

THE COMBINED EFFECTS OF NANO-MONTMORILLONITE AND HALLOYSITE NANOCCLAY TO THE WORKABILITY AND COMPRESSIVE STRENGTH OF CONCRETE

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ABSTRACT: In consideration of higher specifications for concrete, particularly in strength, the proportion of ingredients is usually modified to satisfy the mix design requirements. However, its practicality is not always appropriate in construction because of the expense and availability of the materials. Hence, additives and supplementary materials are adopted in the mix design with present studies directed to the application of nanoclay constituents to concrete technology. Consequently, the study is concerned with the utilization of nano-montmorillonite and halloysite nanoclay as partial substitutes to cement in which the workability and compressive strength of concrete are investigated at combined replacements of these nanoclays. The results show that the workability of fresh concrete generally decreased at the addition of nanoclay in the mix wherein a maximum loss of 50.000 % in the slump is observed for 5% replacement of the nanoclay combination. In addition, a 28th-day compressive strength of 44.541 MPa is achieved as the highest among the concrete samples at 3% replacement which demonstrates an increase by 27.430 % compared to a control specimen with a strength of 34.954 MPa. It is also recognized that there is a parabolic trend of compressive strength with respect to the amount of nanoclay replacement which indicates that the strength of concrete continues to increase until the optimal value of nanoclay replacement is attained. It is established that the optimal replacement of nanoclay combination for a curing period of 28 days is 2.562 % corresponding to a theoretical peak value of 46.060 MPa.

Keywords: Concrete, Additives, Nanoclay, Workability, Compressive strength

1. INTRODUCTION

Clay minerals have been a part of society and human existence since the very beginnings of civilization [1]. Clay, due to its varying mineral composition, has several substantial properties like its plasticity and cohesiveness [2]. As a result, it has been widely utilized as a constituent for industrial and commercial uses. Furthermore, clay can be associated with nanotechnology to have nanoclays, a mineral used in materials application. And with the development of nanotechnology throughout the years, endless advancements concerning nanoclays await to be discovered.

Nanoclay, through various researches and investigations, exhibits notable characteristics and properties which can be beneficial for the reinforcement of materials. In addition, nanoclays can be activators as it also demonstrates pozzolanic properties making it viable for the production of concrete [3]. Taking this into account, it is significant to look into the capabilities of nanoclay and its possible influence on the manufacturing and mechanical behavior of concrete.

Construction of concrete typically depends on its design mix. In fact, particular concrete designs and specifications heavily rely on the quality of the constituents used in production and this includes the

availability of these products with respect to location and transportation [4]. Furthermore, cement and concrete manufacturer is enveloped with several issues particularly relating to its sustainability. This includes economic, environmental, and social sustainability issues which pertain to matters such as local market volatility, wide usage of chemical substances and admixtures, and the high risk of impact on local communities [5]. Accordingly, nanomaterials, especially nanocomposites, may provide an adequate solution to these problems by creating an alternative to comply with the specifications of concrete.

This prompts the making of this study, particularly pertaining to the applications of nanoclay in cement and its potential influence in the properties of concrete. As previously mentioned, nanoclays possess pozzolanic compositions. With this in mind, nanoclays can be employed to develop an alternative form of cement or serve as a partial substitute for specific components of cement. Consequently, the feasibility of the nanoclay induced cement to the mechanical characteristics of concrete is looked upon as it would indisputably generate changes to the structure and composition of the concrete. Considering this, the probable improvement to the concrete incorporated with nanoclay, compared with

conventional concrete, is highly sought.

For the past century, several advancements have complied with the expectation of observing the effects of nanoclay on concrete. Among these experiments is a study by Chowdary and Kumar [6] which incorporates partial amounts of nanoclay to composite materials. The purpose of their study is to produce a composite reinforcing material with an overall better tensile and bending properties.

