the flexural strength as compared to the control specimen.

The increase in compressive strength shows that Cloisite 30B particles and finely ground WGP improves the mechanical properties of the cement paste.

Salami et al., 2013 presented the physico-mechanical characteristics of blended white cement pastes containing thermally activated ultrafine nanoclays. In this case nano-metakaolin was added in different proportions i.e. 2%, 4%, 6%, 8%, 10%, 12% and 14% by the weight of cement. In this case there is replacement of cement to the proportion of nano-metakaolin added.

From **Fig. 2.8** it is clear that flexural strength of cement paste composite with the addition of nano-metakaolin at different proportions was checked at 28 days. It is clear from the **Fig. 2.8** that optimum value of strength obtained at 10% with the

addition of nano-metakaolin. **Fig. 2.8** represents that at 28 days there is 36.2% increase in flexural strength.

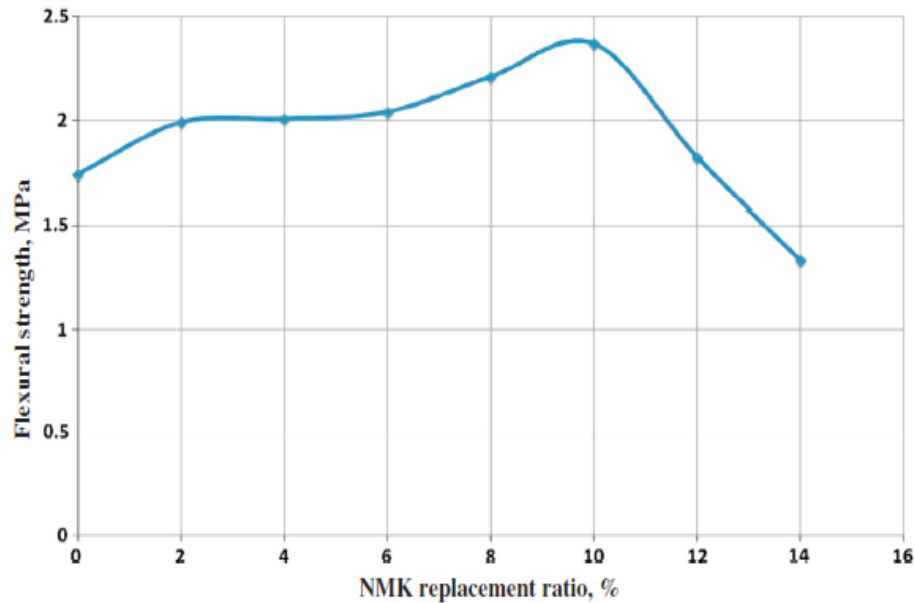


Fig. 2.8: Variation of flexural strength of NMK- modified cement pastes with NMK ratio at 28days of curing (Salami et al., 2013)

The nano-metakaolin particles act as filler which act as a fiber between hydration products which lead to bridging of micro cracks in the matrix and provide resistance to the crack propagation and also due to the formation of C-S-H which is formed by the reaction of alumino-silicate containing NMK with calcium hydroxide which makes the cement paste denser.

Hakamy et al., 2014 presented the characteristics of hemp fabric reinforced nanoclay cement nanocomposites. In this case Cloisite 30B nanoclay was added at different proportions i.e. 1%, 2% and 3%.

From **Fig. 2.9** it is clear that flexural strength of cement paste composite with the addition of Cloisite 30B nanoclay at different proportions was checked at 28 days. It is clear from the figure that optimum value of strength obtained at 1% with the addition of Cloisite 30B nanoclay. Figure represents that at 28 days there is 26.2% increase in flexural strength as compared to HF reinforced cement composite.

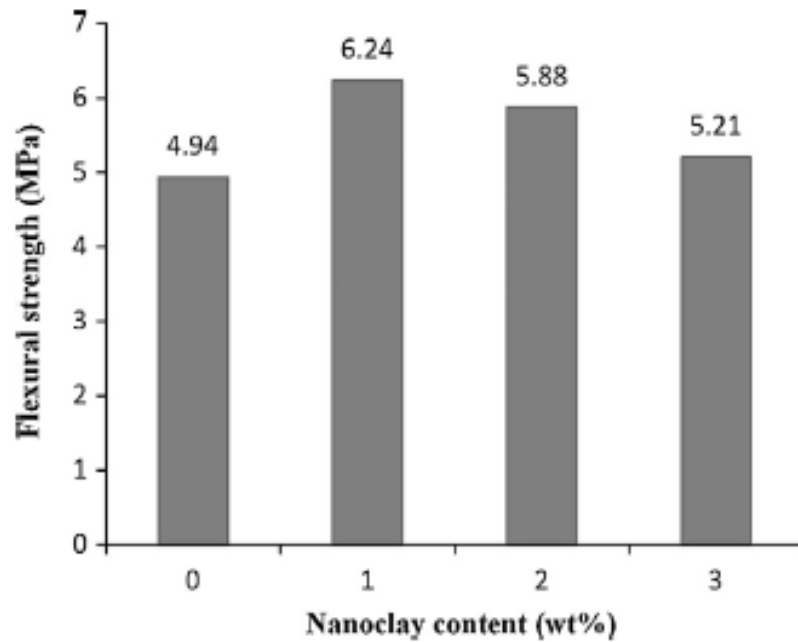


Fig. 2.9: Variation of flexural strength as a function of nanoclay content for HF reinforced cement composite and HF reinforced nanocomposite (Hakamy et al., 2014)

The improvement of flexural strength is mainly due to filling effect in which nanoclay particles filled the voids or pores in cement paste in which nanoparticles are uniformly dispersed and also due to the formation of C-S-H which is formed by the reaction of aluminosilicate containing NMK with calcium hydroxide which makes the cement paste denser.

2.4 Effect of NC on Split Tensile Strength

Morsy et al., 2010 presented the effect of nano-clay on mechanical properties and microstructure of Ordinary Portland cement mortar. In this case nano-metakaolin was added at four different proportions i.e. 2%, 4%, 6% and 8% as shown in **Fig. 2.10**.

From **Fig. 2.10** it is clear that split tensile strength of cement paste composite with the addition of nano-metakaolin at different proportions was checked at 28 days. It is clear from the figure that optimum value of strength obtained at 8% with the addition of nano-metakaolin. It is observed from the figure that tensile strength of NMK mortar increases with increase in the percentage of NMK ratio. Figure represents that at 28 days there is 33.33% increase in flexural strength as compared to control mix.

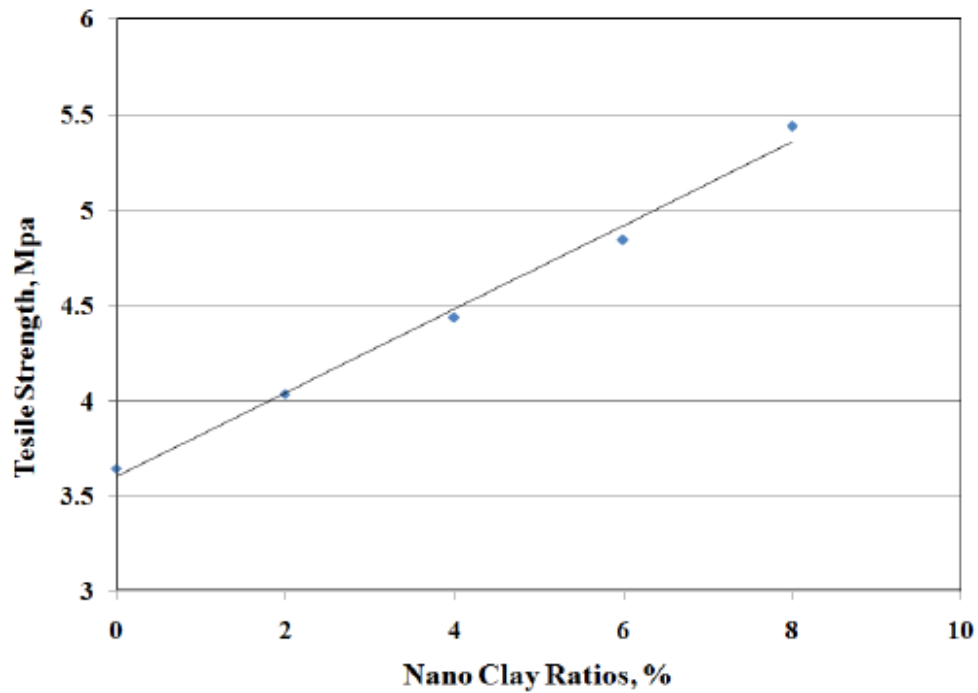


Fig. 2.10: Tensile strength of NMK mortar hydrated for 28 days (Morsy et al., 2010)

The nano-metakaolin belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of nano-metakaolin fills the voids of the cement mortar and make the mixture denser and the mechanical property is improved due to pozzolanic reaction of nano-metakaolin with free lime.

2.5 Effect of NC on Water Absorption Test

Farzadnia et al., 2013 presented the effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars. In this case halloysite nanoclay was added in different proportions i.e. 1%, 2% and 3% by the weight of cement.

From **Fig. 2.11** it is clear that water absorption test of cement paste composite with the addition of halloysite nanoclay at different proportions was checked at 28 days and then oven dried at 105°C for 48 hours. From **Fig. 2.11** it is clear that with the addition of nanoclay the rate of water absorption decreases in the voids and shows denser microstructure. Figure represents that at 28 days for NC2 samples there must be an exception due to decrease in gel/space ratio.

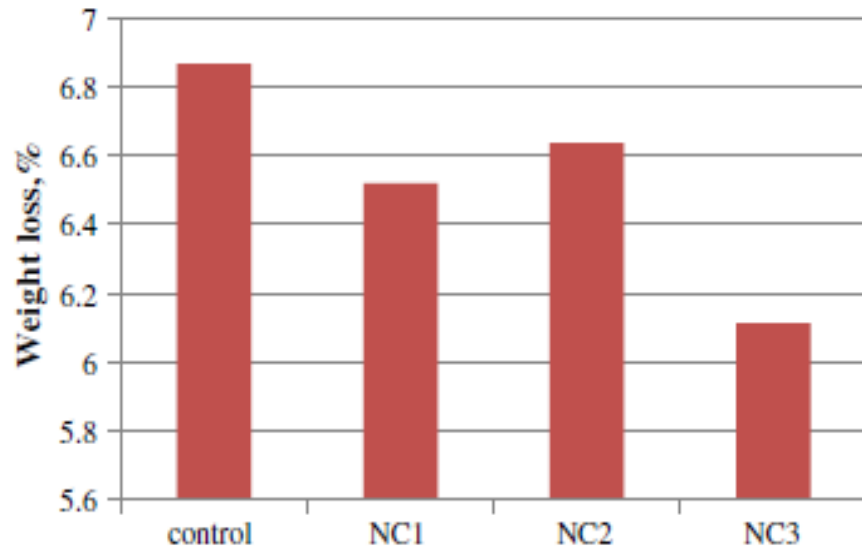


Fig. 2.11: Weight loss of control, NC1, NC2 and NC3 samples due to water evaporation (Farzadnia et al., 2013)

The NC2 samples have more permeable pores than NC1 and NC3 samples which may be due to high shrinkage after 48 hours of oven drying.

2.6 Effect of NC on pH level

Farzadnia et al., 2013 presented the effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars. In this case halloysite nanoclay was added in different proportions i.e. 1%, 2% and 3% by the weight of cement.

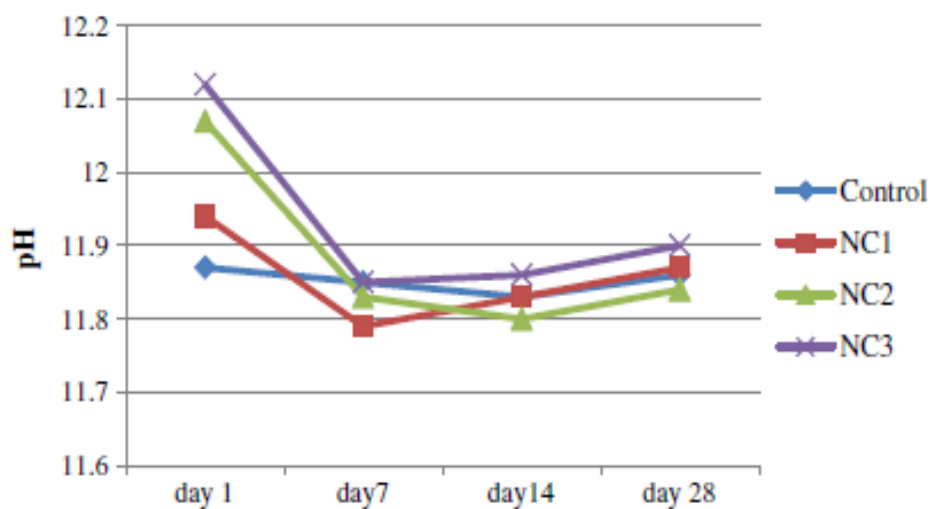


Fig. 2.12: pH levels of control, NC1, NC2 and NC3 samples at 1st, 7th, 14th and 28th days (Farzadnia et al., 2013)

From **Fig. 2.12** it is clear that ph test of cement paste composite with the addition of halloysite nanoclay at different proportions was checked at 1st, 7th, 14th and 28th days. From **Fig. 2.12** it is clear that with the addition of nanoclay the rate of water absorption decreases in the voids and shows denser microstructure. Figure represents that at 28 days for NC2 samples there must be an exception due to decrease in gel/space ratio.

The NC2 samples have more permeable pores than NC1 and NC3 samples which may be due to high shrinkage after 48 hours of oven drying.

2.7 X- Ray Diffraction (XRD) Examination

Chang et al., 2007 studied the material properties of Portland cement paste with the addition of montmorillonite nanoclay. In this case samples are observed under XRD examination.

In this case two samples were studied under XRD. In which first sample having composition of hardened cement paste and second sample having composition of hardened cement paste with montmorillonite nanoclay in which the amount of clay is 0.6% which was added along with cement paste in the second composition.

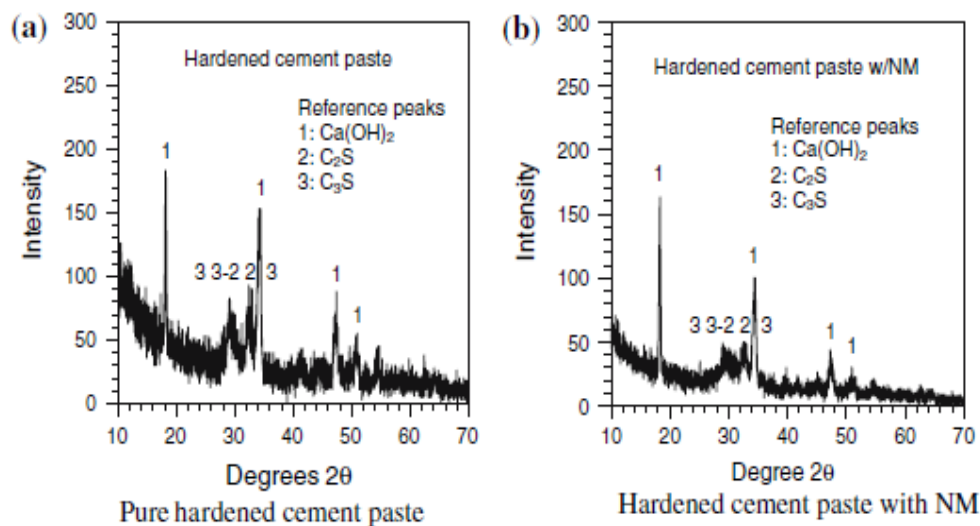


Fig. 2.13: Typical XRD patterns of hardened Portland cement paste (a) without NM (b)with 0.6% added NM (Chang et al., 2007)

The CH has a composition of a well defined crystalline structure. From **Fig. 2.13** it has been concluded that four major peaks were formed at 18.00°, 34.10°, 47.12° and 50.81°.

From **Fig. 2.13** it is clear that the diffracted intensity in case of pure hardened cement paste is 183.0 where as the diffracted intensity in case of 0.6% added NM is 163.0 which imply that there is 10.93% decrease in diffracted intensity with the addition of nanoclay.

From **Fig. 2.13** it is also clear that the microstructure of tricalcium silicate (C_3S) and dicalcium silicate (C_2S) exist at 2θ from 29° to 35° of XRD. It has been concluded that with the addition of nano-clay, the intensities of tricalcium silicate (C_3S) and dicalcium silicate (C_2S) of hardened Portland cement also becomes smaller due to the production of C-S-H gel from pozzolanic reaction.

Salami et al., 2013 presented the physico-mechanical characteristics of blended white cement pastes containing thermally activated ultrafine nanoclays. In this case nano-metakaolin was added in different proportions i.e. 2%, 4%, 6%, 8%, 10%, 12% and 14% by the weight of cement. In this case there is replacement of cement to the proportion of nano-metakaolin added.

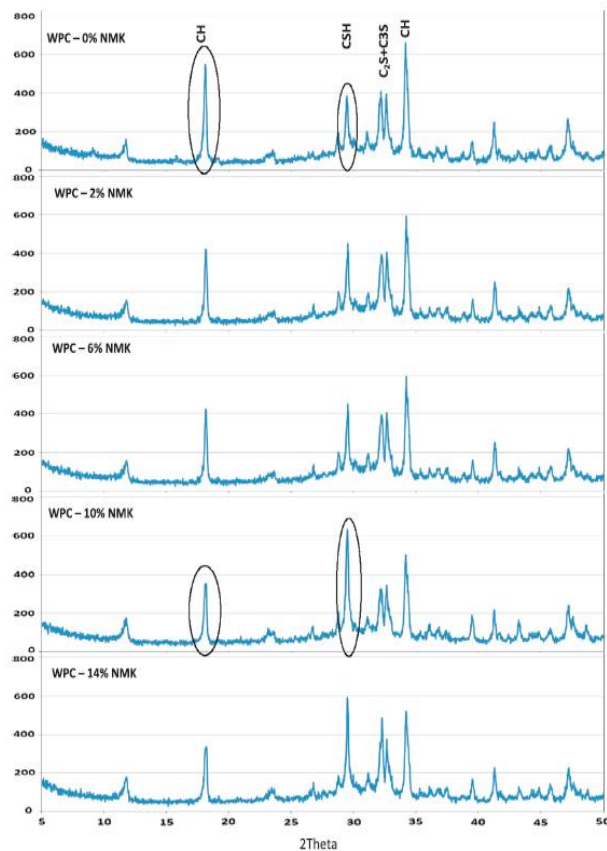


Fig. 2.14: XRD patterns for plain and NMK-modified cement pastes hydrated for 28days (Salami et al., 2013)

In this case samples were studied under XRD. **Fig. 2.14** shows the XRD pattern for plain cement and NMK modified cement pastes with the addition of nanoclay from 2% to 14%. These samples were hydrated for 28 days.

