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Halloysite Nano Clay in Construction Material – A Review

Anusha S.B[1], Chethan Kumar S[2]

[1]Student, Dept. of Civil Engineering, Dayananda Sagar College of Engineering, Bengaluru, 560078, India

[2]Assistant Professor, Dept. of Civil Engineering, Dayananda Sagar College of Engineering, Bengaluru, 560078, India

Abstract: Nowadays, the application of Nano materials has received great attentions to improve the conventional concrete properties. The ordinary/normal concrete has low tensile strength, so it was supplied with steel rebars in order to improve the tensile strength of the structural concrete. It was found that partial substitution of cement by pozzolanic materials enhance concrete steel bond strength. Nano-clay is one of the pozzolanic material which researchers have focused on investigating its effect on cement mortar and concrete recently.

Keywords: Halloysite, Nano-clay, Construction material, HNC

1. INTRODUCTION

Ordinary cement concrete is widely used construction material due to its high compressive strength, low cost and abundance in raw material. However, the common problem of plain/ordinary concrete is its low resistance to tensile load so steel rebars were provided with it in order to enhance the tensile strength to be used in structural concrete. In recent years, Nanotechnology has received special attention in many fields of applications, to manufacture materials with new different characteristics. It was found that supplementary pozzolanic Nano-materials such as silica fume, fly ash, slag and Nano clay have great potential in improving the hardened properties of concrete and it was also evident that concrete flow decreases upon incorporating nanoparticles in cementitious matrix. (Dungca et al., 2019; Elfeky et al., 2017)
Although certain Nanomaterials such as CNT's have found to have an adverse effect on the environment yet some other materials such as HNC seem more eco-friendly. CNT's have been regarded as ideal reinforcing agents because of their incredible strength and binding properties which increase the compressive and flexural-strength to a much greater level. CNT's are graphite sheets with carbon atoms bonded in a hexagonal pattern. However, CNT's are not considered free from harm for humans as well as the environment because of their toxicology potencies. With the advancement of research in the Nanocomposite field, another material has emerged as a safe option. Halloysites are naturally occurring eco-friendly Nanotubes with low cost. (Anjum & Kumar, n.d., 2018)
Halloysite Nano-clay (HNC) is an Aluminosilicate clay. Al2Si2O5(OH)4.H2O) is the chemical formula of HNC with Nano tubular and hollow micro structure and this Nano-material composed of Aluminum, Silicon, Hydrogen, and Oxygen. Halloysites have an outer diameter of 10-15nano-meter and 5-10 nano-meter of inner dimeter with 2-40 mm in length. (Anjum & Kumar, 2018) Halloysite nano-clay is a two-layered aluminosilicate with a predominantly hollow nanotubular structure. Chemically, the outer surface of the halloysite nanotubes had properties similar to SiO2 while the inner cylinder core was related to Al2O3. Halloysite has a 1:1 Al:Si ratio. (Farzadnia et al., 2013) Halloysite Nano Clay are unique and versatile Nano materials and are mined from natural deposits in countries like China, New Zealand, America, Brazil, and France. (Khan & Kumar, n.d.) The effect of halloysite nano-clay, which has a similar chemical composition with kaolin, on the mechanical properties, thermal behavior and microstructure of cement mortars. The formation of halloysite is due to hydrothermal alteration, and it is often found near carbonate. For instance, halloysite samples found in Wagon Wheel Gap, Colorado and United are suspected to be the weathering product of rhyolite by downward moving waters. (Khan & Kumar, n.d.) In general, the formation of clay minerals is highly favored in tropical and sub-tropical climates due to the immense amounts of water flow. (Khan & Kumar, n.d.) Halloysite has also been found overlaying basaltic rock, showing no gradual changes from rock to mineral formation.(Khan & Kumar, n.d.) Halloysite occurs primarily in recently exposed volcanic-derived soils, but it also forms from primary minerals in tropical soils or periglacially weathered materials. Igneous rocks, especially glassy basaltic rocks are more susceptible to weathering and alteration forming halloysite. (Khan & Kumar, n.d.)