In accordance with previous sources and writings, nanoclay has been incorporated in several scientific fields such as the food industry, bioplastic development, and material modification. Mechanically, the predominance of nanoclay can be observed primarily in asphalt pavement modification as a result of its capability to increase shear complexity and reduce rutting and cracking [7]. Successively, nanoclay, together with concrete, exhibits high permeability and high-density competencies. As a result, nanoclay can be applied to structures in need of such properties including bridges, cut-off walls, tunnel linings, and damping systems.

Contrary to the past related studies and literature, this paper intends to scrutinize the effects of different types of nanoclay to concrete. Nanoclays such as nano-montmorillonite (NMT) and halloysite nanoclay (HNCL) are considered and discerned to produce alternative concrete as each type brings forth distinct enhancements to the properties of concrete [8]. Other types of nanoclays can also be considered due to the availability of the materials. Nevertheless, nanoclays are intended to be utilized as partial replacements to cement. The study proposes to replace significant amounts of cement with multiples kinds of nanoclay.

However, as previous studies only suggest partial replacements, specifically indicating and recommending the use of optimal percentage replacements. Likewise, this literature focused more on incorporating cement mortars and pastes with nanoclay or similar constituents. As such, a preliminary approach is to be developed by partly superseding nanoclay to cement in small incrementing ratios and testing for the concrete's specific mechanical properties, particularly its compressive strength and workability, for any significant deviations while observing compliance to the preferred optimal nanoclay ratio in established literature. Subsequently, if tests depict an increasing trend, large to full replacement of cement can possibly be conducted given the circumstance, else the study would focus on the determination of varying effects brought by the different types of nanoclay to concrete.

2. MATERIALS AND METHOD

2.1. Experimental Setup

The study incorporated nano-montmorillonite (NMT) and halloysite nanoclay (HNCL) as a partial replacement to cement wherein individual and combined effects of these nanocomposites in concrete were investigated in terms of compressive strength and workability. Apparently, the setup of the samples is divided into two main groups, namely, the 'A' samples for individual replacements of NMT and HNCL and the 'B' samples that represent specimens with a combination of these nanoclays.

The partial replacement of NMT and HNCL for 'A' samples are 0.5 % and 2.5 %, respectively, by cement weight as shown in Table 1. These percentage replacements were established based on the literature of Farzadnia, Ali, Demirboga, & Anwar [9] and Chang, Shih, Yang, & Hsiao [10] as the effective amount of nanoclay in cement paste and mortar. Meanwhile, in 'B' samples, as shown in Table 1, the replacement of nanoclays are done for 1 %, 3 % and 5 % of cement at a constant NMT to HNCL ratio of 1:5 with reference to the percentage replacements in 'A' samples. The incremental replacements in 'B' samples were intended to determine the trend of compressive strength and workability at an increasing amount of nanoclay replacement. It is also included in the study to investigate the progression of concrete's compressive strength at different ages such that 5 specimens are needed to establish a reliable data for strength in every 7-day increment of curing until the 28th day which totals to 20 specimens per sample.

Table 1 Concrete Specimens

Sample	Nanoclay 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

The selection of proportions and specification for the concrete mix design of the specimens were based

on the standards of American Concrete Institute (ACI) 211.1. Meanwhile, the preparation of concrete specimens as well as the assessment of concrete behavior, particularly with compressive strength and workability, are referenced from the American Society for Testing and Materials (ASTM).

2.2. Properties of Nano-Montmorillonite and Halloysite Nanoclay

The nanoclays were provided by I-Minerals Inc. and Guangzhou Xijia Chemical Co., Ltd. for HNCL and NMT, respectively wherein the physical properties of these nanoclays are summarized in Table 2. In addition, a Scanning Electron Microscope (SEM), is used to characterize these nanoclays (Figures 1 and 2) with great contrast and spatial resolution and ancillary capability for element analysis and imaging [11].

