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Comparison between the Effect of Additionof Nano-Calcium Carbonate and Nano-Kaolineon developing the Properties of Reinforced Concrete

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ملخص البحث:

إن الغرض من هذا البحث هو دراسة تأثير إضافة نانو كربونات الكالسيوم, ونانو الكاولين بنسب مختلفة إلى الخلطات الخرسانية لدراسة تأثيرهم على مقاومة الضغط والشد والنفاذية. وتم تطبيق المسح المجهري بالميكروسكوب الإلكتروني السطحي على العينات المثالية . ولقد اظهرت النتائج ان استخدام جزيئات النانو كاولين فى الخرسانة تؤثر على خواصها الفيزيائية وتحسن خواصها الميكانيكية والمعمرية**.** كما ان هذه الخلطات سواء فى الاعمار المبكرة او المتاخرة تعطى افضل اداء لمقاومة الضغط باستخدام نسبة احلال 7% وذلك بالمقارنة بالخلطة المرجعية بدون النانو. وفى حالة استخدام جزيئات النانو لكربونات الكالسيوم وجد ان الخلطة ذات نسبة الاحلال 1% تعطى اقضل اداء لمقاومة الضغط مقارنة بالخلطة المرجعية بدون النانو.

واعتمادا على صور الفحص بالميكروسكوب الالكترونى اثبتت النتائج ان النانو اكاولين يساهم فى تعزيز البنية للخلطة الخرسانية ، وجعل البنية اكثر كثافة ، واكثر احكاما وموحدة عن طريق ملء مسام المصفوفة للخلطة الخرسانية وهذه الاسباب المسئولة عن تحسين الخواص الميكانيكية مع جزيئات النانو.

Abstract

This current study is carried out to investigate effect of some nano materials on the properties of concrete, experimental program included nano particles of both calcium carbonates (CaCO3) and Kaoline (K) with different percentages. The nano-CaCO3 was added at rates1, 2, 3, 4 and 5% as a partial mass replacement for cement. NK was added at rates 5,6,7,8,9 and 10%.The experiment results showed that adding these nano materials did not reduce the flowability of concrete significantly, but the early compressive strength of concrete was both improved some extent when the dosage of both was suitable. The optimum amount of nano-CaCO3 and NK are1% and 7%respectively. Results of microstructure analysis were in agreement with the strength results

Keywords: NanoCalcium Carbonate**,** nanoKaoline, nano materials

1-Introduction:

Some of previous researches concerning the effect of adding nanoclay as partial replacement of cement are as follows:

Hakamy, et al [(1)] 2014 carried out an investigation about "Characteristics of Hemp Fabric Reinforced Nanoclay–Cement Nanocomposites" they studied and fabricated cement eco-nano composites reinforced with hemp fabric (HF) and nanoclay platelets (Cloisite 30B) in terms of X-ray diffraction, scanning electron microscopy, physical and mechanical properties. They found that, the optimum content of nanoclay was 1 wt%.

The HF-reinforced nano composites containing 1wt% nano clay decreased the porosity (15.5%) and also increased the density (5.3%), flexural strength (26.2%) and fracture toughness (24.9%). Adding more than 1% nanoclay to the HF-reinforced cement composites affects negatively the fracture toughness and the flexural strength. Potential applications may include ceilings, on-ground floors, roofing sheets, and concrete tiles.[1•]

A.S. Prince, et al[2]2013, showed in their paper; "Experimental Investigation on Concrete Containing NanoMetakaolin" they attempted to know the effect of Nano-Metakaolin as a replacement material for cement in concrete. They also have determined the compressive strength, split tensile strength, they also comparedbetween the cost of Normal Concrete and concrete with Nano-Metakaolin. From their study, they found that the partial replacement with Nano-Kaolin effects on the strength parameters of concrete, its optimum percentage is 10%. The increase in Compressive strength reaches between 5-38% for M20 grade, 2-37% for M30 grade, 3-13% for M40 grade and 3-18% for M50 grade of concrete. The increase of SplittingTensile strength was between 5-36% for M20 grade, 2-13% for M30 grade, 2-34% for M40 grade and 2-26% for M50 grade of concrete. The increase in cost for 10% replacement ranged between 11-13% for all grades of concrete.

S.I. Zaki, et al [3]2012, discussed in their following paper: "The Use of Activated Nano Clay to Develop the Compressive Strength and Microstructure of High Performance Concrete", nano clay was added with percentage 0, 3, 5, 7 & 10% by weight of cement. They concluded that the properties of concrete improved by the use of nano clay since it fills the voids and consume a part of Calcium Hydroxide leading to more formation of C-S-H and more improvement of interface structure. The application of nano clay particles with newly developed super plasticizers improved the workability and strength of high performance concrete since nanoKaoline interpenetrates polymer network and causes the mentioned improvements. The improvement percentages were 36-39-7.6 %, at the ages 3- 7- 28 days respectively.