The main compounds which are detected under XRD are calcium silicate hydrate (CSH), calcium aluminate hydrate (CAH) and calcium hydroxide (CH). From **Fig. 2.14** it is clear that with increasing NMK amount CH peaks goes on decreasing whereas in case of C-S-H with addition of more NMK the peaks goes on increasing.

Aly et al., 2011 presented the effect of nanoclay particles on mechanical, thermal and physical behaviours of waste-glass cement mortar. In this case waste-glass is added at different proportions i.e. 5%, 20%, 30% and 50% and the proportion of Cloisite 30B nanoclay in each case remain same i.e. 2.5% with the replacement of equal proportion of the Ordinary Portland cement.

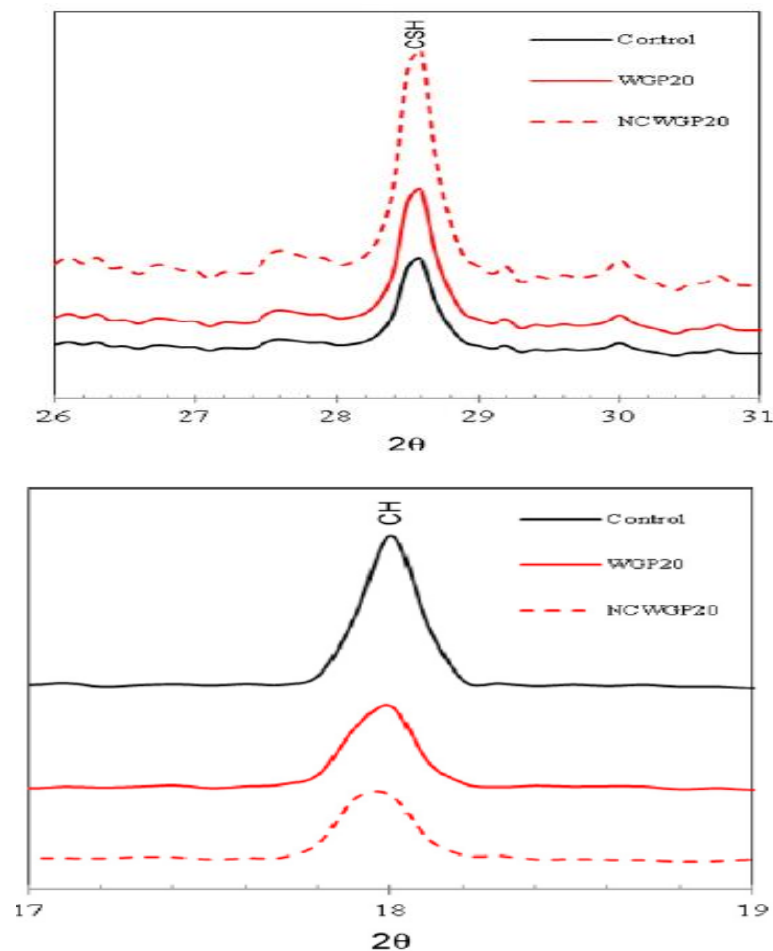


Fig. 2.15: XRD pattern for control, WGP 20 and NCWGP 20 specimens (Aly et al., 2011)

From **Fig. 2.15** it is clear that XRD examination was conducted on some of the specimens of Portland cement which include control mix, WGP 20 and NCWGP 20 which are hydrated for 28 days. For comparison the peak of CH is selected at 18° and the peak of CSH is selected at 28.6° as shown in **Fig. 2.15**.

From **Fig. 2.15** it is clear that sharp peak of CH is observed in control mix which represents the pure hydration product. With the addition of WGP20 and NCWGP20 the intensity of CH peak goes on decreasing due to consumption of CH in the pozzolanic reaction. It is also clear from the figure that intensity of CSH is more in NCWGP20 as compared to control mix.

Farzadnia et al., 2013 presented the effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars. In this case halloysite nanoclay was added in different proportions i.e. 1%, 2% and 3% by the weight of cement.

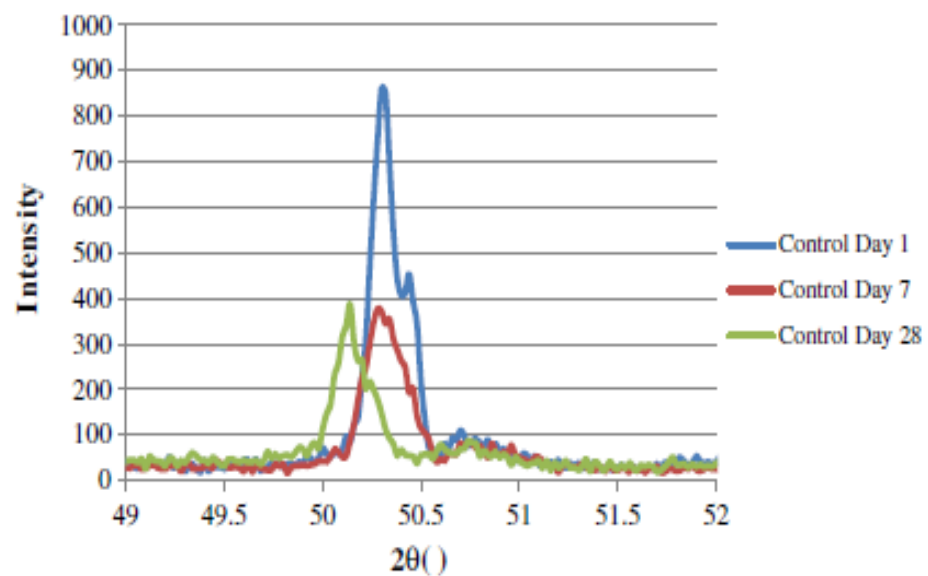


Fig. 2.16: XRD analysis in control samples at 1st, 7th and 28th days (Farzadnia et al., 2013)

From **Fig. 2.16** it is clear that control samples are examined under XRD analysis at the age of 1, 7 and 28 days. For control samples the amount of CH is much higher in the first week as we compare it with 7 and 28 day samples. At 7 and 28 days the amount of CH is nearly same for control samples because of the addition of silica fume which accelerated the consumption of Portlandite and formation of calcium silicate hydrate.

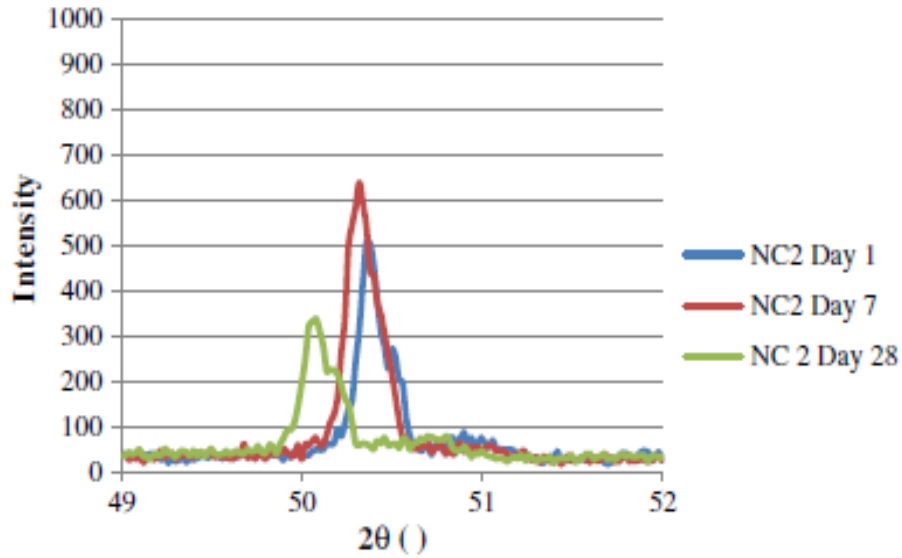


Fig. 2.17: XRD analysis of $\text{Ca}(\text{OH})_2$ in NC2 samples at 1st, 7st and 28th days (Farzadnia et al., 2013)

From **Fig. 2.17** it is clear that samples containing nanoclay are examined under XRD analysis at the age of 1, 7 and 28 days. In this case the CH sample at 1st day is less than 7th day which means that addition of nanoclay increased the consumption of Portlandite.

2.8 Scanning Electron Microscopy (SEM)

Morsy et al., 2010 presented the effect of nanoclay on mechanical properties and microstructure of Ordinary Portland cement mortar. In this case nano-metakaolin was added at four different proportions i.e. 0%, 4%, and 8% and the samples are hydrated for 28 days.

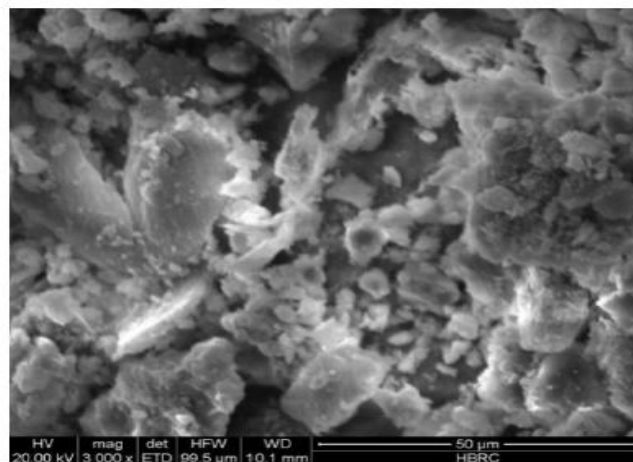


Fig. 2.18: SEM micrograph of cement mortar containing 0%NMK (Morsy et al., 2010)

It is clear from the **Fig. 2.18** that micrograph represents the hydrated products such as CSH, CH and calcium silicate aluminates hydrate. It is clear from the figure that CSH gel existed in the form of clusters, lapped and joined together by many needle hydrates and CH crystals are also present in the cement paste. In this case the texture of the cement paste is not compact and denser as there is no material used which act as filler and fills the pores.

In case of samples containing 4% and 8% nano-metakaolin, nanoclay act as a filler material which fills the pores and makes the material denser and compact. The samples containing NMK are shown in **Fig. 2.19** and **2.20**.

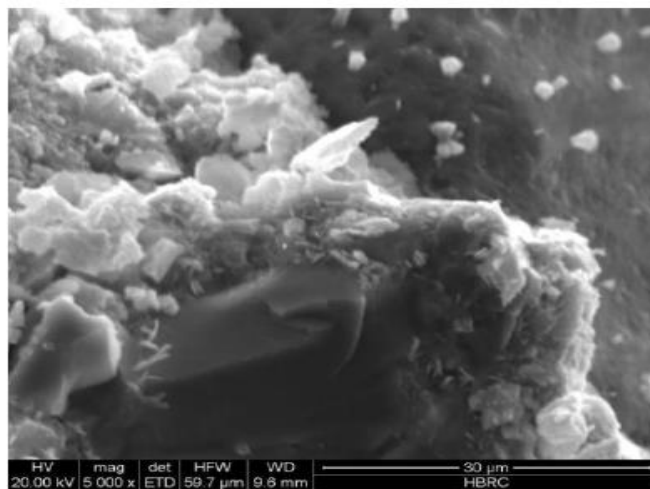


Fig. 2.19: SEM micrograph of cement mortar containing 4%NMK (Morsy et al., 2010)

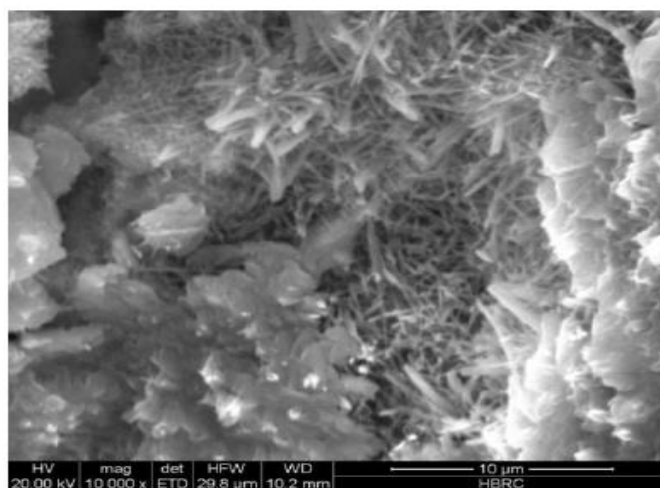


Fig. 2.20: SEM micrograph of cement mortar containing 8%NMK (Morsy et al., 2010)

The addition of NMK in cement mortar improves the microstructure and strength. When small quantity of nano-particles are uniformly dispersed in the cement mortar then the hydrate products which are formed gets deposited on the nano-particles due to its greater surface energy during hydration.

In case when the nano-particles are not dispersed well, that is a case of extensive nano-particles content, the aggregating nano-particles creates weak zones in the form of voids. In that case homogeneous hydrate was not formed and results into low strength.

Morsy et al., 2010 presented the hybrid effect of carbon nano-tube and nanoclay on physico-mechanical properties of cement mortar. In this case CNT is added at different proportions i.e. 0.005%, 0.02%, 0.05% and 0.1% and the proportion of nano-metakaolin in each case remain same i.e. 6%. The samples are hydrated for 28 days.

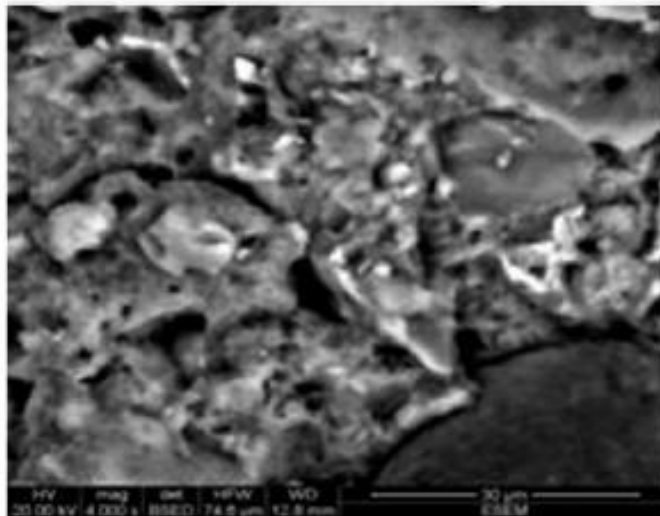


Fig. 2.21: SEM micro graph of control mortar (Morsy et al., 2010)

From **Fig. 2.21** the microstructure of the OPC shows the presence calcium silicate hydrates (CSH). The presence of calcium hydroxide (CH) crystals and air voids between the hydrated phases are also shown in the **Fig. 2.21**.

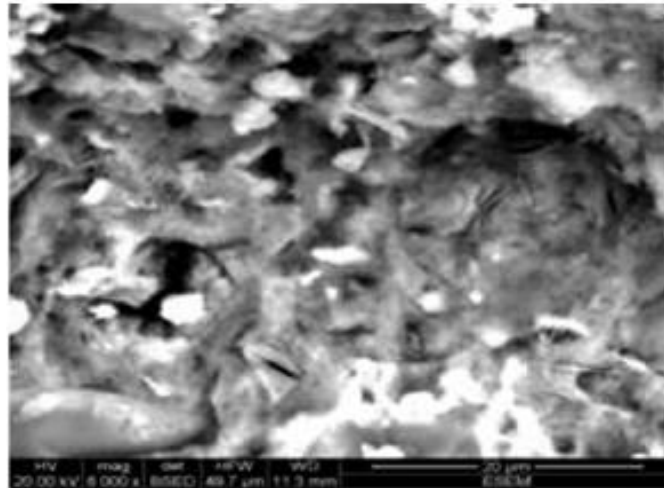


Fig. 2.22: SEM micrograph of cement mortar containing 6% NMK (Morsy et al., 2010)

In this case 6% NMK was added in the cement mortar. The presence of NMK in the cement mortar indicates that the hydration products formed in it are of perfectly dense structure. The production of C-S-H gel and ill crystals of CH due to pozzolanic reaction improves the mechanical properties of the blended mortar.

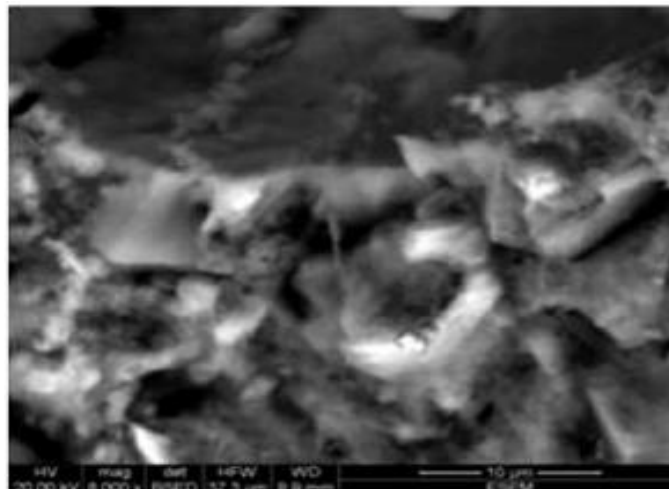


Fig. 2.23: SEM micrograph of cement mortar containing 6% NMK and 0.005% CNT (Morsy et al., 2010)

From **Fig. 2.23** and **2.24** it is clear that CNT's are found embedded as individual fibers in the paste and which act as bridges between hydrates and across cracks. The presence of NMK particles disrupts the fiber-fiber interactions which can held CNT's together as clumps.