Advantages of Halloysite Nano-clay

- Halloysites are naturally occurring eco-friendly nanotubes and harmless to humans. (Anjum & Kumar, n.d.)
- Abundant availability. (Anjum & Kumar, n.d.)
- They are highly dispersive with fine particle size and high surface area. (Anjum & Kumar, n.d.)
- Implementable in many forms such as powders, creams, gels. (Khan & Kumar, n.d.)

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- Superior loading rates to other carriers, Fast adsorption rate. (Khan & Kumar, n.d.)
- They are non-swelling compounds with high aspect ratio and high porosity. (Anjum & Kumar, n.d.)

2. REVIEWS

An experimental study conducted by Vidhya C.R [1] et al in 2014 on behavior of Halloysite Nano Tubes & Clay as an in –fill to Composite Steel tubes. To determine the ultimate load & deflection in HNC's composite steel hollow tubes under monotonic loading and further, SEM (scanning electron microscope) image are taken during mixing of the materials, before testing the specimen and after testing and for buckled steel tube, fracture analysis was carried out using Radiographic testing. Experiment was carried out on four different specimens with four variations in each specimen, which varies in length of 50, 75, 100, 125, 150 and 200mm with constant diameter of 25mm. And mixed with Cement, Sand & Halloysite nano-clay (0.5%, 1%, 1.5% and 2%). Tests are being conducted for the compressive strength of HNC's. When mixed with only cement, only sand & all the three. **Halloysite nano clay:** The source of the HNC used is New-Zealand and Sigma Aldrich being the manufacturer

Table 1: The Physical and chemical properties of HNC provide by the supplier

Synonyms	Kaolin clay
Formula	$H_4Al_2O_9Si_2 \cdot 2H_2O$
Appearance Form	Powder
Colour	White to tan
Diameter	30-70nm
Length	0.25-4microns
Relative density	2.53g/cm3
Molecular weight	294.19g/mol
pH value	6.5-6.9
Pore volume	1.26-1.34ml/gm

Fig.1: Halloysite Nano-clay

Ghazala Anjum [2] et al in 2016 used Carbon Nanotubes (Single walled and Multi walled) and Halloysite nano-clay to study the effect of nano-clays on compression and split tensile strength of cement mortar in comparison with plain cement paste. For both compression and split tensile strength, the specimens of constant diameter of 20mm and constant length of 40mm and materials of OPC 53 grade cement and sand passing through 2.3mm IS sieve been used. Single walled Nanotubes, Multi walled nanotubes and Halloysite nano clay was added into the specimen in dosages of 0.5, 0.75 and 1 wt% of the cement for both compression and split tensile tests and placed for testing after 7, 14 and 28 day of curing. Images during mixing, before testing and after testing are taken to study the SEM (scanning electron microscope) and Energy-dispersive X-ray spectroscopy (EDX) Analysis.

Fig 2(a): Single Walled CNT

Fig. 2(b): Multiwalled CNT

Fig. 2(c): HNC.

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Sara Allalou [3] et al in 2018 used Calcined Halloysite nano-clay to study the mechanical properties and microstructure of High-volume slag (HVS) cement mortar. Total of seven different cementitious materials were formulated. The first sample of High-volume slag cement mortar was formulated from 30% OPC and 70% GBFS. The remaining six samples were formulated by Calcined Halloysite nano clay was added into the specimen in dosages 1, 2, 3, 4, 5 & 6% of cement. The specimens of size 3cm*3cm cubes were casted for compression test and the cubes were tested after 2, 7, 28 and 90 days of curing and prismatic test specimens of size 40mm*40mm*160mm were used for flexural strength test. The results of the samples containing CHNC (Calcined halloysite nano-clay) as a partial replacement for HVSC were compared with the normal specimens.

Another experimental study on HNC done by Nima Farzadnia [4] et al in 2013 using Halloysite Nano-clay (1, 2, 3%) to study their effect on mechanical properties, thermal behavior and microstructure of cement mortars. A constant of 5% silica fume were added as a replacement for cement and 2% naphthalene sulfonate base superplasticizer (Darex Super 20) were applied for all the specimens. The specimens of size 5 cm × 5 cm × 5 cm cubes and 2 cm × 5 cm cylinders were used for compression test and permeability test respectively. 1, 2, 3% HNC were added to the mortars to study the mechanical properties, flowability, thermal behavior and durability. The results of the specimens containing HNC were compared with the specimens having zero HNC.