Table 2 Physical Properties of Nanoclay Composites

Nanoclay Composite	Particle Shape	Size	Form
NMT	Spherical	1 nm ~ 100 nm	Powder
HNCL	Tubular	Length: 1 μ m Diameter: 20 nm	Powder

It is determined that for the kaolinite group of clays, such as halloysite nanoclay (HNCL), a chemical formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is the same for different members in the group however its structure varies per member [12]. The predominant structure of HNCL is a hollow nanotube of a two-layered aluminosilicate which is able to grow into long multi-walled tubules similar to multi-walled carbon nanotubes. It has a 1:1 ratio of Aluminum to Silicon with a stoichiometry of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. In addition, the outer surface of the nanotubes is similar to SiO_2 while the inner cylinder core is related to Al_2O_3 [9]. In comparison, the montmorillonite group exhibits larger particles with a general formula of $(\text{Ca}, \text{Na}, \text{H})(\text{Al}, \text{Mg}, \text{Fe}, \text{Zn})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$ wherein silicate sheets enclose layers of Aluminum Oxide/Hydroxide ($\text{Al}_2(\text{OH})_4$) [12].

The clay particles manifest a pozzolanic behavior when silica and aluminum are present while, at the same time, acts as nuclei of hydration and because of its nano-size particles, it becomes an effective filler in the cement matrix that develops the performance of concrete. Furthermore, due to the chemical reactions that transpire in the mix, a dense cement matrix with a high calcium silicate hydrate (C-S-H gel) and less calcium hydroxide is produced [12].

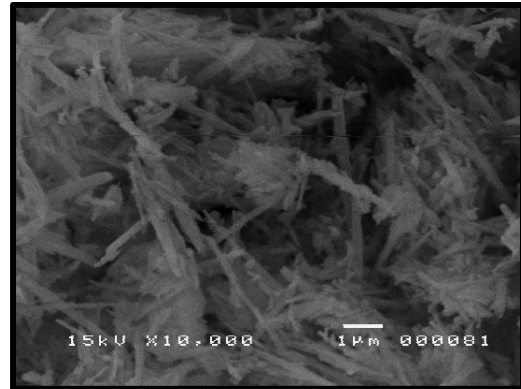


Fig. 1. SEM Image of HNCL at 10k Magnification

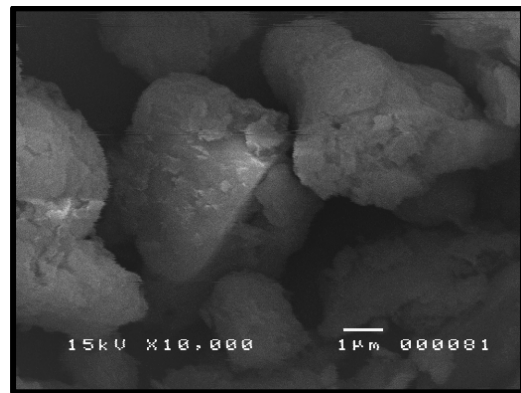


Fig. 2. SEM Image of NMT at 10k Magnification

2.3. Specification and Proportion of Concrete Mix Design

The selection of proportion, as well as the specification, for the mix design of concrete samples was accomplished based on the standards of American Concrete Institute (ACI) 211.1 with reference to the literatures of Farzadnia, Ali, Demirboga, & Anwar [9] and Chang, Shih, Yang, & Hsiao [10]. In addition, the cement and aggregates utilized in the study were sponsored by DEMA Hardware and Construction Supply. Meanwhile, the tests to determine the properties of these materials, which serves as a basis in performing the design, were done by the Universal and Testing Laboratory and Inspection, Inc. The summary of results on the background data of cement and aggregates are shown in Tables 3, 4, & 5 and the specifications of the mix design are indicated in Table 6.