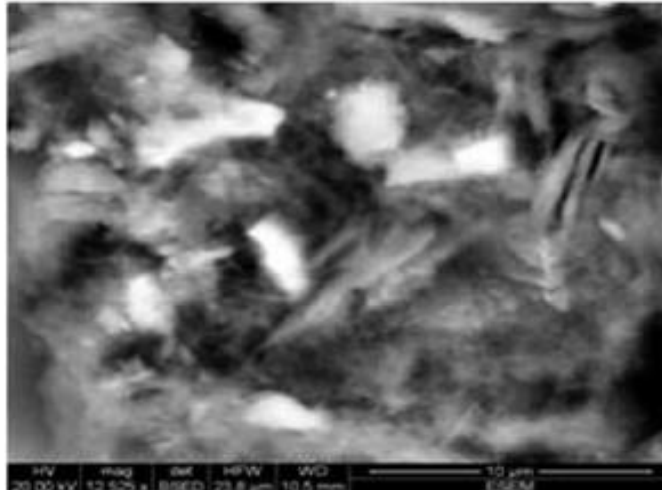


Fig. 2.24: SEM micrograph of cement mortar containing 6% NMK and 0.02% CNT (Morsy et al., 2010)

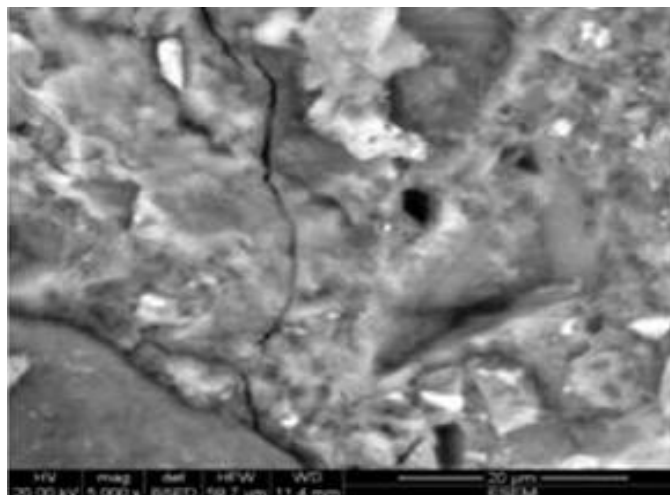


Fig. 2.25: SEM micrograph of cement mortar containing 6% NMK and 0.01% CNT (Morsy et al., 2010)

As the CNT addition increases in the cement mortar the SEM micrograph indicates the appearance of micro-cracks, which causes due to higher concentration of CNT's in the cement mortar due to which bonds becomes weak in the microstructure and produces less strength.

Aly et al., 2011 presented the effect of nanoclay particles on mechanical, thermal and physical behaviors of waste-glass cement mortar. In this SEM micrographs are studied on control and 20% samples, and the proportion of Cloisite 30B nanoclay in each case remain same i.e. 2.5% with the replacement of equal proportion of the Ordinary Portland cement.

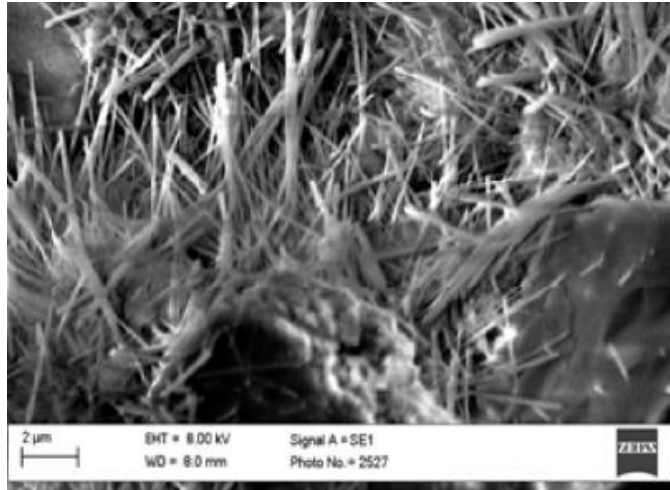


Fig. 2.26: SEM micrograph of control sample (Aly et al., 2011)

Fig. 2.26 represents the micro-structure of the control sample which was hydrated for 28 days. The presence of CSH gel which is surrounded by and connected with many needle-hydrates is shown in the **Fig. 2.26**.

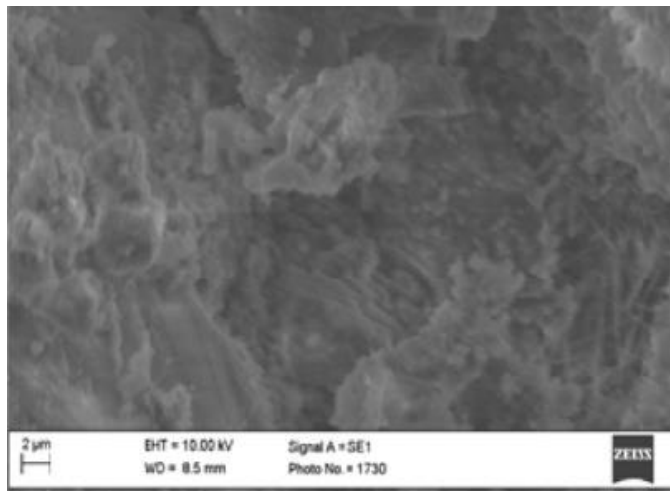


Fig. 2.27: SEM micrograph of WGP 20 (Aly et al., 2011)

Fig. 2.27 represents the micro-structure of WGP 20. In this case equal amount of cement is replaced with the addition of glass powder. With the addition of glass powder the CSH becomes more fine and dense because the glass powder particles fill the voids.

NCWGP20 as shown in **Fig. 2.28** showed a perfectly dense and compact formation of hydration products. The SEM micrographs represents the densest mortar structure was observed for the specimen with a hybrid combination of 20% glass and 2.5% NC particles, followed by the mix with 20% glass powder (WGP20).

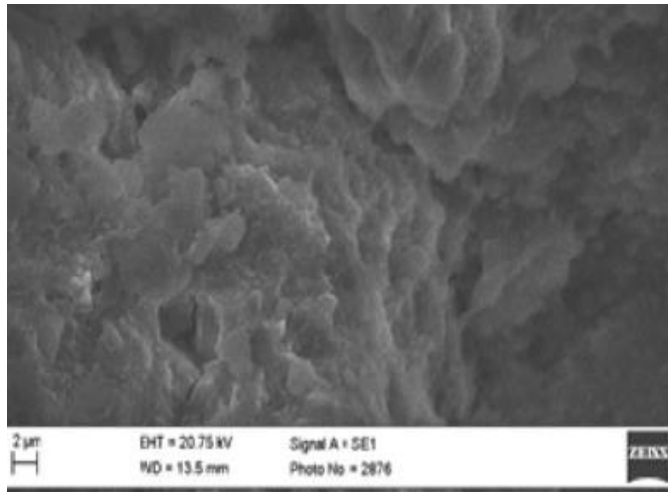


Fig. 2.28: SEM micrograph of NCWGP 20 (Aly et al., 2011)

The improvements in microstructure of NCWGP20 could be due to the packing effect of NC particles in the voids, due to their great surface area, which leads to increases in toughness and strength.

Farzadnia et al., 2013 presented the effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars. In this case halloysite nanoclay SEM micrographs of control and 2% nanoclay were studied.

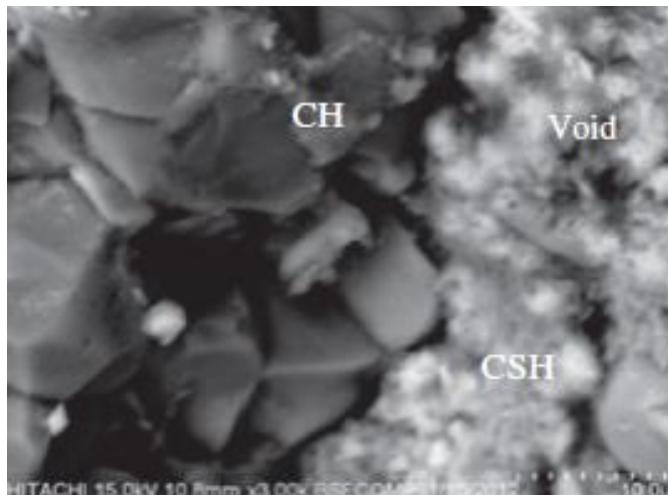


Fig. 2.29: SEM micrograph of control (Farzadnia et al., 2013)

Fig. 2.29 and **2.30** represents the microstructure of samples which shows that 2% nanoclay was denser than control samples and silica fume is also present in both images. Denser microstructure can be due to the fact that nanoclay can act as filler and fills voids which lead to denser microstructure of mortar as compared to control samples.

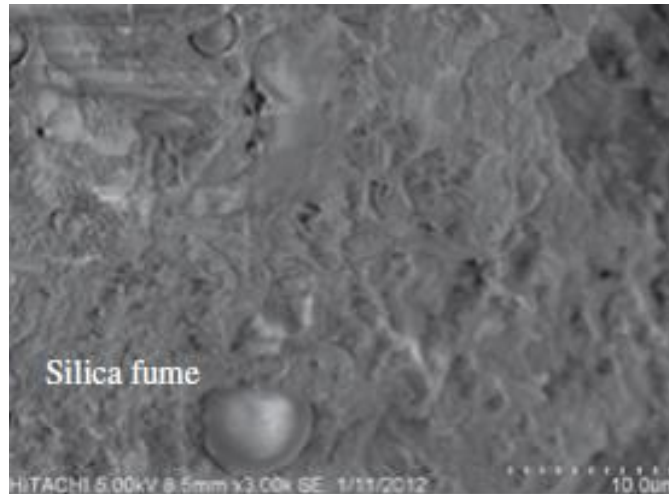


Fig. 2.30: SEM micrograph of 2% NC (Farzadnia et al., 2013)

The large amount of SiO_2 in halloysite nanoclay increases the rate of CSH due to consumption of Portlandite in cement matrix. The water which was entrapped in nanoclay can be released gradually which cause further hydration and increase both strength and density.

Salami et al., 2013 presented the physico-mechanical characteristics of blended white cement pastes containing thermally activated ultrafine nanoclays. In this case nano-metakaolin was added in different proportions and for those SEM micrographs was studied on control, 8%, 10% and 12% samples. In this case the samples were hydrated for 28 days.

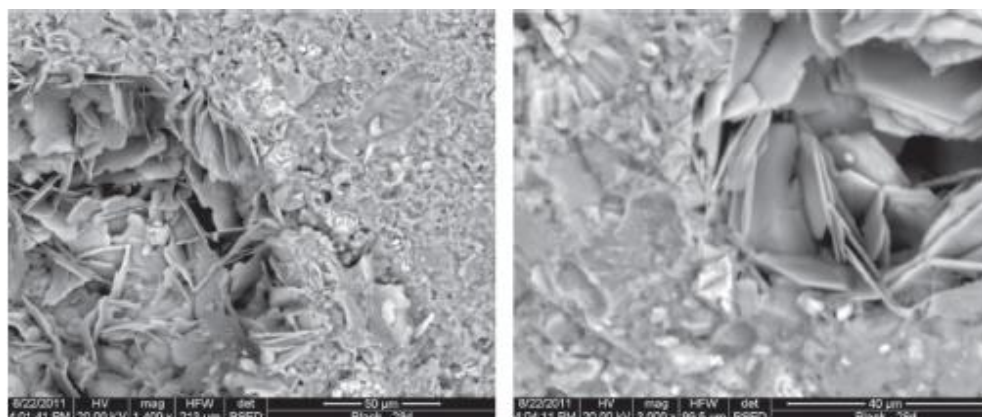


Fig. 2.31: SEM micrograph of control sample (Salami et al., 2013)

Fig. 2.31 represents the micrographs of control sample which indicates the presence of hydrated products such as CSH, CH and CAH. SEM micrograph represents needle like mono sulfate and it was found out that CSH exist in gel form and CH crystals are also distributed in the cement paste.

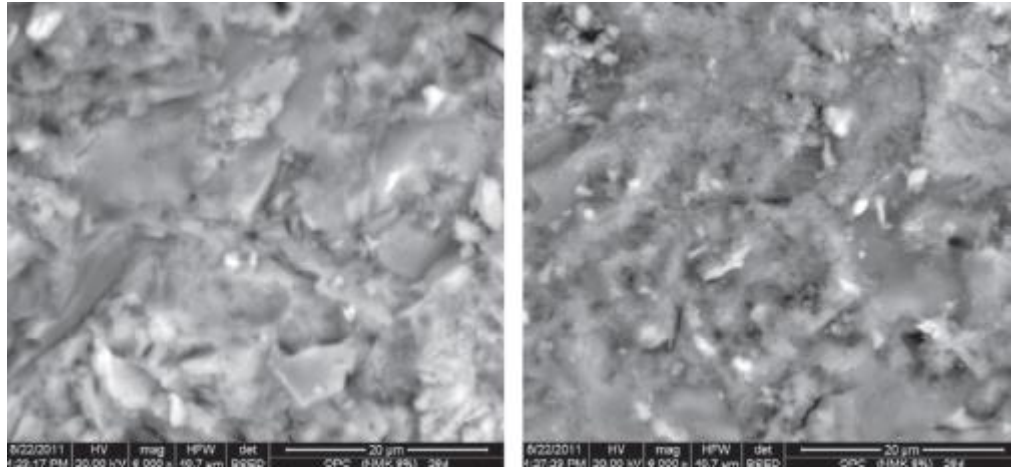


Fig. 2.32: SEM micrograph of 8% NMK (Salami et al., 2013)

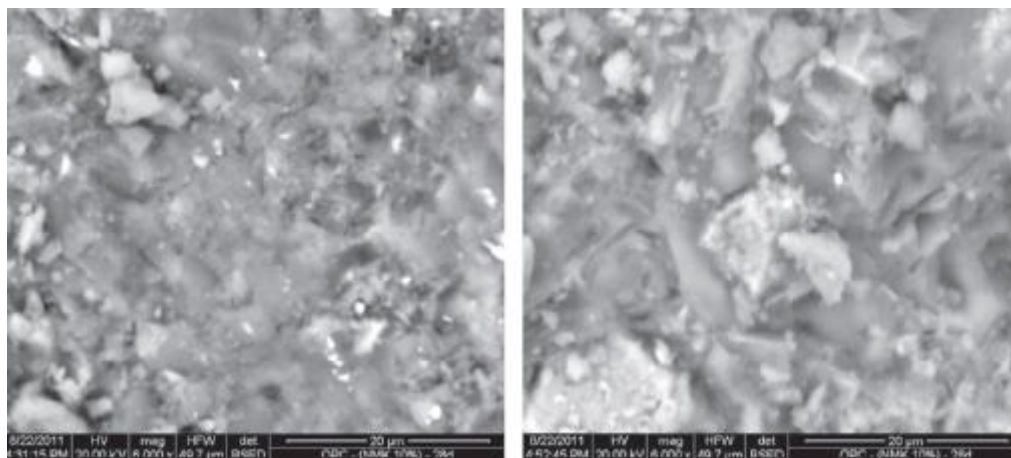


Fig. 2.33: SEM micrograph of 10% NMK (Salami et al., 2013)

Fig. 2.32 and **2.33** represents the microstructure of the mixture which contains 8% and 10% NMK. In case of 8% and 10% NMK micro-structure is dense and compact as compared with control sample. In this case large CH crystals are absent. With the addition of NMK the mechanical properties such as compressive and flexural strength improves.

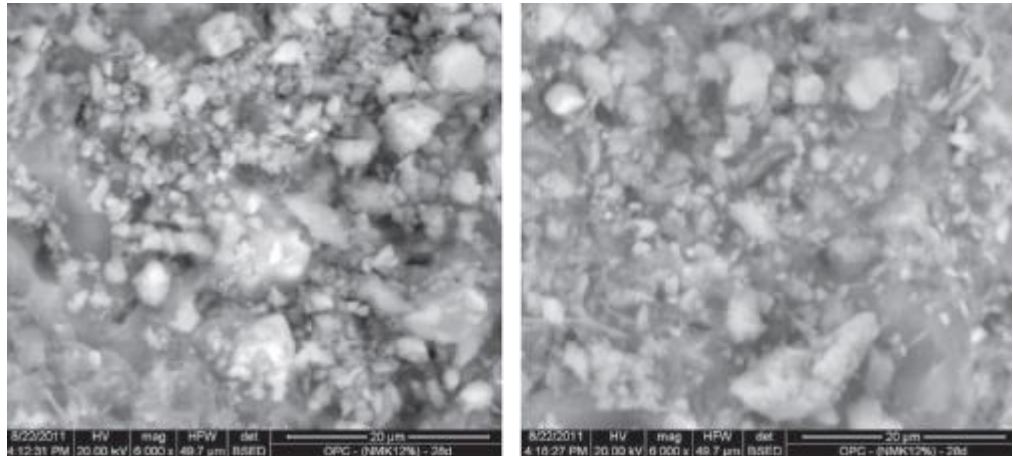


Fig. 2.34: SEM micrograph of 12% NMK (Salami et al., 2013)

Fig. 2.34 represents the microstructure of the mixture containing 12% NMK. Figure shows that the texture is poor and in this case unhydrated cement grains appears which leads to lower strength.

2.9 Differential Scanning Calorimeter (DSC)

Chang et al., 2007 studied the material properties of Portland cement paste with the addition of montmorillonite nanoclay. In this case montmorillonite nanoclay was added. In this case samples were examined under DSC.

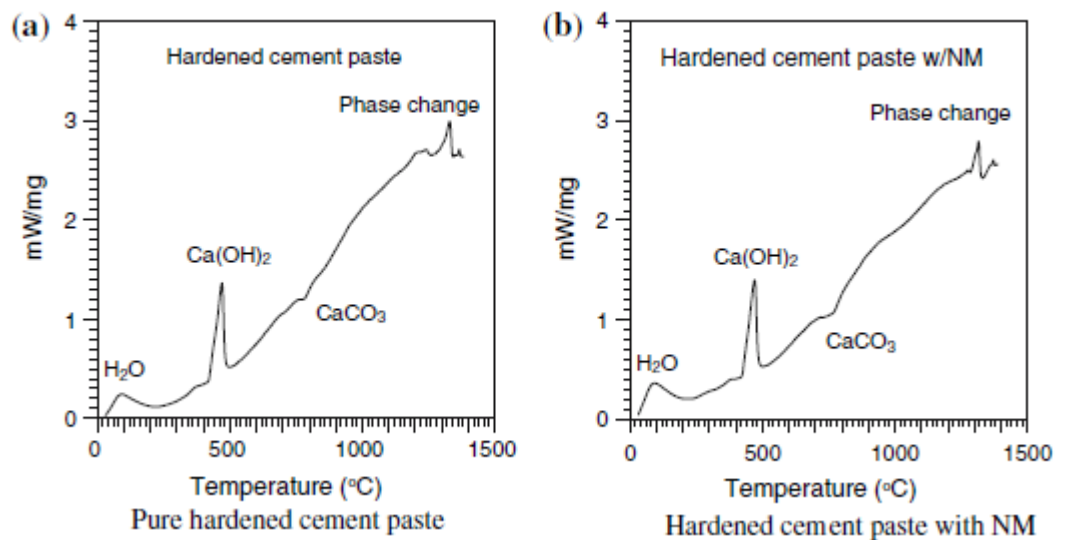


Fig. 2.35: Typical DSC curve of hardened Portland cement paste (a) without NM (b) With 0.6% added NM (Chang et al., 2007)

Fig. 2.35 (a, b) represents the four endothermic peaks which appear around 100°C, 470°C, 720°C and 1300°C. From figure it is clear that the peak variation of CH appears to be sharpest. There is only 1°C difference between the two temperatures of

469.63°C and 470°C on the dehydroxylation of CH for two types of hardened cement paste whereas, in case of glass-transition temperature (T_g), temperature raises from 1296.62 to 1301.78°C with an increase of 5°C which indicates that cement paste with addition of nanoclay have higher melting point.