Table 2: Materials quantity

Mixes	**OPC**	**SF**	**Nano-clay**
Control	95	5	-
NC1	94	5	1%
NC2	93	5	2%
NC3	92	5	3%

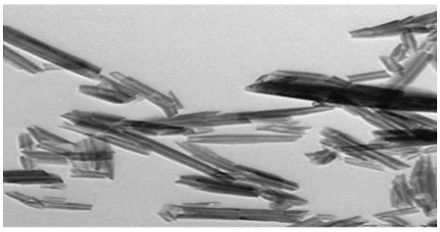

Fig 3: HNC

An experimental study done by Jonathan R. Dungca [5] et al in 2019 using Nano-montmorillonite and Halloysite nano-clay. This study is involved with the use of nano-montmorillonite (NMT) and halloysite nano-clay 9HNC) as partial substitutes to cement in which the workability and compressive strength of concrete are investigated at individual and combined replacements of these nano-clays. The chemical formula of Halloysite nano-clay is Al2Si2O5(OH)4 and the montmorillonite group exhibits larger particles with a general formula of (Ca, Na, H)(Al, Mg, Fe, Zn)2(Si, Al)4O10(OH)2 X H2O wherein silicate sheets enclose layers of Aluminum Oxide/Hydroxide (Al2(OH)4). The Halloysite nano-clay was provided by I-Minerals Inc. and Nano-montmorillonite by Guangzhou Xijia Chemical Co., Ltd.

Table 3: Percentage of replacement of Nano-clay

Samples	**Nano-clay Additive**	**% Replacement**	**Specimen samples**
Control	-	-	20
A1	NMT	0.5%	20
A2	HNCL	2.5%	20
B1	NMT & HNCL	1%	20
B2	NMT & HNCL	3%	20
B3	NMT & HNCL	5%	20

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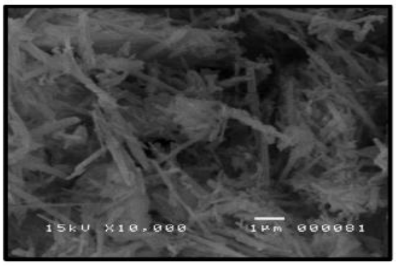

Fig. 4(a): SEM image of HNCL

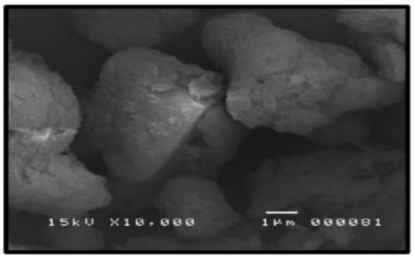

Fig. 4(b): SEM image of NMT

Table 4: Physical and chemical properties of nano-clay composites

Nano-clay composites	Particle shapes	Size	Form
NMT	Spherical	1nm~100nm	Powder
HNCL	Tubular	Length: 1micro-meter Diameter: 20nm	Powder

The proportions of water, fine aggregate, and coarse aggregate were specified per batch of 20 specimens. Meanwhile, the amount of HNCL and NMT incorporated as a partial replacement to cement in each sample.

A study by M. S. EL-FEKY [6] et al into the Coupled effect of nano-clay and carbon nano-tubes on the mechanical properties of concrete where CNTs are used to reinforce cement paste at the nanoscale while NC is used to increase strength by forming additional CSH gel. The Nano-clay added to the specimen in dosage 2.5%, 5% and 7.5% of cement by weight and CNTs added to the specimen in dosage 0.01%, 0.02% and 0.04%by weight of cement using the optimum percentage of NC. The Nano-clay (NC) which was used in the experiment is an off-white powder, calcined at 850o C for 3 hours, with particles size less than 150nm and Carbon nanotubes are mainly graphene sheets folded in cylindrical shape with length from 10 to 100 micro-meter with internal diameter from 1.5 to 15 nano-meter and external diameter to 50 nano-meter.