Table 3 Background Data on Cement

Type and Classification	Type IP, General Purpose
Specific Gravity	3.150

Table 4 Background Data on Fine Aggregates

Specific Gravity, Dry	2.343
Moisture Content (%)	6.195
Absorption (%)	4.384
Fineness Modulus	2.950

Table 5 Background Data on Coarse Aggregates

Specific Gravity, Dry	2.789
Moisture Content (%)	1.349
Absorption (%)	0.802
Maximum Size (mm)	19
Dry Rodded Density (kg/m ³)	1682

Table 6 Specifications of Mix Design

Target Slump (mm)	50
Strength Requirement (MPa)	30
Water Per Cubic Meter of Concrete (kg/m ³)	190
Water to Cement Ratio by Weight	0.54
Entrained Air (%)	2, Non-Air Entrained
Quantity Coarse Aggregates (%)	60.5

The proportions of the initial mix were determined from the design specifications and background data of cement and aggregates. There were adjustments made on the proportions of the mix design based on the yield results of the trial mixes to achieve the target slump of fresh concrete. The working mix design is accomplished at the second adjustment of the proportions wherein a 50-millimeter slump is obtained. In Table 7, the proportions of water, sand, and gravel were specified per batch of 20 specimens. Meanwhile, the amount of HNCL and NMT incorporated as a partial replacement to cement in each sample per batch is indicated in Table 8.

Table 7 Proportion of Water, Sand, & Gravel Per Batch of 20 Specimens in Kilograms

Water	Sand	Gravel
7.177	20.447	37.807

Table 8 Amount of Nanoclays in Samples as Partial Replacement to Cement Per Batch of 20 Specimens in Kilograms

Sample	Cement	NMT	HNCL
Control	14.313	-	-
A1	14.242	0.072	-
A2	13.956	-	0.358
B1	14.170	0.024	0.119
B2	13.884	0.072	0.358
B3	13.598	0.119	0.596

3. RESULTS AND DISCUSSION

The study involved an analysis of concrete specimens with cement partially replaced by nanomontmorillonite (NMT) and halloysite nanoclay (HNCL) in which the individual and combined effects of these nanoclays were investigated in terms of workability and compressive strength of concrete. Furthermore, the details of the discussion elaborate on the results of the nanoclay combination in 'B' samples based on the correlation of fresh concrete workability, as well as, its compressive strength in the hardened state to the amount of cement that is partially replaced by nanoclay with reference to 'A' samples with only individual replacements.

3.1. Workability of Fresh Concrete

It is recognized from the results in Table 9 and the bar plot in Figure 3 that the workability of fresh concrete generally decreased when there is nanoclay present in the samples. The largest decline in workability is observed in B3 wherein there is a noticeable 50 % reduction in the slump for a 5 % replacement of NMT and HNCL combination. However, the addition of nanoclay in the mix also produced a slight rise in the slump in one of the samples as the workability in A1 increased by 3.704 %. Nevertheless, the increase in A1 is minor compared to the loss of workability in the other samples, not to mention, that only 0.5 % of cement is replaced by NMT in A1.

Table 9 Slump Test Results

Sample	Slump (mm)	% Decrease from Control
Control	54	-
A1	56	-3.704 %
A2	36	33.333 %
B1	39	27.778 %
B2	33	38.889 %
B3	27	50.000 %

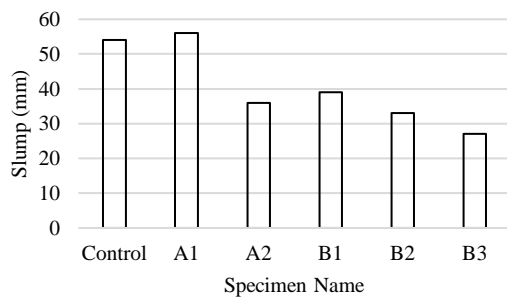


Fig. 3 Bar Plot of Slump Per Sample

The plot in Figure 4 relates the workability of fresh concrete to the increasing increment of nanoclay combination replacement in 'B' samples. It illustrates a decreasing trend in the slump as the replacement of nanoclay is increased. Furthermore, there is a sudden decrease of slump observed when nanoclay is introduced in the mix with reference to the control sample and a gradual reduction of workability at further increments of nanoclay replacement. The loss in workability is the result of the influence of clay particles in the water distribution of the mix [12].