Morsy et al., 2010 presented the effect of nanoclay on mechanical properties and microstructure of Ordinary Portland cement mortar. In this case DSC was checked at control, 4% and 8% as shown in **Fig. 2.36**.

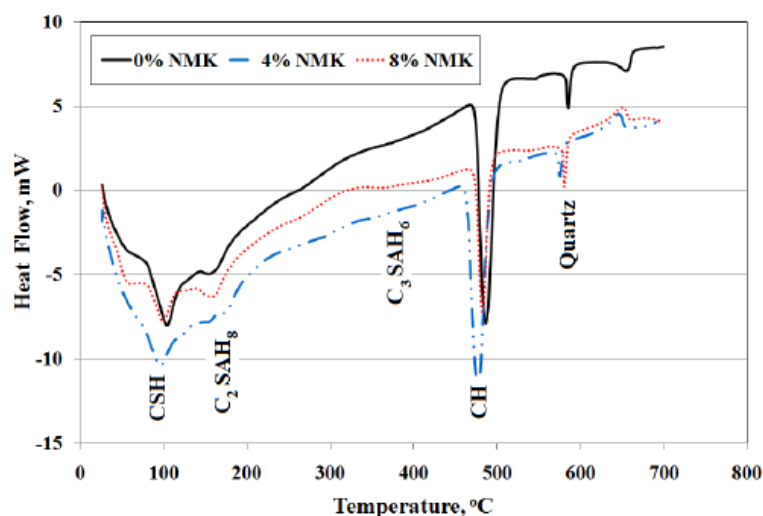


Fig. 2.36: DSC thermograms of NMK mortar hydrated for 28 days (Morsy et al., 2010)

In this case there are four endothermic peaks are located at 105°C, 160°C, 350°C and 580°C. These peaks shows the decomposition of calcium silicate hydrate, gehlenite hydrate (C_2ASH_8), hydrogarnet (C_3ASH_8), CH and quartz. As the quantity of NMK increases up to 8% the formation of CH during hydration decreases from 30.23J/G to 14.17J/g. In this case there is increase in phase enthalpy which indicates the formation of well crystalline phases.

Morsy et al., 2010 presented the hybrid effect of carbon nano-tube and nanoclay on physico-mechanical properties of cement mortar.

In this case CNT is added at different proportions i.e. 0.02% and 0.1% and the proportion of nano-metakaolin in each case remain same i.e. 6%. The samples are hydrated for 28 days

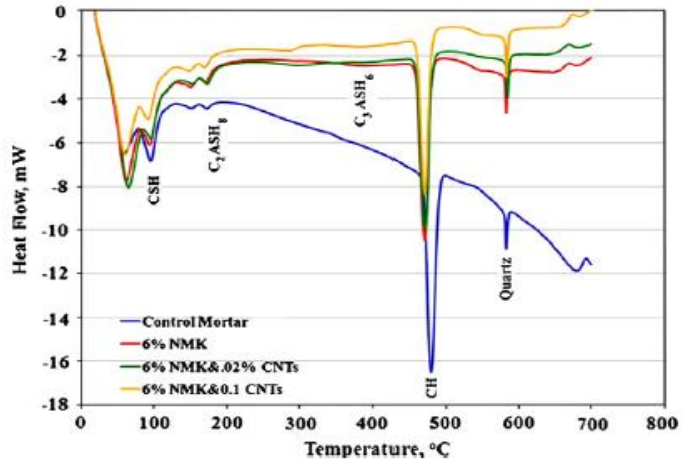


Fig. 2.37: DSC thermograms of blended cement mortar containing exfoliated 6% NMK versus CNTs ratios at 28 days of hydration (Morsy et al., 2010)

Fig. 2.37 indicates five endothermic peaks which are located at 95°C, 174°C, 380°C, 470°C and 580°C. These peaks show the decomposition of Calcium silicate hydrates (C-S-H), gehlenite hydrate (C₂ASH₈), hydrogarnet (C₃ASH₈), CH and quartz. During hydration the enthalpy of formed CH in case of control and blended cement which contains nanoclay shows a decrease from 35.73J/g to 33.57J/g.

Farzadnia et al., 2013 presented the effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars. In this case halloysite nanoclay DSC thermograms of control and 2% nanoclay were studied.

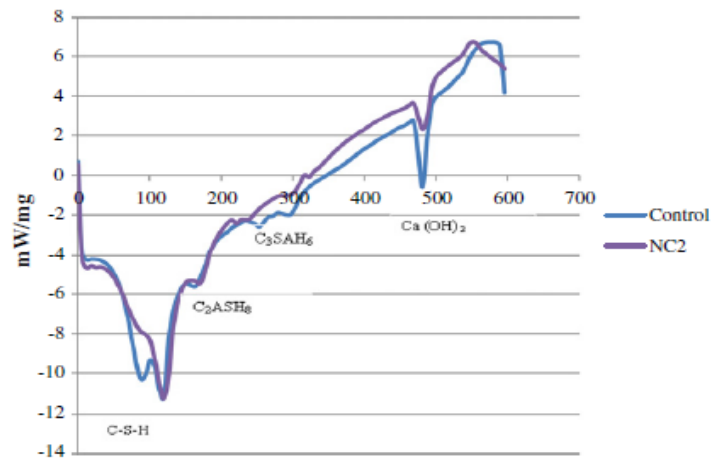


Fig. 2.38: DSC thermograms of control and 2% NC samples at 28 days (Farzadnia et al., 2013)

In this case the endothermic peaks are observed at 120°C, 170°C, 295°C and 490°C. **Fig. 2.38** also represents the decomposition of calcium silicate hydrate, gehlenite hydrate (C₂ASH₈), hydrogarnet (C₃ASH₈) and CH. Figure shows increase in the peak

area of C_2ASH_8 and C_3ASH_8 which lead to high heat of hydration which causes formation of more C-S-H gel.

Salami et al., 2013 presented the physico-mechanical characteristics of blended white cement pastes containing thermally activated ultrafine nanoclays. In this case nano-metakaolin was added in different proportions and for those DSC thermograms was studied on control, 8% and 10% samples. In this case the samples were hydrated for 28 days.

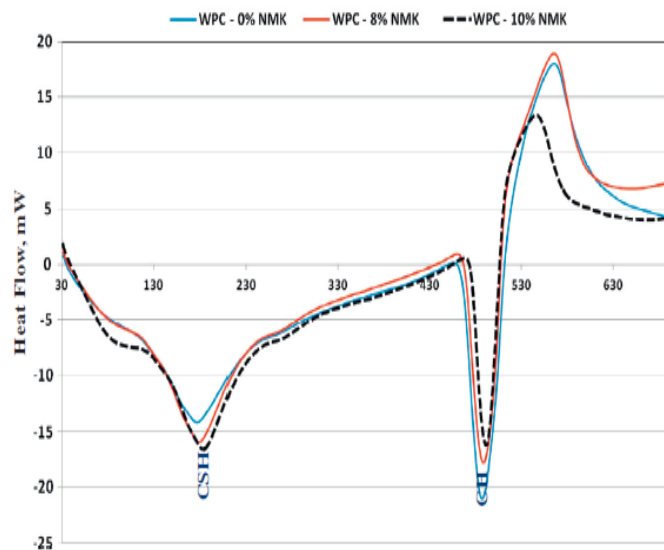


Fig. 2.39: DSC thermograms for plain and NMK modified cement pastes hydrated for 28days (Salami et al., 2013)

In this case the endothermic peaks are observed at 170°C and 475°C. **Fig. 2.39** also represents the decomposition of calcium silicate hydrate and CH. The addition of more NMK with the replacement of Ordinary Portland cement leads to change in the phase of calcium hydroxide from well crystalline to ill-crystalline. The crystallization which was produced by NMK and CH fill the pores and thus enhances the mechanical properties of the material.

2.10 Closing Remarks

In this chapter, the research done so far on nanoclay in cementitious material. It is very clear from the review of literature that addition of nanoclay in vary proportions, with their high surface, have improved the compressive, flexural and split tensile strength and other properties such as SEM, XRD of the cement mortar. In the

following chapter, the experimental study carried out in this research using nanoclay as addition to cement mortar has been elaborated and detailed.

CHAPTER 3

EXPERIMENTAL PROGRAM AND METHODOLOGY

3.1 General

The basic aim of the research is to investigate the effect of addition of nanoclay in varying proportions to cement mortar as filler to the cement mortar paste. The effect on the mechanical, thermal and the micro-structure property by the addition of nanoclay was studied. Cement mortar samples with cement: sand ratio as 1:3 was prepared and nanoclay was added as filler in varying proportion. Water/cement ratio was kept constant at 0.41.

3.2 Properties of Constituent Materials

3.2.1 Cement

Cement is a fine powder which is grey in color. Cement and water forms a paste that binds the other materials. The cement used in the study was Ordinary Portland Cement (OPC) and the properties of the cement used are presented below in **Table 3.1**.

Table 3.1: Properties of cement used

Properties	Observed Values		
Initial Setting Time (minutes)	95		
Final Setting Time (minutes)	185		
Specific Gravity	3.01		
Normal Consistency	29%		
Compressive Strength(N/mm ²)	3 days	7 days	28 days
	24.8	36.08	45.65

3.2.2 Sand

Standard sand was used throughout the research work obtained from Tamil Nadu Ennore. The specifications provided by the supplier are shown in **Table 3.2** and match with the requirements of the specification given by IS: 650-1991.

Table 3.2: Particle size distribution

Type of Grade	Particle size
Grade1	Particle size smaller 2mm and greater than 1mm.
Grade2	Particle size smaller 1mm and greater than 500microns.
Grade3	Particle size smaller 500 microns and greater than 90 microns.

3.2.3 Water

Portable water was used for preparing cement mortar samples. The water/cement ratio for making samples was 0.41.

3.2.4 Nanoclay used (Cloisite 30B)

Cloisite 30B used in this work was obtained from Connell Bros, Mumbai, Maharashtra. It was white in color as shown in **Fig. 3.1**.



Fig. 3.1: Cloisite 30B sample

Specifications of Cloisite 30B provided by supplier are as below in **Table 3.3**.

Table 3.3: Specifications of Cloisite 30B

Properties of Cloisite 30B	
Density	1.98g/cm ³
Moisture content	<2%

Average size	6 μ m
Basal Spacing, d_{001}	18.5 \AA
Colour	Off-White
Modifier concentration	90meq ^a /100g clay

Cloisite 30B nanoclay has extreme fineness of the nanoclay and very high amorphous silicon dioxide content makes Cloisite 30B nanoclay extremely reactive pozzolanic material. As the Portland cement in mortar begins to react chemically, it releases calcium hydroxide. The Cloisite 30B nanoclay reacts with this calcium hydroxide to form additional binder material called calcium silicate hydrate (CSH), which is very similar to the calcium silicate hydrate formed from Portland cement. It is an additional binder that gives improved properties to the cement mortar.

3.3 Sample Preparation

3.3.1 Cement mortar samples with nanoclay

Mortar prepared according to ASTM provisions with cement to sand ratio of 1:3. The nanoclay was properly dispersed in the cement matrix. The Cloisite 30B nanoclay dispersion can be done by two methods i.e. aqueous mixing (AM) and powder mixing (PM).

- (a) **Aqueous mixing:** In aqueous mixing the dispersion of Cloisite 30B nanoclay was done by using ultra-sonicator.
- (b) **Powder mixing:** In case of powder mixing Cloisite 30B nanoclay was mixed vigorously with cement in dry state for 30 minutes for the proper dispersion of nanoclay in the cement mortar.

3.3.2 Samples for mechanical properties

Table 3.3 Specimen details

Specimen	Specifications(mm)	Test Conducted
Mortar Cubes	70.6 \times 70.6 \times 70.6	Compressive Strength Split tensile
Mortar Beams	40 \times 40 \times 160	Flexural Beams

3.3.2 Samples for thermal properties

Table 3.4 Specimen details

Specimen	Test Conducted
Powder retained at respective days of curing	TGA DSC

3.3.2 Samples for chemical and micro-structure properties

Table 3.5 Specimen details

Specimen	Test Conducted
Powder retained at respective days of curing	XRD SEM

3.4 Experimental Program & Methodology

3.4.1 Mechanical properties

Mechanical properties test was performed to investigate the effect of incorporation of Cloisite 30B NC in various proportions of 0.5%, 1%, 2%, 4% and 6%. In mechanical properties; compressive strength, flexural strength and split tensile strength was investigated at the ages of 3, 7 and 28 days. In case of compressive strength and split tensile strength the loading rate was taken as 70 kN/min and in case of flexural strength the loading rate was taken as 2.65kN/min.

Table 3.6 Details & nomenclature of cement mortar samples

Details of addition of NC in CM by weight of cement	Nomenclature
0% Nanoclay/Plain CM sample	C (Control)
0.5% Nanoclay	NC0.5
1% Nanoclay	NC1
2% Nanoclay	NC2
4% Nanoclay	NC4
6% Nanoclay	NC6

3.4.2 Thermal properties

In thermal properties TGA and DSC test are performed, tests indicate the formation of different endothermic peaks. In case of TGA and DSC the samples are analyzed from room temperature to 1000°C which have the uniform heating rate of 20°C.

3.4.3 Chemical composition and micro-structure of mortars

The chemical composition of the samples are investigated using X-ray diffractometer analysis (XRD) with Cu radiation and also graphite 30 kV and voltage of 40 mV was used with diffraction intensity in the range of 10-80°.

The micro-structure of the mortar samples are examined by using scanning electron microscopy (SEM) analysis which is used to identify the changes which occurs in the micro-structure and also the formation and deformation of phases in the mortar sample.

The experimental program of the research work thesis work is shown in **Fig. 3.2**

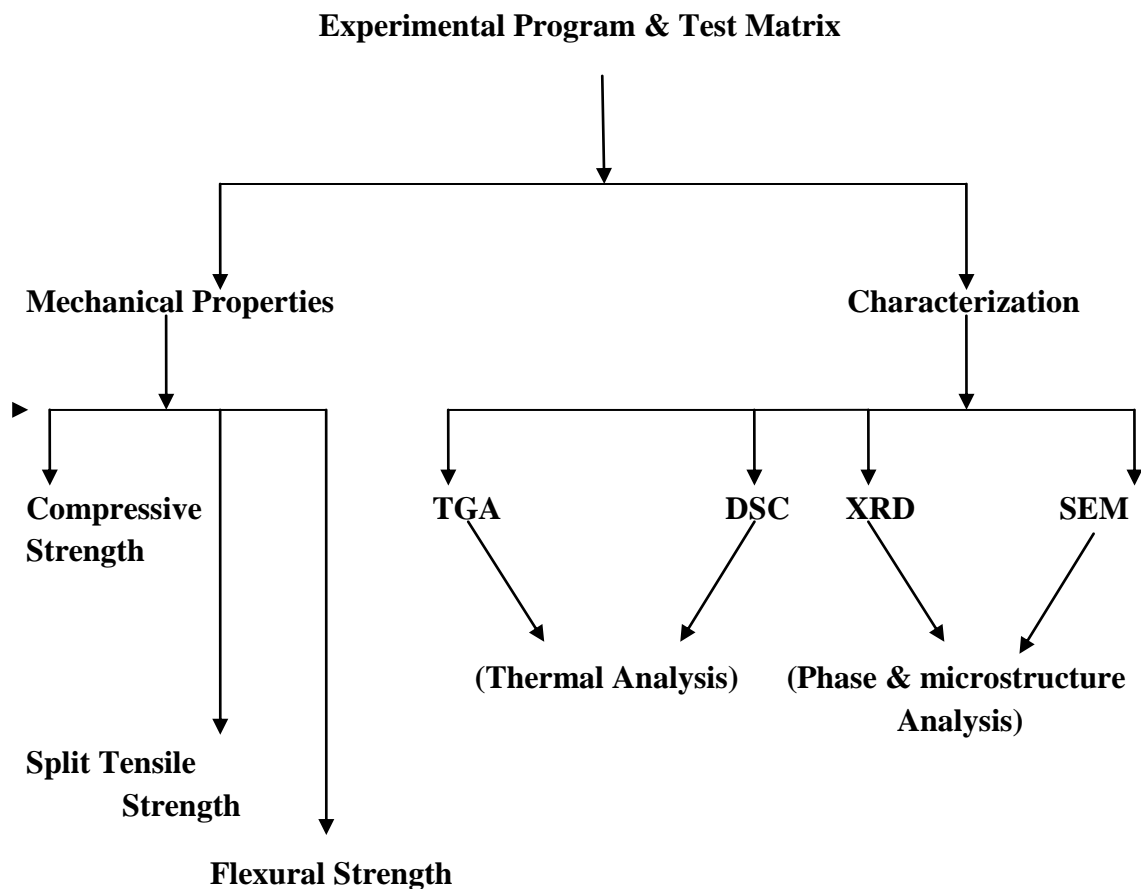


Fig. 3.2: Experimental Program and test matrix

3.5 Casting

Before casting the moulds should be properly cleaned and oiled. The screws should be tightened properly in the perfect dimension before casting. Care should be taken that no gap should be left in mould so that mortar starts coming out. The three grades of standard sand should be weighed with perfect accuracy. The mortar was prepared by hand mixing on the non absorbing platform. Then cement was added to this mixture. Then water was added to the mixture. For each mix 18 cubes (70.6×70.6×70.6mm), 9 for compressive strength for 3,7 and 28 days and 9 for split tensile test for 7, 14 and 28 days was casted. For the same mix 9 beams (40×40×160mm) for flexural strength test for 7, 14 and 28 days were casted.

3.6 Test Conducted

3.6.1. Compressive strength Test (IS: 516-1959)

The compressive strength test is performed on cubes to determine compressive strength at various ages.