Table 5: The chemical composition of NC

Element	SiO2	FeO3	Al2O3	CaO3	MgO	TiO2	Na2O	Na2O
Content %	61.24	1.06	20.89	0.16	0.22	1.61	0.71	13.12

For the experiment, ordinary Portland cement, Natural available clean sand with particles size smaller than 0.5 mm, For the coarse aggregate, a clean crushed dolomite of 12mm maximum size and Naphthalene sulfonate-based superplasticizer was used.

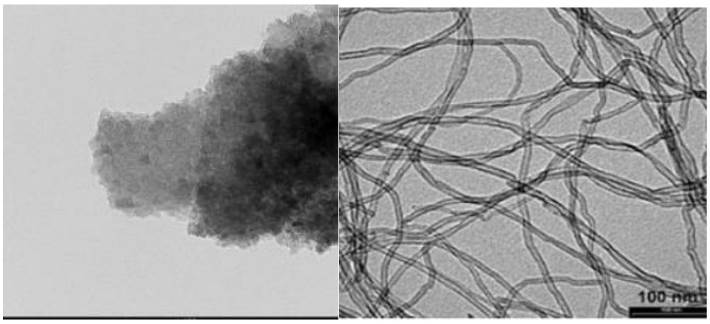

Fig 5: transmission electron micrographs (TEM) of nano-clay and carbon nano-tubes

The preparing compaction and curing of all specimens were executed in accordance to ASTM C31. Six cubes with dimensions (100*100*100mm3) were casted for implementing compressive strength test after 7 and 28 days of curing according ASTM C109. To find the optimization of CNTs, 3 cylinders with dimension (100 diameter *200 height mm2) were casted and tested after 28days of curing for investigation the tensile strength according to ASTM C496.

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3. RESULTS and DISCUSSIONS

[1] Vidhya C. R. in her study showed that, for specimens of length 300mm, diameter 22mm, thickness 5mm and M20 grade of concrete, the ultimate load obtained are 85.68, 88.25, 89.11 and 82.32 for the partial replacement of HNC's 0.5, 1.0, 1.5, and 2.0% respectively. As percentage of HNC's increases load also increases and reached optimum and started decreasing between 1.5 to 2%.

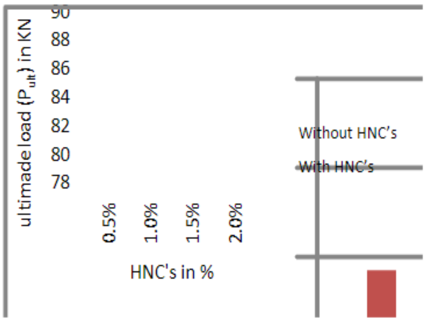

Fig 6: The graph ultimate load v/s HNC's in %

[2] The study by Ghajala Anjum, The Experimental Investigation on Influence of Carbon Nanotubes & Halloysite Nano-clay on Strength of Cement Mortar yielded the following graphs,