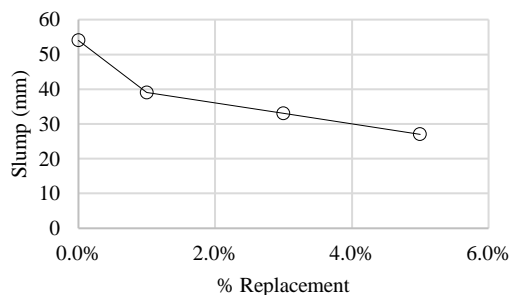


Fig. 4 Plot of Slump at Increasing Percentage Replacement of Nanoclay Combination in 'B' Samples

3.2. Compressive Strength of Hardened Concrete

The values in Table 10 are the mean compressive strength of the samples with the outliers removed. In addition, the significance of the change in 28th day compressive strength of these samples is established through an analysis of variance (ANOVA) and a t-test of the mean results with reference to the control sample as shown in Table 11 and Table 12. There are two conditions to determine the significance of the results; the F critical is less than the F value and the P value is less than the specified alpha level [13], which in this case is 0.05.

Table 10 Mean Compressive Strength of Samples Per 7 Day Increments in Megapascals

Sample	7 th Day f_c	14 th Day f_c	21 st Day f_c	28 th Day f_c
Control	23.875	28.747	32.579	34.954
A1	25.122	26.511	34.651	35.198
A2	31.274	34.232	40.130	41.792
B1	32.501	36.497	39.737	44.129
B2	34.423	39.280	43.373	44.541
B3	27.425	33.171	36.103	37.248

The results indicate an apparent increase in the compressive strength of concrete samples upon the addition of NMT and HNCL at individual and combined replacements for cement. The trend of compressive strength in 'A' samples, as illustrated in Figure 5, suggests that HNCL at 2.5 % replacement in A2 samples produces a higher value of strength compared to A1 samples with 0.5 % replacement of NMT. Likewise, the 'B' samples in Figure 6 also establish an increase in compressive strength wherein B3 at 5 % replacement of NMT and HNCL combination shows the lowest trend of increase, followed by B1 at 1 % replacement and B2 with the highest trend among the 'B' samples at 3 % replacement.

It is also observed that the trend of compressive strength at combined replacements of nanoclay in 'B' samples generally yields a greater change in strength compared to individual replacements of 'A' samples with reference to a control variable. In fact, the difference of the trends indicates that there is an apparent reaction between NMT and HNCL in 'B' samples with combined nanoclays that produces a

higher strength in the concrete specimens. However, in 'A' samples with single nanoclay substitution, percentage replacements are only based from single values such that the relationship of concrete strength to the amount of nanoclay is not considered for samples with individual replacements.