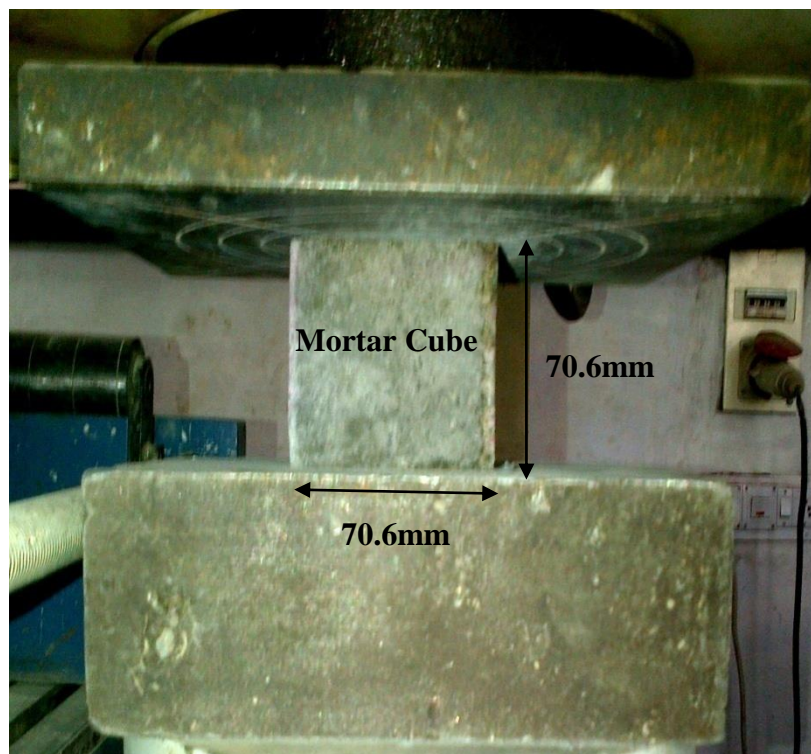


Fig. 3.3 Compressive strength test on cube

Testing Machine: The testing machine may be of any reliable type, of sufficient capacity for the tests and capable of applying the load at the rate specified which is 70kN/min for 70.6×70.6×70.6 mm size of mould. The permissible error shall be not

more than ± 2 percent of the maximum load. The testing machine shall be equipped with two steel bearing platens with hardened faces. One of the platens (preferably the one that normally will bear on the upper surface of the specimen) shall be fitted with a ball seating in the form of a portion of a sphere, the centre of which coincides with the central point of the face of the platen. The other compression platen shall be plain rigid bearing block. The bearing faces of both platens shall be at least as large as, and preferably larger than the nominal size of the specimen to which the load is applied.

Age at test

Tests shall be made at recognized ages of the test specimens, the most usual being 3, 7 and 28 days. Test at age of 56 days can also be performed. Ages of 13 weeks and one year are recommended in case tests at greater ages are required. Where it may be necessary to obtain the early strengths, tests may be made at the ages of 24 hours $\pm 1/2$ hour and 72 hours ± 2 hours. The ages shall be calculated from the time of the addition of water to the dry ingredients.

Number of specimens

At least three specimens, preferably from different composition, shall be made for testing at each selected ages of 3, 7 and 28 days.

Formula used

Compressive Strength = **Error! Reference source not found.**..... (3.1)

Where P = Load at fracture (kN)

3.7.2 Flexural strength test

The flexural strength test is performed on mortar beams to determine the flexural strength at various ages.

Testing Machine: The testing machine may be of any reliable type, of sufficient capacity for the tests and capable of applying the load at the rate specified which is 2.65 KN/min for 40×40×160 mm size of mould. The permissible error shall be not more than ± 2 percent of the maximum load. The testing machine shall be equipped with two steel bearing platens with hardened faces. One of the platens (preferably the one that normally will bear on the upper surface of the specimen) shall be fitted with a ball seating in the form of a portion of a sphere, the centre of which coincides with the central point of the face of the platen. The other compression platen shall be plain

rigid bearing block. The bearing faces of both platens shall be at least as large as, and preferably larger than the nominal size of the specimen to which the load is applied.

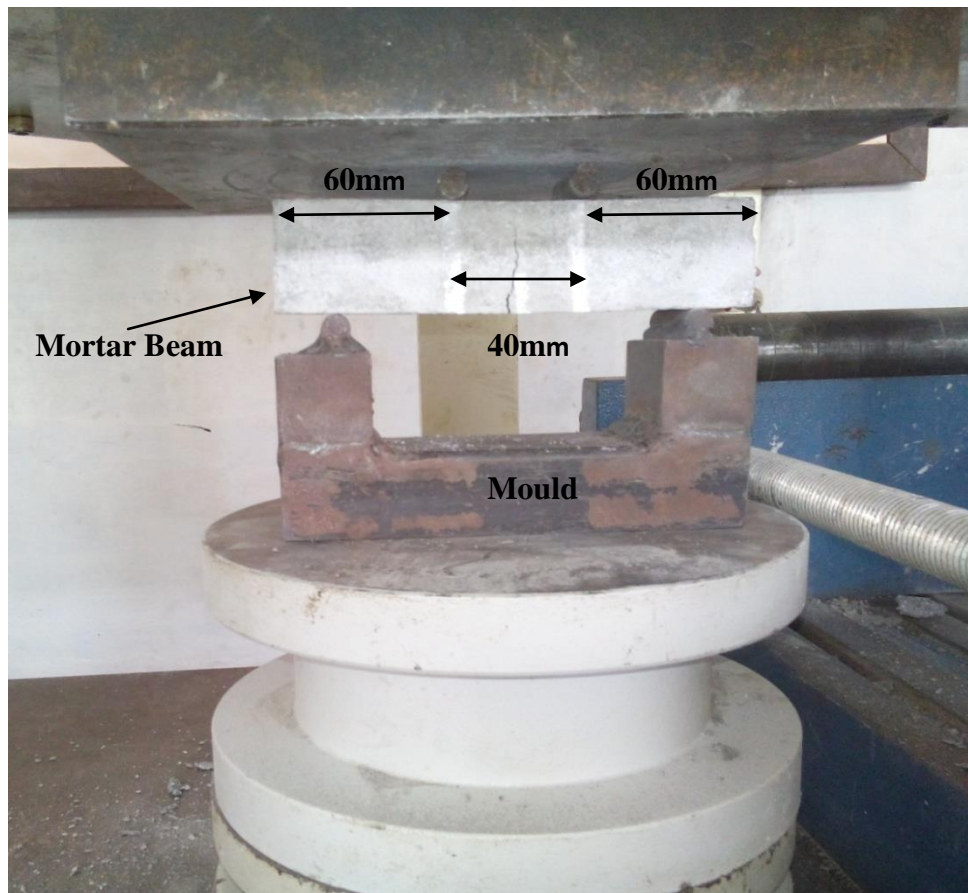


Fig. 3.4 Beam under two point loading

Age at test

Tests shall be made at recognized ages of the test specimens, the most usual being 7, 14 and 28 days. Test at age of 56 days can also be performed. Ages of 13 weeks and one year are recommended in case tests at greater ages are required. Where it may be necessary to obtain the early strengths, tests may be made at the ages of 24 hours \pm ½ hour and 72 hours \pm 2 hours. The ages shall be calculated from the time of the addition of water to the dry ingredients.

Number of specimens

At least three specimens, preferably from different composition, shall be made for testing at each selected ages of 7, 14 and 28 days.

Formula used

f_t (Flexural strength/ Modulus of rupture) = **Error! Reference source not found.**
= **Error! Reference source not found.**

$$f_t = \frac{P}{bd} \quad \text{N/mm}^2 \dots \dots \dots (3.2)$$

Where P = Load at which beam fails (kN)

3.7.3 Split tensile strength test

Apparatus

Testing Machine: The testing machine may be of any reliable type. The machine should have sufficient capacity to perform the tests and capable of applying the load at the rate of 70 kN/min on 70.6×70.6×70.6 mm size of the mould. It shall comply with the requirements given in IS 516 as far as applicable except that the bearing faces of both platens shall provide a minimum loading area of 12 mm x the length of the cube, as the case may be so that the load should be applied over the entire length of the specimen.

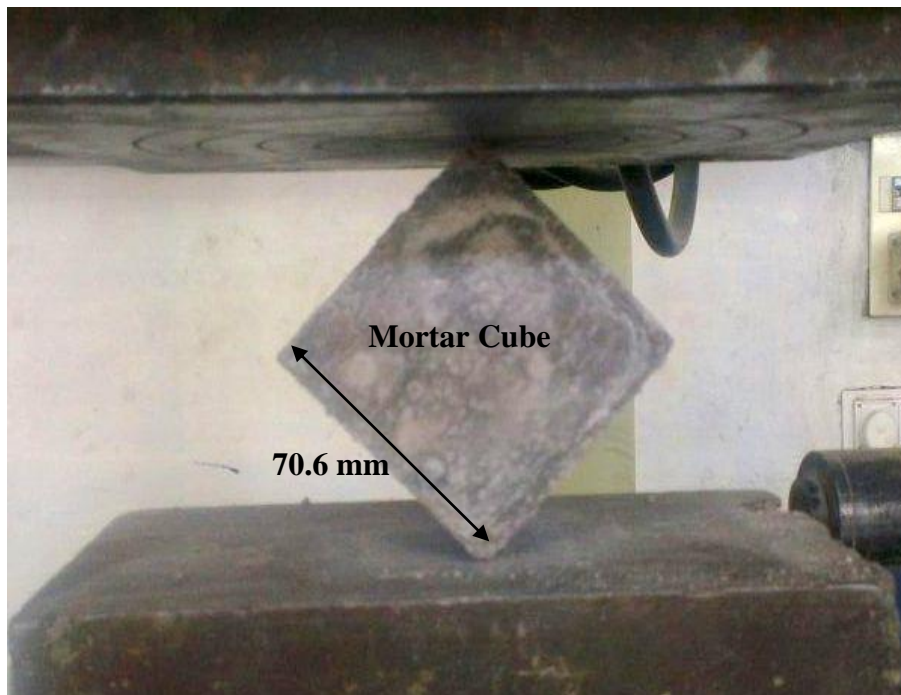


Fig. 3.5 Cube under split tensile test

Age at test

Tests shall be made at recognized ages of the test specimens, the most usual being 7, 14 and 28 days. Test at age of 56 days can also be performed. Ages of 13 weeks and one year are recommended in case tests at greater ages are required. Where it may be necessary to obtain the early strengths, tests may be made at the ages of 24 hours \pm ½ hour and 72 hours \pm 2 hours. The ages shall be calculated from the time of the addition of water to the dry ingredients.

Number of specimens

At least three specimens, preferably from different composition, shall be made for testing at each selected ages of 7, 14 and 28 days.

Formula used

Split tensile strength= **Error! Reference source not found.**..... (3.3)

Where P= Load at fracture

S= Side of cube

3.8 Characterization Techniques

3.8.1 X-ray diffraction (XRD)

X-ray investigation on the samples were characterized by X-ray diffractometer with CuK_α radiation for the identification of existing phases, crystal structure, lattice parameter of the crystalline solids. The sample is irradiated with monochromatic X-rays and the counters record the reflected radiation. The X-ray diffraction pattern were recorded using Bruker’s diffractogram with CuK_α ($\lambda=1.54\text{\AA}$) obtained from Cu target using an inbuilt Ni filter. The 2Θ values for XRD patterns, in the range of 10° - 90° . The X-ray diffraction peaks were identified using Powder Diffraction Files (PDF).

3.8.2 Scanning electron microscopy (SEM)

SEM is conducted to study the micro-structure properties of the samples. The samples which are already casted and cured for 28 days are used for the test. This test is used to identify the changes which had occurred inside the micro-structure and also the formation and deformation of the phases.

3.8.3 Thermo-gravimetric analysis

TGA conducts on the prepared samples to measure the amount of weight change of samples, either as function of increasing temperature, or isothermally as a function of time, in atmosphere of nitrogen, helium, air, other gas, or in vacuum. For TGA temperature can range from 25° to 1000°C and sample weight range from 1mg to 150mg and samples can be analyzed in the form of powder or small pieces so the interior sample temperature remains close to the measured gas temperature.

3.8.4 Differential scanning calorimeter (DSC)

DSC measures the amount of energy absorb or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat released) reactions. For DSC temperature can range from -120°C to 725°C, in atmosphere of nitrogen, argon, air, controlled mixed gases, or in vacuum. The inner atmosphere is required above 600°C. The sample size can range from 0.5mg to 100mg.

3.9 Closing Remarks

In this chapter, the experimental details of various tests and the methodology for investigating effect of NC on mechanical, thermal, chemical composition and micro-structure properties have been discussed. In the following chapter the experimental results obtained is presented.

4.1 General

In this chapter the results of the cement samples and the mortar samples made with the addition of Cloisite 30B nanoclay in the varying proportions by weight of cement are presented and discussed. The properties such as Compressive Strength, Splitting Tensile Strength, Flexural Strength and thermal behaviour of final product are discussed and the comparisons between different mixes are represented.

4.2 Compressive Strength

To study the effect of addition of Cloisite 30B nanoclay in different proportions with cement on compressive strength. The addition level of Cloisite 30B NC is 0.5%, 1%, 2%, 4% and 6% by weight of cement. Specimens are cured in water and tested at ages of 3, 7 and 28 days.

4.2.1 Results by aqueous mixing

The test results of aqueous mixing are shown in **Fig. 4.1** and **Table 4.1**. In this case the dispersion of Cloisite 30B NC was done by using ultra-sonicator.

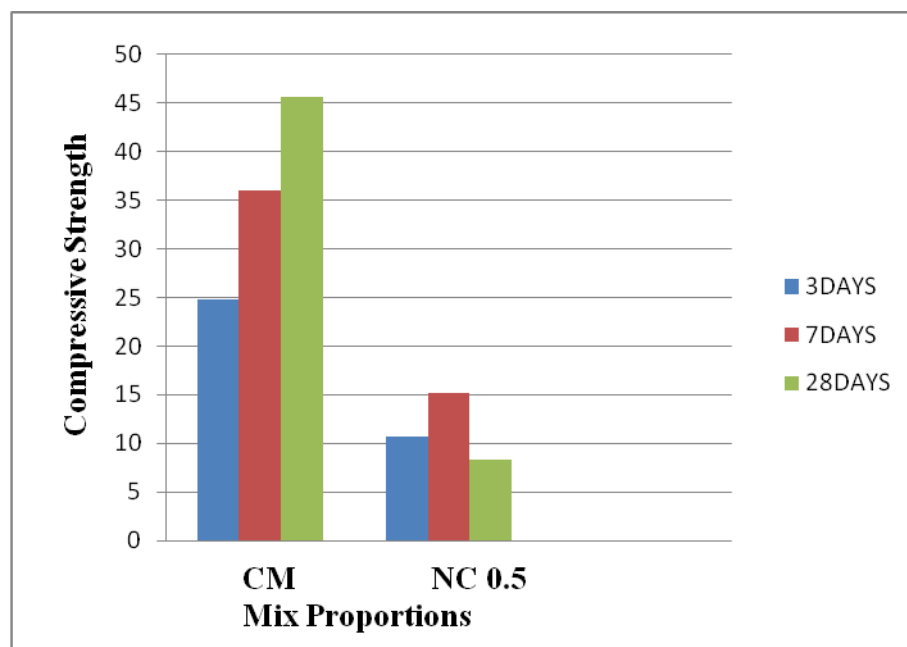


Fig. 4.1: Compressive strength of cement mortar with Cloisite 30B NC<1% by aqueous mixing

Table 4.1: Compressive strength of cement mortar with Cloisite 30B NC<1%

MIX	Compressive Strength (N/mm ²)			Average Compressive Strength (N/mm ²)		
	3 days	7 days	28days	3 days	7 days	28days
C	23.1	35.27	43.92	24.8	36.03	45.65
	24.2	35.64	46.65			
	27.2	37.17	47.64			
0.5% NC	10.46	11.17	5	10.73	15.11	8.27
	10.87	16.83	9			
	10.87	17.33	10.8			

The water cement ratio in all cases discussed above remains same i.e. 0.41. The test results indicated that, when 0.5 percent of Cloisite 30B nanoclay was added by the weight of cement was done, for 3 days compressive strength decreases progressively by 43.26%, for 7 days the compressive strength decreases by 41.2% and for 28 days the compressive strength decreases by 81.88% as shown in **Fig.4.1**.The decrease in strength occurs mainly due to improper dispersion of nanoclay in the cement and also coagulation occurs in the mortar mix.The results in the case aqueous mixing was not appropriate so other method for dispersion of nanoclay was adopted i.e. dispersion of Cloisite 30B NC by powder mixing.

4.2.2 Results by powder mixing

The test results of powder mixing are shown in **Fig. 4.2** and **Table 4.2**. In this case the dispersion of Cloisite 30B NC was done by mixing Cloisite 30B NC manually by mixing NC for 30 minutes so that NC get properly dispersed.

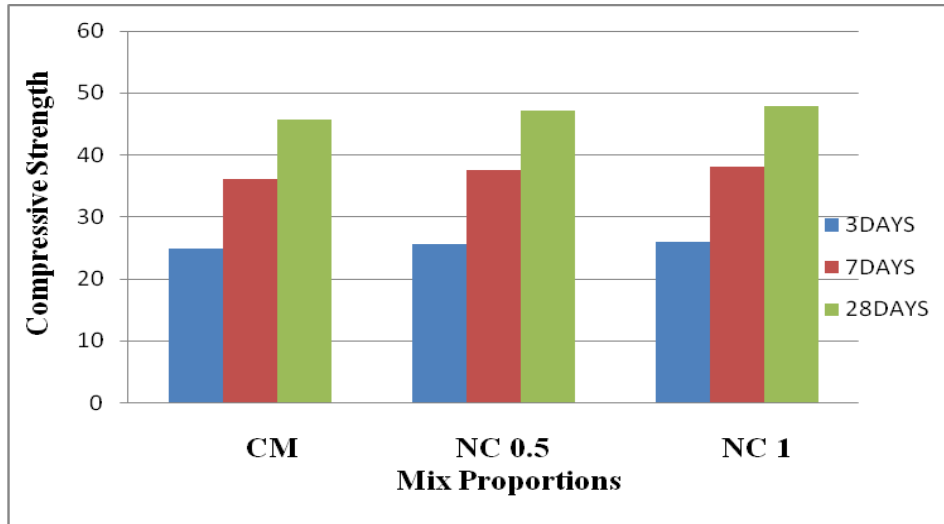


Fig. 4.2: Compressive strength of cement mortar with Cloisite 30B NC ≤ 1%

Table 4.2: Compressive strength of cement mortar with Cloisite 30B NC ≤ 1%

MIX	Compressive Strength (N/mm ²)			Average Compressive Strength (N/mm ²)		
	3 days	7 days	28days	3 days	7 days	28days
C	23.1	35.27	43.92	24.8	36.03	45.65
	24.2	35.64	46.65			
	27.2	37.17	47.64			
NC0.5	23.38	37.24	46.25	25.54	37.52	47.11
	26.11	37.45	47.21			
	27.13	37.88	47.88			
NC1	23.801	36.31	45.57	25.85	38.14	47.84
	26.51	36.36	46.93			
	27.26	41.76	44.21			

From Fig. 4.2 it is clear that with the addition of Cloisite 30B NC compressive strength goes on increasing. In case of NC0.5 for 3 days the strength increases up to 4.15% where in case of NC1 the strength increases by 7.58% as compared to control samples. For 7days in case of NC0.5 the strength increases by 5.95% whereas in case

of NC1 the strength increases by 9.46% as compared to control samples. For 28 days in case of NC0.5 and NC1 there was small increase in strength i.e. strength increases by 1.39% as compared to control samples.