(a) Compression test at 28 days testing

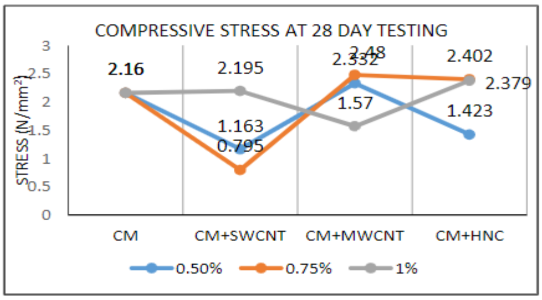

Fig 7(a): Compressive stress at 28 days testing

(b) Splitting tensile strength at 28 days testing

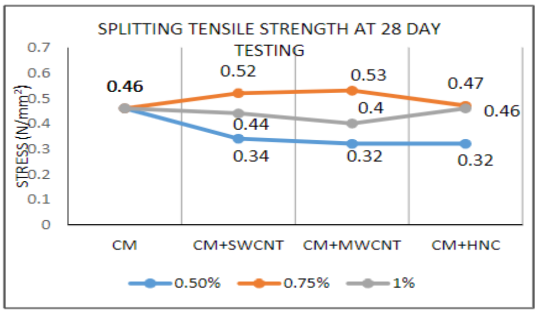

Fig 7(b): (b) Splitting tensile strength at 28 days testing

[3] The experimental study by Sara Allalou into the Effects of calcined halloysite nano-clay having the following results
(a) Substitution of 6% CHNC to the High-volume slag cement increased the w/c ratio from 0.25-0.267 to achieve the constant/standard consistency.
(b) Reduction of initial and final setting time of HVS cement with increasing the CHNC content.
(c) The HVS with partial replacement of 5%HNC mortar showed about 105, 29.70 and 36.21% higher compressive strengths at 2, 7 and 28 days, respectively and which also showed about 73.71, 16 and 16.40% higher flexural strength at 2, 7 and 28 days, respectively than the control specimen.

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[4] The study by Nima Farzadni revealed that,
(a) Flowability of samples containing nano-clay decreased as nano-clay was added into the mixture which was due to the high surface area of Nano-clay which needed more water to cover the surface area of NC

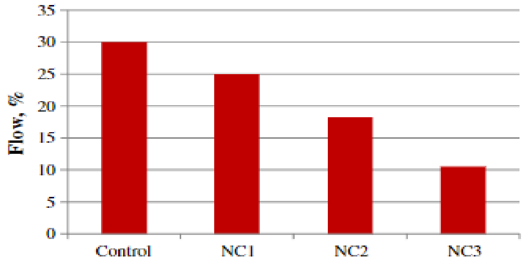

Fig. 8(a): Flowability

(b) Addition of 3% nano-clay increased the 28 days compression strength up to 24% compared to the control specimens.

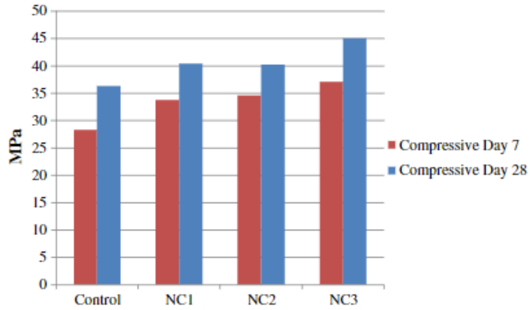

Fig. 8(b): Compression strength

(c) The addition of Nano-clay in mortars reduced the gas permeability. Adding 2% NC (Nano-clay) decreased Gas permeability up to 56%.

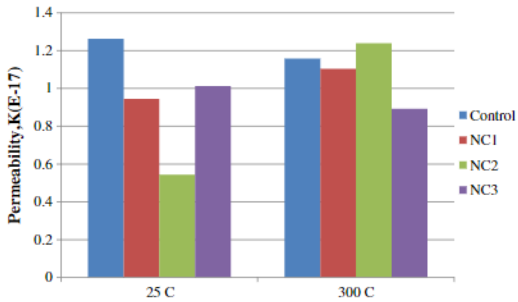

Fig. 8(c): Gas permeability

[5] The experimental study by Jonathan R. Dungca study the individual and combined effect of HNCL (Halloysite Nano-clay) and NMT (Nano-montmorillonite). In which effect of these nano-clays were investigated in terms of workability and compressive strength of concrete.
(a) Workability of fresh concrete: The addition of 2.5% HNC showed 3.704% rise and 0.5% NMT replacement showed 33.33% reduction of slump. The largest of 50 % reduction in the slump for a 5 % combined replacement of NMT and HNCL.
(b) Compressive Strength of Concrete: Result showed increase in the compressive strength of concrete specimens upon the partial replacement of cement by NMT (Nano-montmorillonite) and HNCL (Halloysite Nano-clay) at individual and combined replacements. The 28 days compression strength of control specimen showed 34.954MPa and for individual replacement the strength was 41.792MPa and 35.198MPa for HNCL and NMT respectively.
The combined replacements of Nano-clay (HNCL+NMT) generally showed a greater change in strength compared to individual replacements. The compressive strength of 3% combined replacement of HNCLNMT is 44.541MPa.