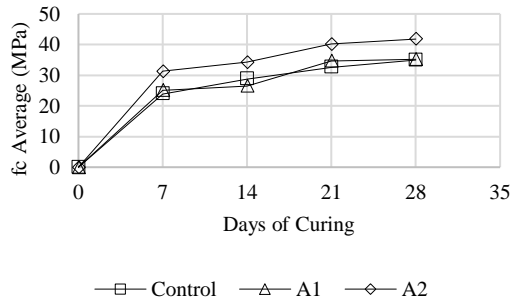


Fig. 5 Plot of Mean Compressive Strength in 'A' Samples for 7 Day Increments

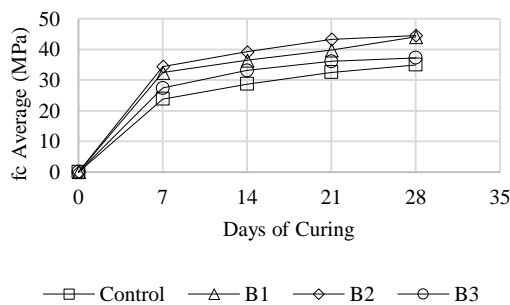


Fig. 6 Plot of Mean Compressive Strength in 'B' Samples for 7 Day Increments

Furthermore, it is determined from the ANOVA results in Table 11 that the difference in the 28th-day strength of the specimens in both groups of 'A' and 'B' samples are significant with respect to a control sample which validates that nanoclay is effective as cement replacement. However, a paired sample t-test for the 28th day strength indicates that A1 with a strength increase of 0.701 % at 0.5 % replacement of NMT is statistically the same with the results of the control sample whereas, for A2, the results are relatively significant with a 19.565 % increase in strength with HNCL at 2.5 % replacement. The results of compressive strength for A1 is the consequence of directly substituting NMT in the concrete mix, wherein, without any prior preparation, the nanoclay is ineffective to concrete because the expansion of silicate sheets in clay particles is not restricted and there are also alkali cations present in these layers that affect the durability of concrete [14]. Meanwhile, the 19.565 % increase in strength for A2 with HNCL replacement of 2.5 % corresponds with the literature of Farzadnia, Ali, Demirboga, & Anwar

[9] wherein for 2 % and 3 % replacement of HNCL in cement mortars there is a 24 % increase in compressive strength.

Table 11 Summary of ANOVA Results for the 28th Day Mean Compressive Strength (MPa) of Control and Samples with Individual and Combined Replacements

Samples in Group	Mean Values	P Value	F Critical	F Value
Control	34.954			
A1	35.198	0.00036	3.885	16.463
A2	41.792			
Control	34.954			
B1	44.129	0.00004	3.239	16.612
B2	44.541			
B3	37.248			

Table 12 Summary of T-test Results for the 28th Day Mean Compressive Strength (MPa) of Samples Paired to Control

Paired Samples	Mean Values	P Value
Control, A1 (One-Tailed)	34.954, 35.198	0.43442
Control, A2 (One-Tailed)	34.954, 35.198	0.00553
Control, B1 (Two-Tailed)	34.954, 44.129	0.00458
Control, B2 (Two-Tailed)	34.954, 44.541	0.00307
Control, B3 (Two-Tailed)	34.954, 37.248	0.06629

In addition, the values in 'B' samples also show a certain degree of significance where an apparent increase of 26.251 %, 27.430 %, and 6.565 % in the 28th-day strength is observed for B1, B2, and B3, respectively. It is also recognized that the increase of strength in 'B' samples, particularly in B1 and B2, is apparently higher than the strength of 'A' samples indicating that the combination of NMT and HNCL produces a relatively higher strength compared to individual replacements. It is considered that the increase of strength in 'B' samples is a requisite to the compatibility of HNCL to restrict the reactions of alkali cations [14] in the layers of NMT particles [15] such that both nanoclays contribute in the

development of concrete strength. Consequently, the t-test determined that only B3 with 5 % replacement of NMT and HNCL combination is not significant among the 'B' samples. The results of t-test for B3 is validated by the plot of compressive strength to percentage replacement in Figure 7 wherein it is observed that the trend decreased at 5 % indicating that the amount of nanoclay in the mix already exceeded the optimal value.

It is then recognized that there is a parabolic trend of compressive strength in correlation to the amount of nanoclay substituted to cement as shown in Figure 7. The curve is from the results of the combined effect of NMT and HNCL in the compressive strength of concrete for 'B' samples. The strength-replacement curve elaborates that the compressive strength increases as nanoclay fills in the voids of the cement matrix resulting in a denser structure [16]. However, there is only a limit to the increase of compressive strength since clay particles have an influence on the water in the mix [12] such that excessive amount of clay results to less distribution of water which then decreases the compressive strength [4].