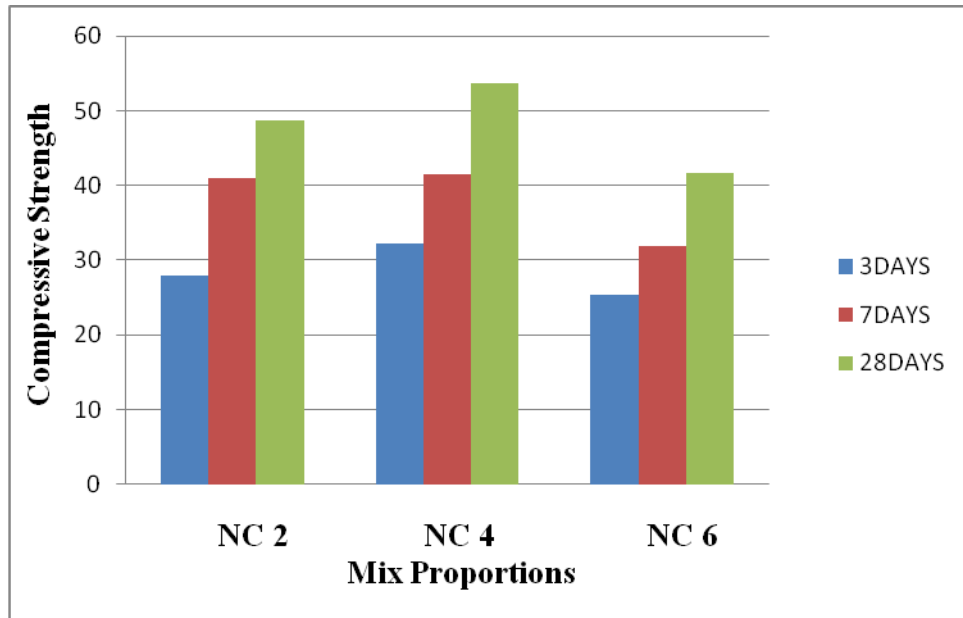


Fig. 4.3: Compressive strength of cement mortar with Cloisite 30B NC > 1%

Table 4.3: Compressive strength of cement mortar with Cloisite 30B NC > 1%

MIX	Compressive Strength (N/mm ²)			Average Compressive Strength (N/mm ²)		
	3 days	7 days	28days	3 days	7 days	28days
NC2	27.85	40.98	48.23	27.97	41.03	48.66
	28.04	40.97	48.24			
	28.04	41.15	49.5			
NC4	31.84	41.2	53.02	32.16	41.45	53.62
	32.21	41.34	53.91			
	32.47	41.77	54.12			
NC6	25.26	31.79	41.36	25.3	31.94	41.66
	25.28	32.16	41.74			
	25.38	31.88	41.95			

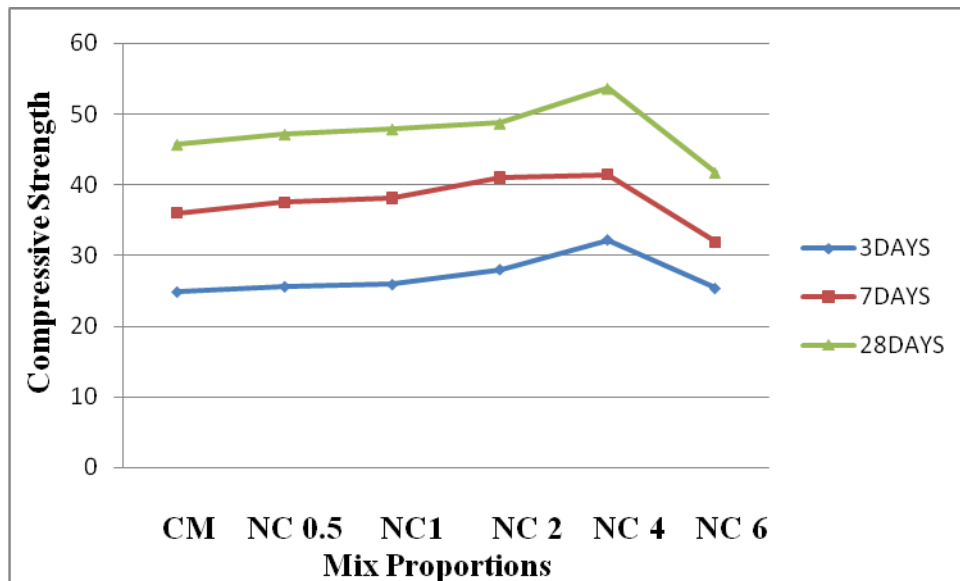


Fig. 4.4: Compressive strength of cement mortar with Cloisite 30B NC

From **Fig. 4.4** it is observed that when NC is added by increasing proportions from 2%, 4% and 6% it is observed that the strength increases progressively up to 4%. In case of NC2 for 3 days strength increases by 24.04% where as in case of NC4 the strength increases by 41.34% as compared with the results of control mix samples where as for NC6 there is only 8.4% increase in strength which is very less as compared to NC2 and NC4 results. For 7 days strength in case of NC2 the strength increases by 20.45% where as in case of NC4 there is 14.81% increase in strength as compared with results of control mix samples where as in NC6 there is 16.34% decrease in strength. For 28 days strength in case of NC2 and NC4 samples the strength increases by 7.78% and 20.58% where as for NC6 strength decreases by 10.32% as compared to 28 days strength of control mix samples.

The test results indicated that, when 2 to 4 percent by weight addition of Cloisite 30B for cement is done, compressive strength increases progressively. When 6NC was added to the weight of cement, strength starts decreasing.

The Cloisite 30B NC belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of Cloisite 30B NC acts as a filler and fills the voids of the cement mortar and make the mixture denser and the mechanical property is improved due to pozzolanic reaction of Cloisite 30B NC with free lime which adds the bonding strength and solid volume which results into higher compressive strength.

4.3 Split Tensile Strength

Split tensile strength studies were carried out at the age of 7, 14 and 28 days. Test results are given below in **Table 4.4** and **4.5**.

As seen in table, test results indicated the addition of Cloisite 30B NC at different percentages. The NC was added with respect to the weight of the cement. It is observed that with increase the addition of NC at 6% strength goes on decreasing. There is increase of 2 to 4% splitting tensile strength of 38% and 43% cement mortar respectively, when compared to control mix at age of 28 days.

These results are represented graphically below in **Fig. 4.5** and **4.6**.

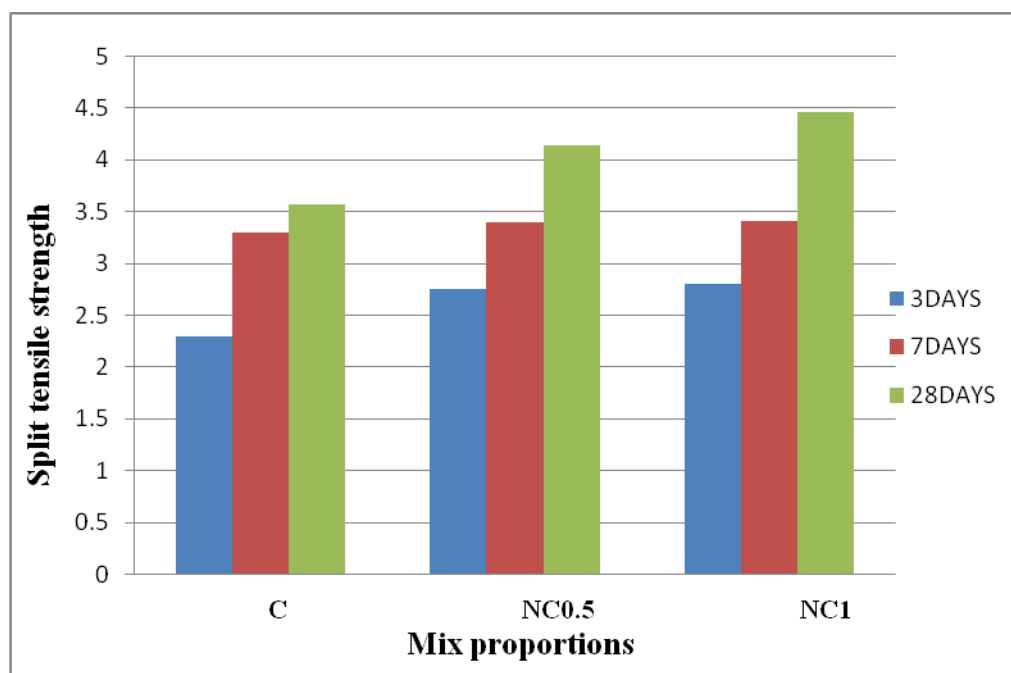


Fig. 4.6: Split tensile strength of cement mortar with Cloisite 30B NC \leq 1%

From **Fig. 4.6** it is clear that with the addition of Cloisite 30B NC split tensile strength goes on increasing. From **Table 4.4** it is clear that for NC0.5 for 7 days the strength increases by 20.52% where in case of NC1 the strength increases by 22.27% as compared to control samples. For 14 days in case of NC0.5 the strength increases by 3.76% whereas in case of NC1 the strength increases by 3.02% as compared to control samples. For 28 days in case of NC0.5 and NC1 there was small increase in strength i.e. strength increases by 16.05% and 25.21% as compared to control samples.

Table 4.4: Split tensile strength of cement mortar with Cloisite 30B NC ≤ 1%

MIX	Split Tensile Strength (N/mm ²)			Average Split Tensile Strength (N/mm ²)		
	7 days	14 days	28days	7 days	14 days	28days
C	2.01	3.11	3.03	2.29	3.19	3.57
	2.03	3.35	3.72			
	2.83	3.45	3.97			
NC0.5	2.74	3.19	4.05	2.76	3.31	4.143
	2.76	3.20	4.19			
	2.80	3.212	4.20			
NC1	2.64	3.126	3.96	2.8	3.41	4.47
	2.7	3.386	4.61			
	2.9	3.714	4.85			

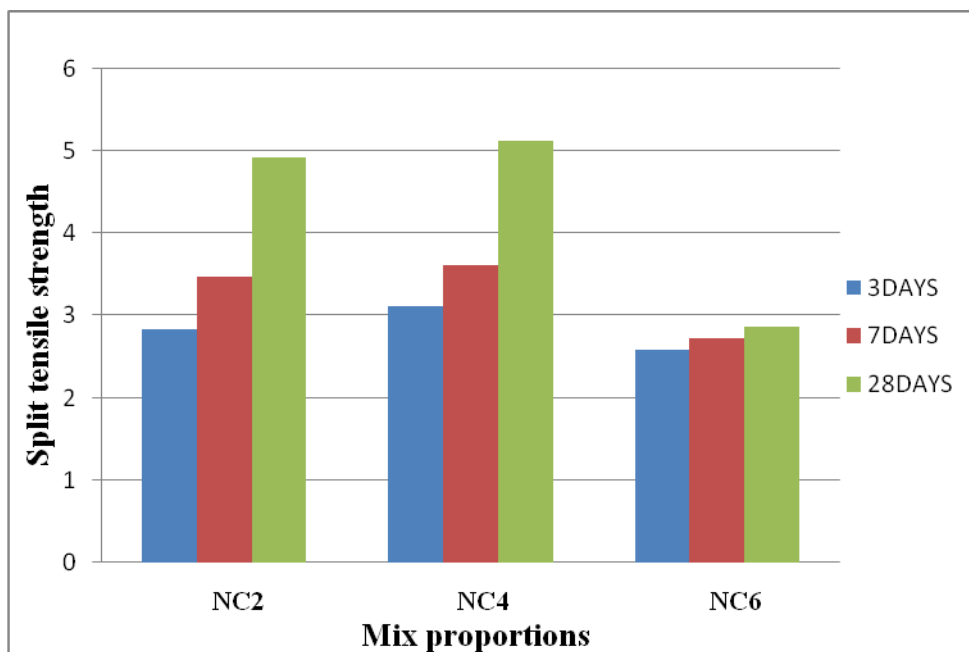


Fig. 4.7: Split tensile strength of cement mortar with Cloisite 30B NC > 1%

Table 4.5: Split tensile strength of cement mortar with Cloisite 30B NC> 1%

MIX	Split Tensile Strength (N/mm ²)			Average Split Tensile Strength (N/mm ²)		
	7 days	14 days	28days	7 days	14 days	28days
NC2	2.77	3.28	4.72	2.81	3.47	4.93
	2.81	3.40	4.98			
	2.85	3.74	5.10			
NC4	3.03	3.59	4.99	3.12	3.61	5.12
	3.15	3.61	5.18			
	3.17	3.63	5.20			
NC6	2.45	2.57	2.35	2.57	2.73	2.86
	2.57	2.71	2.86			
	2.70	2.90	3.37			

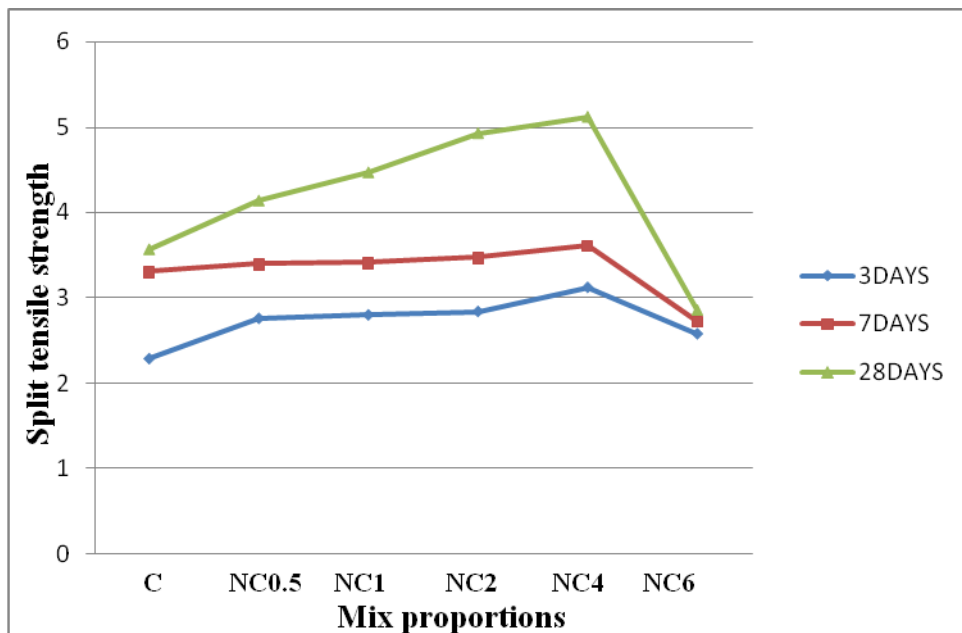


Fig. 4.8: Split tensile strength of cement mortar with Cloisite 30B NC

From **Fig. 4.8** it is observed that when NC is added by increasing proportions from 2%, 4% and 6% it is observed that the strength increases progressively up to 4%. In case of NC2 for 7days strength increases by 22.70% where as in case of NC4 the

strength increases by 36.24% as compared with the results of control mix samples where as for NC6 there is only 12.22% increase in strength which is very less as compared to NC2 and NC4 results. For 14days strength in case of NC2 the strength increases by 4.83% where as in case of NC4 there is 9.06% increase in strength as compared with results of control mix samples where as in NC6 there is 17.52% decrease in strength. For 28 days strength in case of NC2 and NC4 samples the strength increases by 38% and 43.41% where as for NC6 strength decreases by 19.88% as compared to 28 days strength of control mix samples.

The test results indicated that, when 2 to 4 percent by weight addition of Cloisite 30B for cement is done, split tensile increases progressively. When 6% NC was added to the weight of cement, strength starts decreasing.

The Cloisite 30B NC belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of NC fill the voids of the cement mortar and make the mixture denser and the mechanical property is improved due to pozzolanic reaction of Cloisite 30B NC with free lime.

4.4 Flexural Strength

Flexural strength was carried out at the age of 7, 14 and 28 days. Test results are shown below in **Table 4.6** and **4.7**.

As seen in table, test results indicated the addition of Cloisite 30B NC at different percentages. The NC was added with respect to the weight of the cement. There is increase of 38% and 43% strength with 2 to 4% addition of NC in the cement mortar respectively, when compared to control mix at age of 28 days. These results are represented graphically below in **Fig. 4.9** and **4.10**.

From **Fig. 4.9** it is clear that with the addition of Cloisite 30B NC flexural strength goes on increasing. From **Table 4.6** it is clear that for NC0.5 for 7 days the strength increases by 53.17% where in case of NC1 the strength increases by 64.35% as compared to control samples. For 14days in case of NC0.5 the strength increases by 58.06% whereas in case of NC1 the strength increases by 58.06% as compared to control mix. For 28 days in case of NC0.5 and NC1 there was increase in strength i.e. strength increases by 47.88% and 49.89% as compared to control samples.