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[6] Results from the studies by M. S. EL-FEKY,
(a) Workability: The increment in the cement substitution by NC caused decreasing the workability of concrete. The lowest being 200 mm with the replacement 7.5% Nano-clay as compared to the plain/normal concrete 230 mm. The workability slightly increased at the addition of 0.01% CNTs and then began to decrease with increasing the percentage over 0.01%.
(b) Compression strength: It is recorded that the peak of the compressive strength reached to 28.4% at 28 days with 5% NC replacement, as compared to the control mix. The Nano-clay particles with 7.5% replacement affected negatively on the compressive strength. The combined effect improved the compressive strength as compared to the individual replacement of only NC. The 0.04% CNTs + 5%NC mix improved the compressive strength by 26.38% comparing to 5%NC mix.
(c) Tensile strength: As compared to the partial substitution 5% nano-clay, substitution of Carbon Nano-tubes enhanced the tensile strength.
The maximum value of tensile strength reached to 3.819MPa with the partial substitution of 5%NC + 0.02%CNT's of cement with gain about of 40.4% as compared to the 5% Nano-clay mix (2.72MPa). The gain decreased to 2.38% with incorporated 0.04% CNTs.
(d) The SEM images were taken to explain the morphology of experimental samples due to the effect of hybrid nanomaterials as compared to plain concrete without CNT's. The major effect of CNTs are filling effect, bridging effect and nucleation as sub-Centro plasm for C-S-H gel.

4. CONCLUSION

[1] Tests are being conducted for the compression strength of Halloysite Nano-clays when mixed with only cement, only sand and all the three. As percentage of HNC's increases load also increases and reached optimum and started decreasing between 1.5 to 2%. SEM and EDX analysis are shows that HNC's can lead to homogeneous mixture which in turns enhance the load carrying capacity of composite steel column. (Khan & Kumar, n.d.)

[2] Multiwalled Carbon Nano-tubes showed 18.2% more strength whereas Halloysite Nano-clay showed 14% increased in strength after 28days testing but Single-walled Carbon Nano-tubes showed 14% less strength compared to nominal mix. For compression testing, the optimum dosage for HNC found to be 1% by weight and for both Single-walled and multi-walled CNT's is 0.5wt%. Whereas 0.75% for all the nano-tubes for Split tensile strength. (Anjum & Kumar, n.d.)

[3] The water quantity increased with increasing the addition of CHNC contents for standard consistency which is due to the high specific surface area of this nano-clay and also it reduces the initial and final setting time of the cement paste. The High-volume slag cement mortars consisting of CHNC as a partial replacement, revealed higher compression and flexural strength than the control specimens at all ages of curing.
Specimens containing 5wt% CHNC as replacement for cement mortar achieved the highest mechanical strength, while the incorporation of more than 5wt% CHNC contents decreased their mechanical strengths. (Allalou et al., 2019)

[4]. Compared with the control specimen, the sample containing 3% Nano-clay showed 65% decrease in flowability. Partial replacement of 3% nano-clay in mortars improved the Compression strength by up-to 24%. The addition of Nano-clay in mortars reduced the gas permeability. Adding 2% NC (Nano-clay) decreased Gas permeability up to 56%. (Farzadnia et al., 2013)

[5] The workability of fresh concrete decreased when nano-clays were introduced in the mix. The combined replacements of Nano-clay (HNCL+NMT) generally showed a greater change in strength compared to individual replacements. The samples with combined replacement of 1% and 2% NMT and HNCL showed increase of compression strength. The optimum dosage of (NMT+HNCL) found to be 1% which showed 26.251% increase of compression strength and also which showed lowest decrease in workability that it 27.778%. (Dungca et al., 2019)

[6] As the percentage of NC and CNT increase, which workability decreases.
The optimum ratio for cement substitution by Nano-clay was found to be 5% with a rise of 28.4% as compared to the control mix without Nano-clay. However, it is found that adding both Nano-clays in the dosage of (5% NC & 0.01% CNTs) is an adequate ratio as a replacement by weight of cement to qualified microstructure and to improve the mechanical properties with a increase of 12.77% as compared to the control mix without CNTs. (Ahmed Gamal et al., n.d.)

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