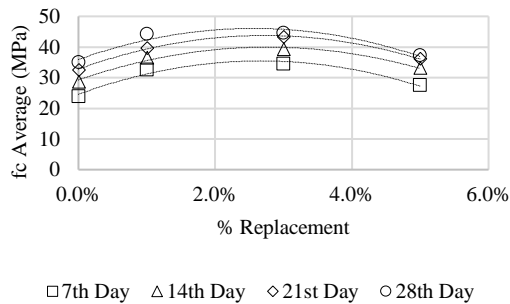


Fig. 7 A plot of Compressive Strength at Increasing Percentage Replacement of Nanoclay Combination in 'B' Samples

The relationship of compressive strength to the amount of combined NMT and HNCL replacement in 'B' samples displays a parabolic curve that suggests an increase of strength at initial replacements and a decline at excessive amounts as the replacement surpasses the optimal percentage. Hence, the optimal values of nanoclay replacement to achieve the highest compressive strengths per 7 days of curing until the 28th day are derived through a first derivative test of the parabolic equations in Table 13 wherein peak values are computed correspondingly as shown in Table 14. The optimal replacements range from 2.5 % to 3.0 % which is consistent with the plotted curve in Figure 5.4.3 that produces theoretical strength values of 35 to 46 MPa.

Table 13 Equations of Parabolic Curve in the Plot of Compressive Strength at Increasing Percentage Replacement Per 7 Day Increments of Curing in 'B' Samples

Curing Days	Parabolic Equation
7	$y = -15436x^2 + 790.83x + 35.931$
14	$y = -14826x^2 + 806.26x + 32.780$
21	$y = -14003x^2 + 775.25x + 29.233$
28	$y = -15274x^2 + 815.60x + 24.570$

The equations of the parabolic curve expressed in Table 13 show the relationship between the compressive strength of the cylindrical specimens as the dependent variable 'y' with the nanoclay percentage replacements as the independent variable 'x'.

Table 14 Optimal Amounts of Nanoclay Combination and the Equivalent Peak Values of Compressive Strength Per 7 Day Increments of Curing in 'B' Samples

Curing Days	Optimal Replacement	Maximum Theoretical f_c (MPa)
7	2.670 %	35.458
14	2.768 %	40.063
21	2.719 %	43.741
28	2.562 %	46.060

4. CONCLUSION

The following conclusions were drawn in the analysis of the results of the workability and compressive strength of concrete in which cement is partially replaced by individual and combined amounts of nanoclays:

- The workability of fresh concrete samples generally decreased when nanoclays were introduced in the mix. In fact, it is recognized that for 'B' samples, there is a sudden decrease of workability by 27.778 % at the initial addition of the nanoclay combination in B1 at 1 % replacement. However, a gradual decline is then observed for further increments of replacement at 3 % and 5 % in B2 and B3 wherein there is a 38.889 % and 50.000 % loss of workability, respectively. The decline in workability is associated with the influence of clay particles in the distribution of water in the mix.

- The increase of compressive strength in concrete specimens for 'B' samples with cement replacement of combined NMT and HNCL, particularly in B1 and B2 at 1 % and 3 % replacement, is speculated due to the compatibility of nanoclays wherein the alkali reactions within the layers of NMT that causes a detrimental effect to the durability of concrete is restricted by HNCL.
- The effective amount of nanoclay replacement for cement is B1 at 1 % replacement of combined NMT and HNCL in which there is an apparent increase of 26.251 % in compressive strength and not to mention that B1 produces the lowest decrease in workability among the samples by 27.778 %.
- There is a parabolic trend of compressive strength at increasing amount of nanoclay replacement such that at minimal amounts of nanoclay, it is observed that there is an increase in strength of concrete wherein nanoclay fills in the voids of the cement matrix resulting to a denser structure. However, at an excessive amount of nanoclay, there is a loss in compressive strength since clay particles have an influence in the distribution of water in the mix.
- The optimal replacements of nanoclay combination in 'B' samples to produce the maximum compressive strengths in the 7th, 14th, 21st, and 28th days of curing ranges from 2.5 % to 3.0 % that corresponds to a theoretical peak strength of 35 to 45 MPa.

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