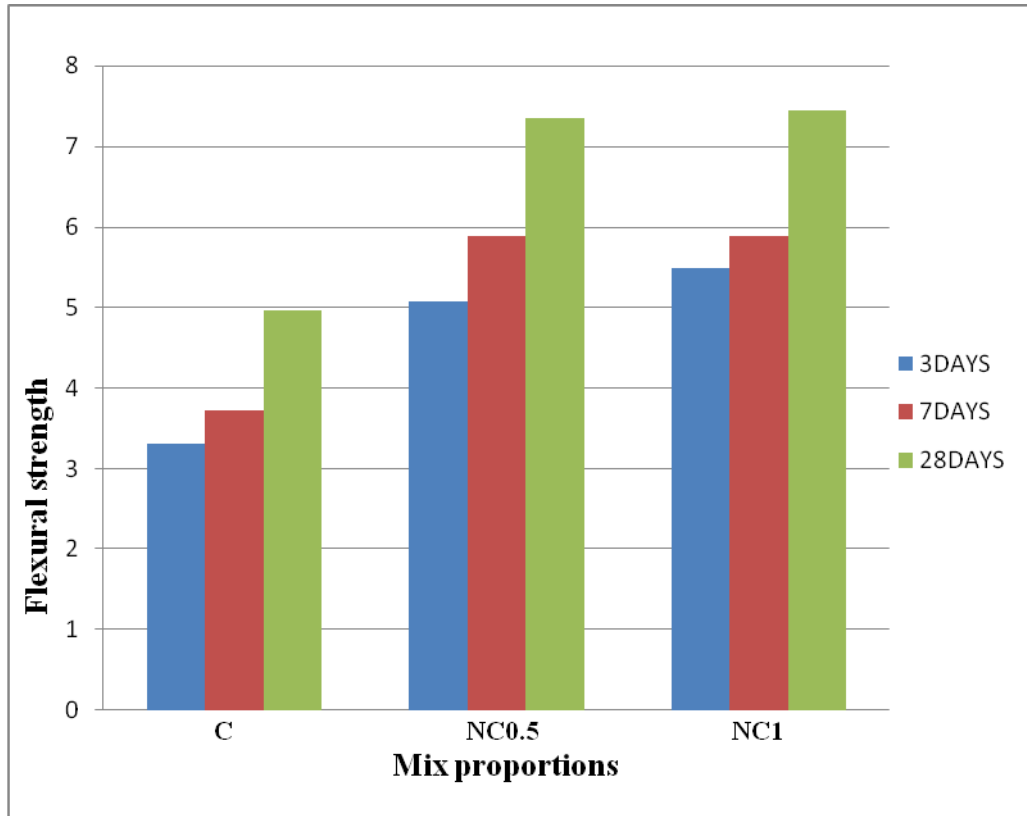


Fig. 4.9: Flexural strength of cement mortar with Cloisite 30B NC ≤ 1%

Table 4.6: Flexural strength of cement mortar with Cloisite 30B NC ≤ 1%

MIX	Compressive Strength (N/mm ²)			Average Compressive Strength (N/mm ²)		
	7 days	14 days	28days	7 days	14 days	28days
C	3.21	3.45	4.9	3.31	3.72	4.97
	3.36	3.75	4.97			
	3.38	3.96	5.03			
NC0.5	4.98	5.85	7.32	5.07	5.88	7.35
	5.10	5.88	7.34			
	5.15	5.91	7.39			
NC1	5.32	5.79	7.12	5.44	5.90	7.45
	5.42	5.82	7.39			
	5.51	6.10	7.84			

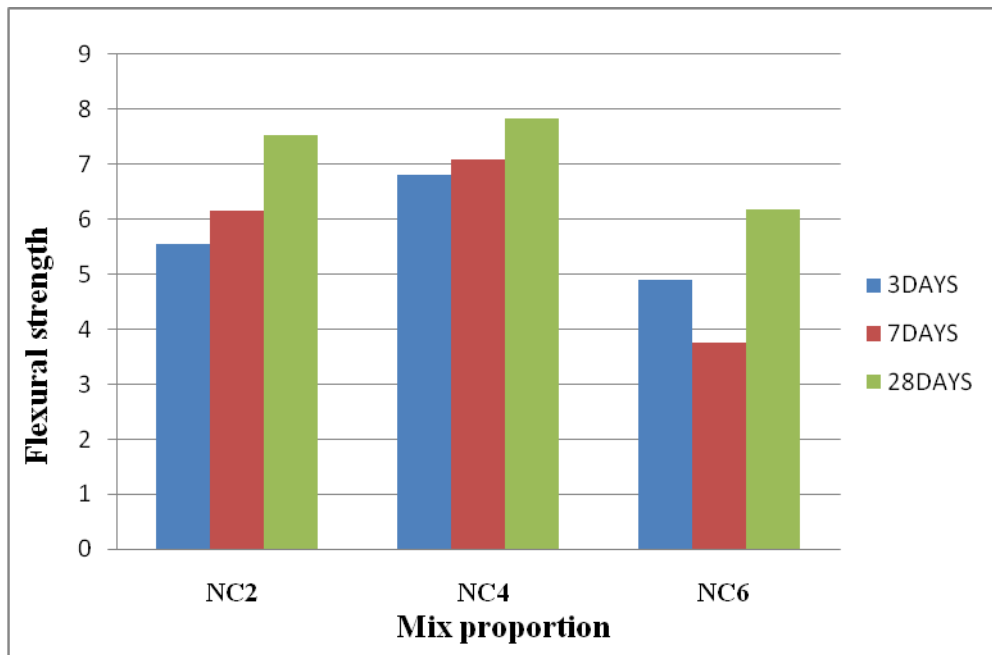


Fig. 4.10: Flexural strength of cement mortar with Cloisite 30B NC > 1%

Table 4.7: Flexural strength of cement mortar with Cloisite 30B NC > 1%

MIX	Flexural Strength (N/mm ²)			Average Flexural Strength (N/mm ²)		
	7 days	14 days	28days	7 days	14 days	28days
NC2	5.96	6.09	7.45	5.98	6.15	7.52
	5.99	6.16	7.54			
	6.02	6.20	7.56			
NC4	6.75	7.04	7.68	6.81	7.08	7.84
	6.84	7.06	7.90			
	6.86	7.14	7.95			
NC6	4.88	3.74	6.13	4.89	3.76	6.18
	4.89	3.77	6.18			
	4.90	3.79	6.24			

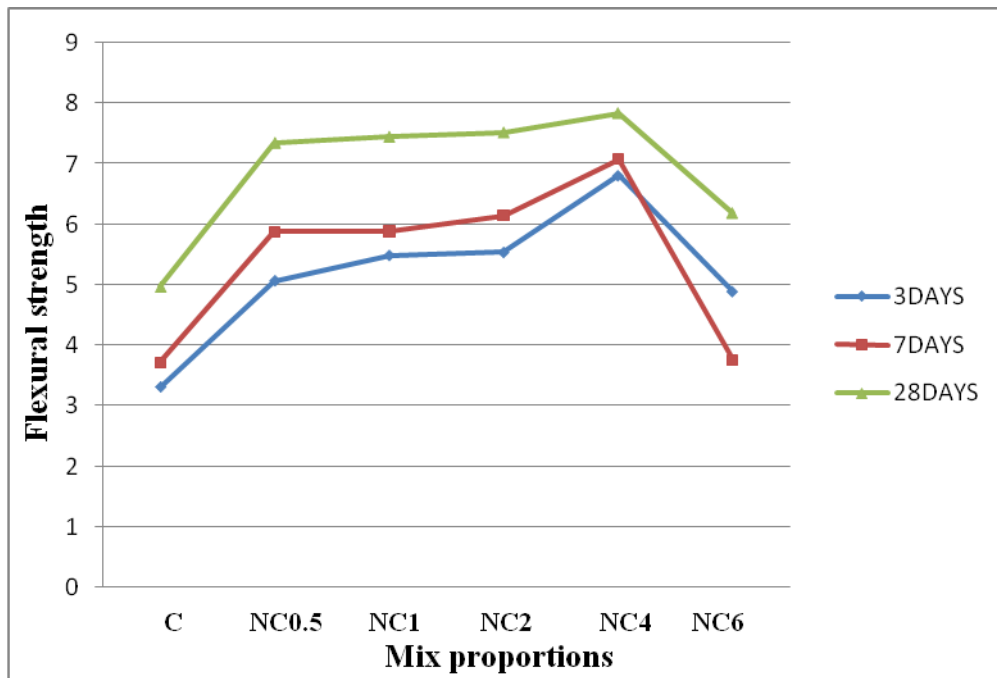


Fig. 4.11: Flexural strength of cement mortar with Cloisite 30B NC

From **Fig. 4.11** it is observed that when NC is added by increasing proportions from 2%, 4% and 6% it is observed that the strength increases progressively up to 4%. In case of NC2 for 7days strength increases by 80.66% where as in case of NC4 the strength increases by 105.74% as compared with the results of control mix samples where as for NC6 there is 47.73% increase in strength which is very less as compared to NC2 and NC4 results. For 14days strength in case of NC2 the strength increases by 65.32% where as in case of NC4 there is 90.32% increase in strength as compared with results of control mix samples where as in NC6 there is 1.07% increase in strength. For 28 days strength in case of NC2 and NC4 samples the strength increases by 51.30% and 57.74% where as for NC6 strength increases by 24.34% as compared to 28 days strength of control mix samples as compared to NC2 and NC4 results NC6 strength is very less.

The Cloisite 30B NC belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of nanoclay fills the voids of the cement mortar and make the mixture denser and the mechanical property is improved due to pozzolanic reaction of Cloisite 30B NC with free lime.

At 6% there is decrease of flexural strength is mainly due to improper filling effect of NC particles at the voids or pores in cement paste, and also due to the lack of

formation of CSH which is actually formed by the reaction of alumino-silicate containing Cloisite 30B NC with calcium hydroxide which makes the cement paste denser.

4.5 Differential Scanning Calorimeter (DSC)

Fig. 4.12 and **4.13** shows the variations of Differential Scanning Calorimeter (DSC) thermographs of plain and Cloisite 30B NC modified cement paste which are hydrated for 7 and 28 days.

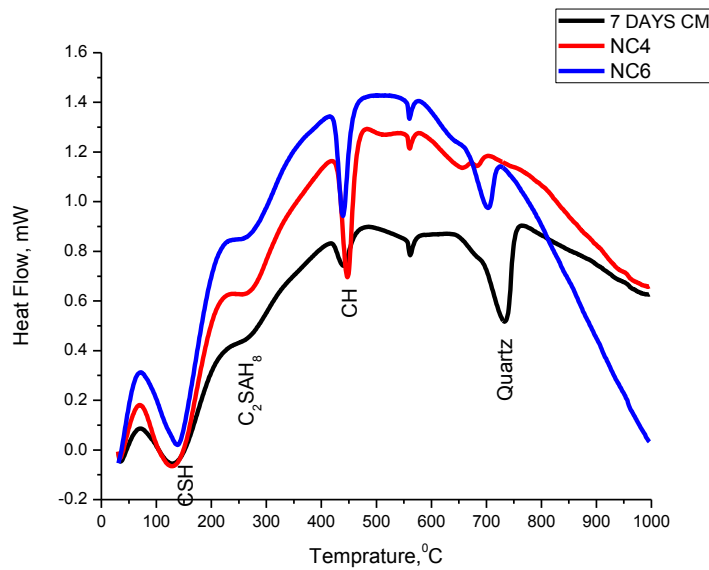


Fig. 4.12: DSC thermograms for plain and Cloisite 30B NC modified cement past hydrated for (7days)

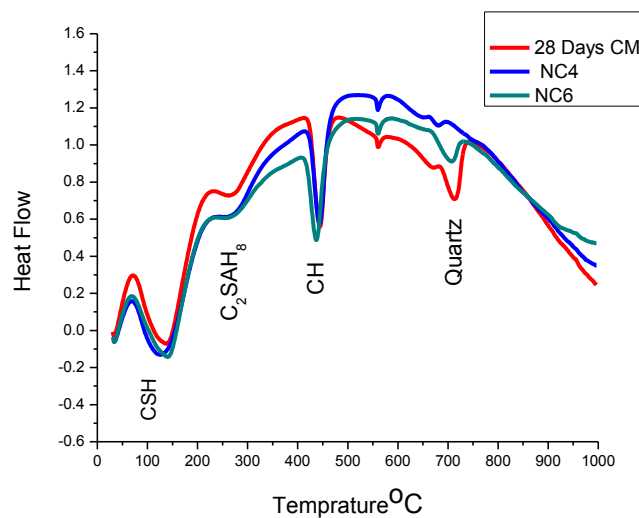


Fig. 4.13: DSC thermograms for plain and Cloisite 30B NC modified cement pastes hydrated for (28 days)

In both the cases at 7 days and 28 days there were almost four endothermic peaks. The first peak located at 120°C which was mainly due to the decomposition of calcium silicate hydrate (CSH). The second endothermic peak observed at 240°C which represents the decomposition of the gehlenite hydrate (C₂ASH₈). In this case the peaks formed at 7 days are wider as compared to 28 days peaks.

The third endothermic peak observed at 440°C which represents the decomposition of CH. The peaks of CH are much ill-crystalline at 28 days as compared with 7 days peaks. The intensity of CH was lower in the blended cement mix. The fourth endothermic peak observed at 740°C which represents the decomposition of quartz. The addition of 4% Cloisite 30B NC led to the transformation of CH phases from well crystalline to ill-crystalline. The presence of NC in the cement paste led to the increment of enthalpy, which represents the formation of well crystalline phases. The crystallizations which are produced by Cloisite 30B NC and CH can fill up the pores and enhance the microstructure and mechanical properties of the cementitious materials.

4.6 TGA

TGA was carried out on the some selective specimens such as control mix, 4% NC addition and 6% NC addition which are hydrated for 7 and 28 days. **Fig. 4.14** and **4.15** represents the TGA profiles.

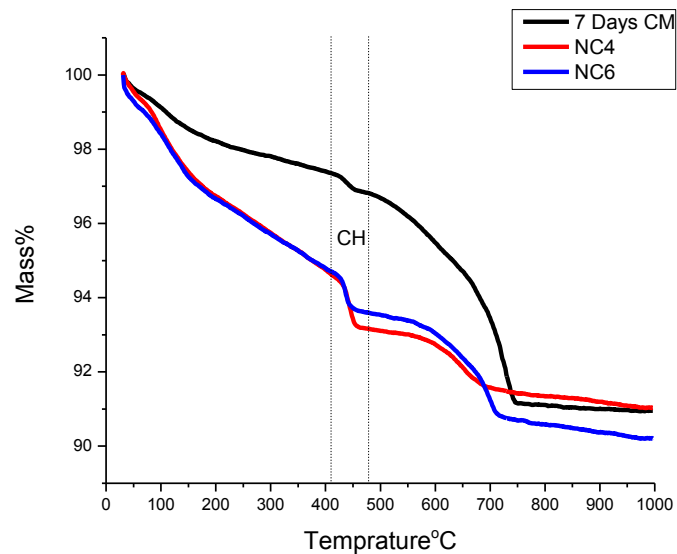


Fig. 4.14: TGA thermograms for plain and Cloisite 30b NC modified cement pastes hydrated for (7days)

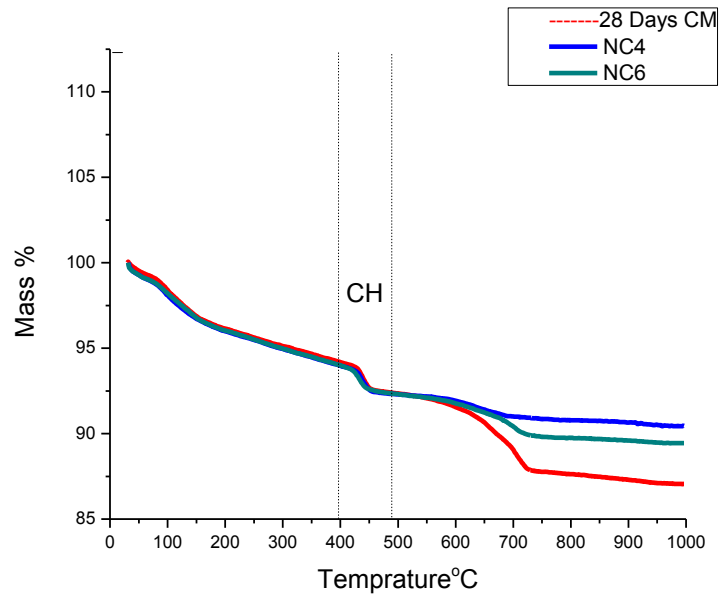


Fig. 4.15: TGA thermograms for plain and Cloisite 30B NC modified cement pastes hydrated for (28 days)

Fig. 4.14 and **4.15** represents TGA profiles of control mix, 4% and 6% addition of NC. The curve represents the reactions which occur in the cement matrix when the samples are subjected to a progressive temperature increase from room temperature up to 1000°C. The TGA curves represent three main endothermic peaks. The first endothermic peak was observed at 120°C, corresponding to the mass loss on the TGA curve up to 120, the mass loss is mainly of bound water in some hydrates like CSH. The second endothermic peak was observed at 440°C which represents the new loss in mass which starts around 420°C which corresponds to the de-hydration of CH. In this case Portlandite decomposes to form free lime at 420°C-480°C. The third peak was observed at 740°C, which occurs due to decomposition of calcium carbonate and also allows the escape of CO₂ from the cement matrix.

4.7 X-Ray Diffraction (XRD)

Fig. 4.16 shows the variations of X Ray Diffraction (XRD) graphs of plain and Cloisite 30B NC modified cement paste in which Cloisite 30B NC added in the proportion of 0.5%, 1%, 2%, 4% and 6% which are hydrated for 28 days.

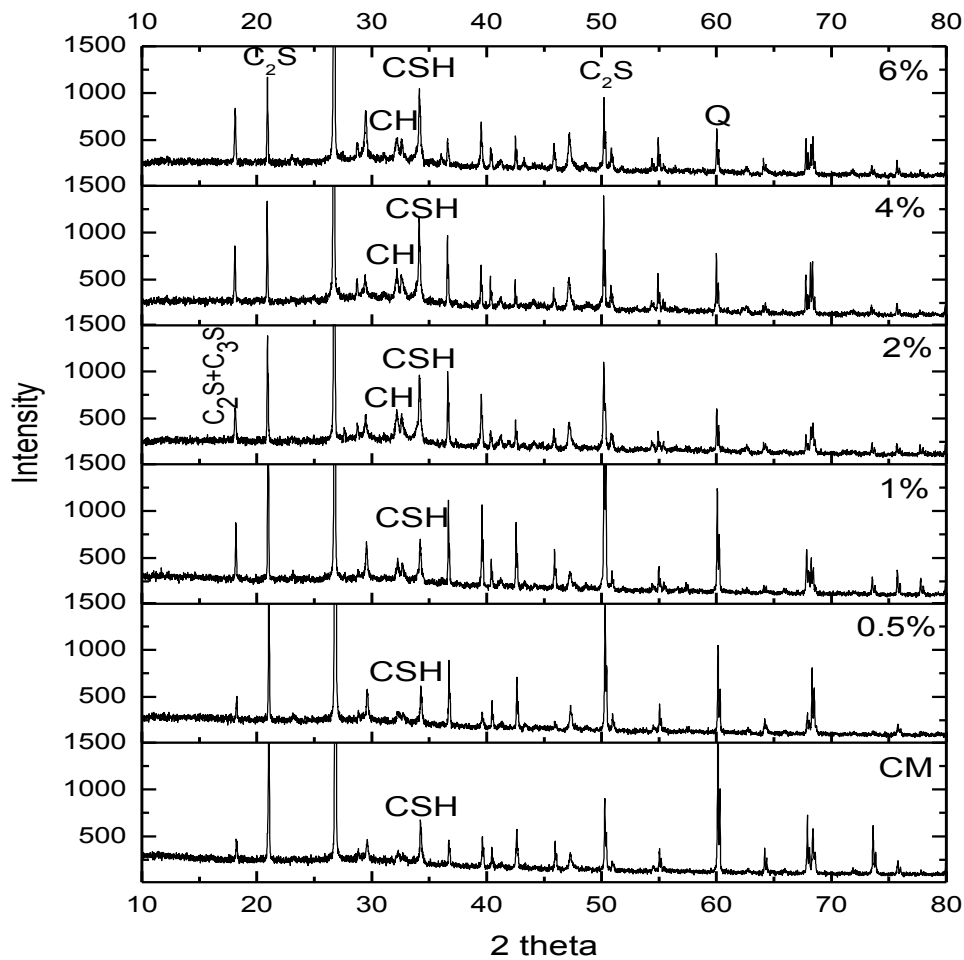


Fig. 4.16: XRD pattern for plain and Cloisite 30B NC modified cement pastes hydrated for 28days (at all additions)

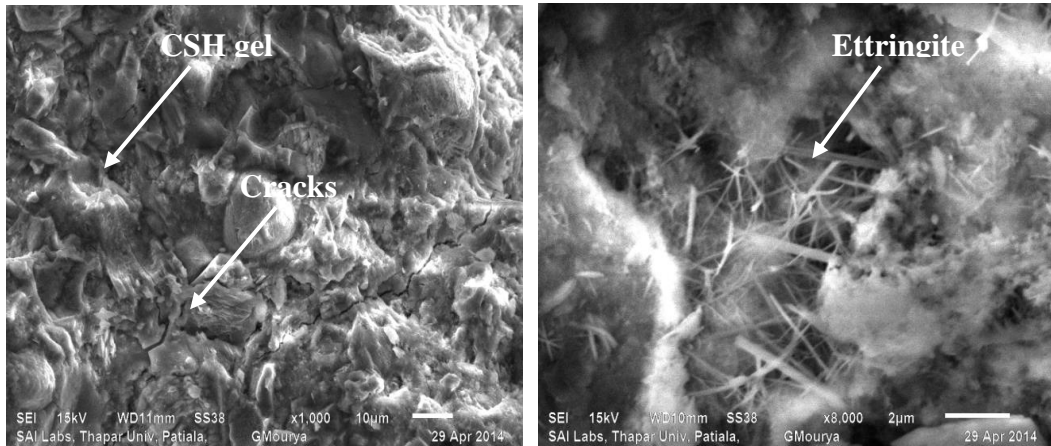
The main compounds detected are calcium silicate hydrate (CSH) and calcium hydroxide (CH). It is clear from the **Fig. 4.16** that CH peaks decreases with increase in the quantity of Cloisite 30B NC whereas, CSH peaks goes on increasing with increase in the quantity of Cloisite 30B NC.

The increase and decrease of CSH and CH intensity phases in Cloisite 30B NC cement paste hydrated for 28 days is mainly due to the pozzolanic reaction of Cloisite 30B NC with the free lime liberated during the process of hydration.

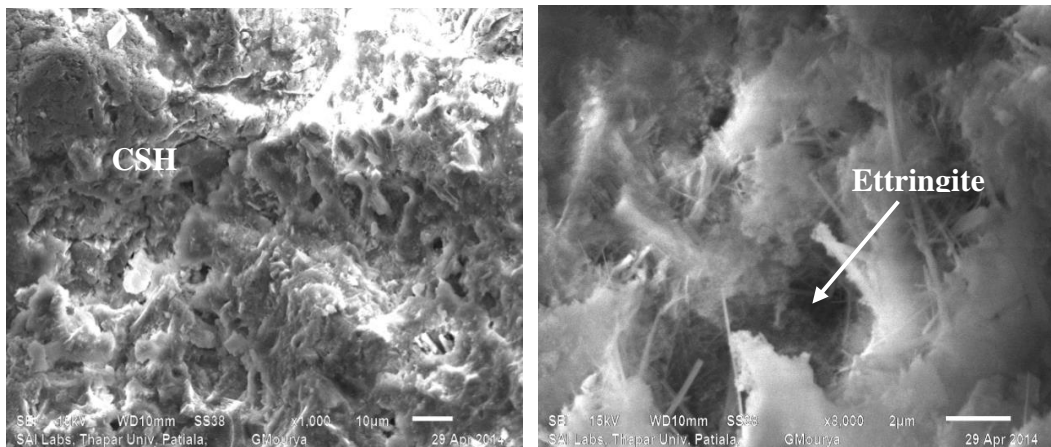
4.8 Scanning Electron Microscopy

SEM was carried out at the age of 28 days for variable proportions of NC. Test results are shown below in **Fig. 4.17**. Test results indicated the addition of Cloisite 30B NC at different percentages. The NC was added with respect to the weight of the cement.

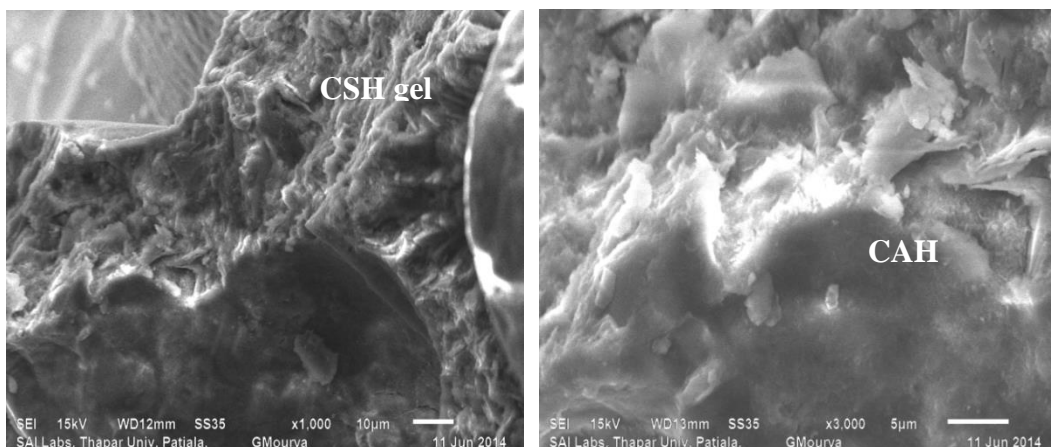
With the increase the addition of NC at 6% strength goes on decreasing. The micro-structure shows the formation of CSH gel, cracks, needle hydrates and voids.



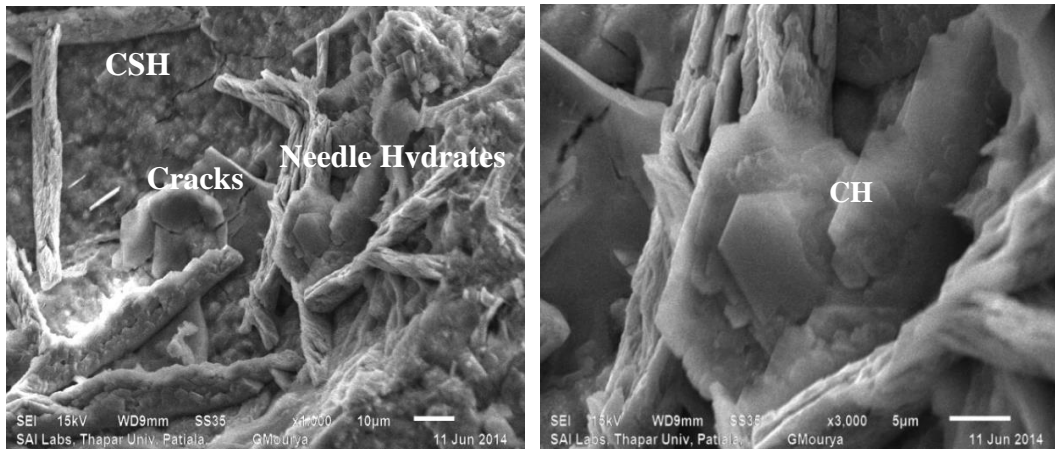
(a) C hydrated for 28 days



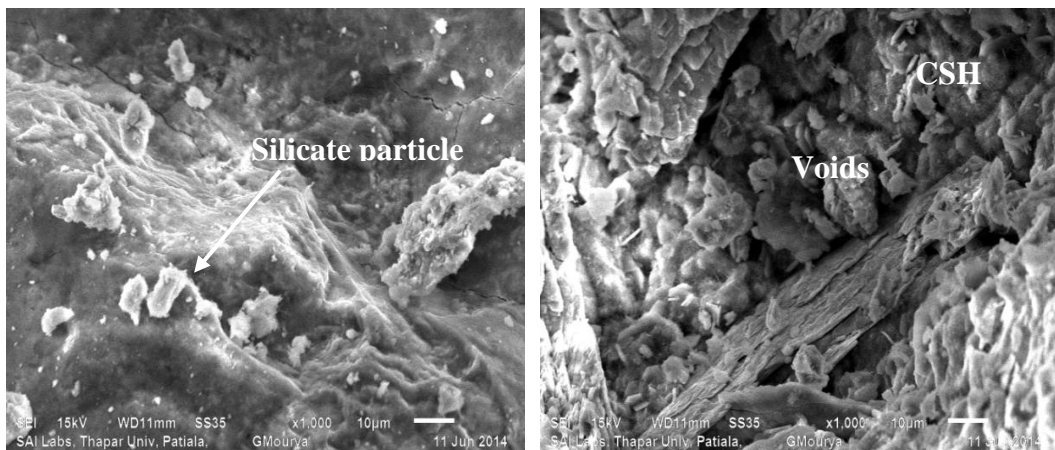
(b) NC0.5 addition in cement mortar hydrated for 28 days



(c) NC2 addition in cement mortar hydrated for 28 days



(d)NC4 addition in cement mortar hydrated for 28 days



(e)NC6 addition in cement mortar hydrated for 28 days

Fig. 4.17: SEM micrographs of Cloisite 30B NC cement pastes hydrated for (28 days)

Fig. 4.17 shows the SEM micrographs of Cloisite 30B NC cement pastes hydrated for 28 days. The test samples of the micro-structure were obtained from the central part of the specimens.

The SEM micrographs show all hydrated products such as CSH, CH etc. **Fig. 4.17 (a)** shows the microstructure of the cement paste without nanoclay. From **Fig. 4.17** it is concluded that CSH existed in the form of gel and SEM image also shows needle like crystals.

Fig. 4.17(b, c, d) represents the micro-structures of the mixture which containing 0.5%, 2% and 4% Cloisite 30B NC as compared to control mix the micro-structure is denser and compact. The improvement of micro-structure improves the mechanical properties of the NC modified cement mortar.

The Cloisite 30B NC improves the micro-structure and strength of the cement paste by a mechanism as follows; when the nano-particles are uniformly dispersed in the cement paste the hydrated products of cement will deposit on nano-particles due to their more surface area during hydration. Cloisite 30B will participate in the hydration process to generate the CSH through reacting with CH therefore the strength increases with the addition of NC.

Fig. 4.17 (e) represents the micro-structure containing 6% Cloisite 30B NC which causes decrease in the strength. The micro-structure represents the poor hydration and unhydrated cement grains. This results in decrease in mechanical properties of the sample.

4.9 Closing Remarks

In this chapter, the testing results were discussed. It is very clear from the results that nano-particles act as filler in the mortar mix to increase the strength. In the next chapter, conclusion were discussed which are drawn out from the results of the previous chapter.

CHAPTER 5

CONCLUSIONS & FUTURE SCOPE

5.1 General

The mechanical, thermal, micro-structure properties and chemical composition have been computed in the present work with the addition of 0.5%, 1%, 2%, 4% and 6% NC in the cement mortar. On the basis of present work the following conclusions are drawn.

5.2 Effect of Dispersion

- Dispersion of Cloisite 30B NC by powder mixing shows better results as compared to aqueous, as the coagulation is less and shows more appropriate results.

5.3 Effect of NC on Compressive Strength

- Compressive strength of NC of cement mortar for aqueous mixing shows progressive decrease in strength for 3, 7 and 28 days i.e. 39.72%, 39.6% and 78.60% with the addition of NC0.5 as compared with control mix sample. The results are not appropriate in this case so powder mixing was adopted.
- Powder mixing shows progressive increase in strength with the addition of NC2 and NC4 for 3, 7 and 28 days. The strength in case of 3 days increases by 24.04% in case of NC2 and 41.34% in case of NC4. In case of 7 days strength increases by 20.45% for NC2 samples and 14.81% for NC4 samples as compared with control mix sample and for 28 days strength increases by 7.78% and 20.58% for NC2 and NC4 samples.
- The addition of more nanoclay i.e. NC6 the strength decreases by 10.28% for 28 days as compared to control mix samples.

5.4 Effect of NC on Split Tensile Strength

- Split tensile strength shows progressive increase in strength with the addition of NC2 and NC4 for 7, 14 and 28 days. The strength in case of 7 days increases by 22.70% in case of NC2 and 36.24% in case of NC4. In case of 14 days strength increases by 4.83% for NC2 samples and 9.06%

for NC4 samples as compared with control mix sample and for 28 days strength increases by 38% and 43.41% for NC2 and NC4 samples.

- The addition of more nanoclay i.e. NC6 the strength decreases by 19.88% for 28 days as compared to control mix samples.

5.5 Effect of NC on Flexural Strength

- Flexural strength shows progressive increase in strength with the addition of NC2 and NC4 for 7, 14 and 28 days. The strength in case of 7 days increases by 80.66% in case of NC2 and 105.74% in case of NC4. In case of 14 days strength increases by 47.73% for NC2 samples and 65.32% for NC4 samples as compared with control mix sample and for 28 days strength increases by 51.30% and 57.74% for NC2 and NC4 samples.
- The addition of more nanoclay i.e. NC6 the strength decreases by 24.34% for 28 days as compared to control mix samples.

5.6 Effect of NC on Thermal and Microstructure Properties

- The results from XRD, DSC and TGA represent the higher formation of CSH and more consumption of CH and SEM micrographs show that the microstructure is appeared quite dense, compact which can be explained by greater surface area and also due to swelling quality of the NC which act as a filler in the pores.

5.7 Future Scope

- Considering all aspects it is suggested that optimized condition to obtain more strengthened cement mortar has to be established.
- Further work would be carried out with other percentages of nano-materials such as nanofibers, nanotubes etc. to get better yield of cement mortar.
- Dispersion of NC through aqueous mixing can be investigated by using various dispersing or stabilizing agents.

REFERENCES

- AL-Salami, A. E., Morsy, M. S., Taha, S., & Shoukry, H. (2013). Physico-mechanical characteristics of blended white cement pastes containing thermally activated ultrafine nano clays. *Construction and Building Materials*, 47, 138-145.
- Anjana, R., & George, K. E. (2012). Reinforcing effect of nano kaolin clay on PP/HDPE blends. *International Journal of Engineering Research and Applications*, 2: 868-872.
- Aly, M., Hashmi, M. S. J., Olabi, A. G., Messeiry, M., & Hussain, A. I. (2011). Effect of nano clay particles on mechanical, thermal and physical behaviours of waste-glass cement mortars. *Materials Science and Engineering: A*, 528(27), 7991-7998.
- Chang, T. P., Shih, J. Y., Yang, K. M., & Hsiao, T. C. (2007). Material properties of Portland cement paste with nano-montmorillonite. *Journal of materials science*, 42(17), 7478-7487.
- Dharaiya, D., & Jana, S. C. (2005). Thermal decomposition of alkyl ammonium ions and its effects on surface polarity of organically treated nanoclay. *Polymer*, 46(23), 10139-10147.
- Hakamy, A., Shaikh, F. U. A., & Low, I. M. (2013). Microstructures and mechanical properties of fabric reinforced organoclay–cement nanocomposites. *Construction and Building Materials*, 49, 298-307.
- Hakamy, A., Shaikh, F. U. A., & Low, I. M. (2014). Characteristics of hemp fabric reinforced nanoclay–cement nanocomposites. *Cement and Concrete Composites*, 50, 27-35.
- IS: 4031 (Part 4, 5&6)-1988: Methods of Physical Tests for Hydraulic Cement, Bureau of Indian Standard, New Delhi-1988.
- IS: 516-1959: Methods of Tests for Strength Of Concrete, Bureau of Indian Standard, New Delhi-1959.
- IS: 5816-1999: Methods of test for Splitting Tensile Strength of Concrete, Bureau of Indian Standard, New Delhi-1999.

IS: 8112-1989 (Reaffirmed 2005): Specification for 43 Grade Ordinary Portland Cement, Bureau of Indian Standard, New Delhi-2005.

Morsy, M. S., & Aglan, H. A. (2007). Development and characterization of nanostructured-perlite-cementitious surface compounds. *Journal of Materials Science*, 42(24), 10188-10195.

Morsy MS, Rashad AM, El-Nouhy HA. (2009). Effect of elevated temperature on physic mechanical properties of metakaolin blended cement mortar. *StructEngMech*, 31:1–10.

Morsy, M. S., Alsayed, S. H., & Aqel, M. (2010). Effect of nano-clay on mechanical properties and microstructure of ordinary Portland cement mortar. *Int J Civ Environ Eng IJCEE-IJENS*, 10(01), 23-27.

Morsy, M. S., Alsayed, S. H., & Aqel, M. (2011). Effect of Nano-Clay on Mechanical Properties and Microstructure of Ordinary Portland Cement Mortar. *International Journal of Civil & Environmental Engineering*.

Morsy, M. S., Alsayed, S. H., & Aqel, M. (2011). Hybrid effect of carbon nanotube and nano-clay on physico-mechanical properties of cement mortar. *Construction and Building Materials*, 25(1), 145-149.

Morsy, M. S., Al-Salloum, Y. A., Abbas, H., & Alsayed, S. H. (2012). Behavior of blended mortars containing nano-metakaolin at elevated temperatures. *Construction and Building Materials*, 35, 900-905.

Rashad, A. M. (2013). A synopsis about the effect of nano- Al_2O_3 , nano- Fe_2O_3 , nano- Fe_3O_4 and nano-clay on some properties of cementitious materials—A short guide for Civil Engineer. *Materials and Design*, 52(Complete), 143-157.

Sabir, B. B., Wild, S., & Bai, J. (2001). Metakaolin and calcined clays as pozzolans for concrete: a review. *Cement and Concrete Composites*, 23(6), 441-454.