K. Patel [4]2012, explained inhis paper**:** "The Use of Nano clay as a Constructional Material" aiming to constitute blended cement mortar with fractional increase in mechanical strength and a greater increase in water-tightness. Nano kaolin (NK) was the kind of nano clay used in this study. The results showed that the microstructure is denser and more uniform than that without nano particles. The NK acts as a nano-fiber due to its morphology. The compressive strength was improved by 300% with 1% NC and by 290% with 2% NC for 7 day testing. At the age of 28 day the improvement reached 310% with 1% NC and 200% with 2% NC. The permeability coefficient of the samples with 1% Nano clay was around 150% more, and with 2% Nano clay it was found to be 200 % more than the control samples.
Other previous researches concerning using Nano Calcium Carbonate were as follows
YameiCai, et al. [5] (2016), studied “Effects of Nano-$CaCO_3$ on the Properties of Cement Paste: Hardening Process and Shrinkage at different Humidity Levels“. The hardening process and volume stability of cement pastes with and without nano-$CaCO_3$ ($NCaCO_3$) were studied through investigations on the setting time and shrinkage. Results showed

that Nano-$CaCO_3$(N$CaCO_3$) shortened the setting time of cement paste and accelerated the hardening process of cement. The initial setting time decreased by 3.9 and 11.1% when 1 and 3% NC were added, and the final setting times were shortened by 6.2 and 15.2%, respectively.NC decreased the shrinkage of cement paste, and the effect was more pronounced when the addition of N$CaCO_3$ was high. Considering the hydration of cement and the volume stability of structure, high curing humidity of samples was an important factor for improving the durability of cement-based materials.

S. Monkman et al.[6](2015), studied “The Effect of In-Situ Development of Nano-Calcium Carbonateon Industrial Concrete“. Industrial trials investigated a method of adding nano Calcium to concrete via an in-situ reaction between gaseous Co2 and freshly hydrating concrete. The addition cause masonry blocks to be harder to compact though this could be addressed with a simple increase in mix water. The compressive strength and water absorption were both improved despite block density being equivalent to the control. The reaction products similarly impacted the fresh properties of ready mix concrete effectively reducing the workability. The compressive strength was comparable or better than the control. The side effects of the carbon dioxide addition are attributable to the new surface area associated with the reaction products as they are created in the fresh concrete.

Wei Li, et al[7] (2015), studied “Study on the status and Development Prospect of the Nano-Concrete”. Nanometer concrete in improving the performance of ordinary concrete (including mechanical properties, durability, etc.) has initially been affirmed, but its specific mechanism of action is not yet in place. The role played by them in concrete does not be mastered clearly and unambiguously. The further research and experimentation is needed. At present, because of the production process of nanomaterials and other reasons, its costs are still relatively high. It is not suitable for us to use in actual construction. Therefore, it is necessary to study and improve the production process to achieve lower costs. Only the costs are reduced, it is possible for it to enter the market, to enter the construction industry.

T. Meng,et al [8] (2013), studied “Influence of nano-$CaCO_3$on compressive strength and microstructure of high strength concrete with hardening accelerator under different curing temperature”. The experiment results showed that adding nano-$CaCO_3$ did not reduce the flow ability of concrete significantly, but the early compressive strength of concrete curing at two different temperatures was both improved by some extent when the dosage of nano-$CaCO_3$ was suitable.The early (3d and 7d) compressive strength of concrete under low temperature curing was obviously lower than that of standard curing. But evening (28d) compressive strength was almost the same.The early compressive strength of concrete with hardening accelerator $Ca(NO2)_2$ was decreased when the dosage of nano-$CaCO_3$ was too low or too high, but improved at an optimum dosage. This indicated that hardening accelerator $Ca(NO2)_2$and nano-$CaCO_3$ restricted each other at the developing of early compressive strength of high strength concrete.

2-Experimental Work

In this work the effect of adding different percentages of two nano materials NK and NCaCO3 as partial replacement of cement was examined to find its influence on concrete mixture mechanical and physical properties.

2.1 Materials:

The materials used to prepare the test specimens for 12 different mixes included sand as fine aggregate. Ordinary Portland cement (CEM I 52.5 N), nano clay, and nano calcium carbonate were used as cement replacement materials by weight. The description and specification of these materials are as follows:

2.1.1 Cement:

Ordinary Portland cement (OPC) (CEM1 52.5 N) was used during this study, obtained from Beni-Suef Cement Factory in Egypt with standard specifications as in (ESS 4756-1)[9]. The chemical analysis of cement is shown in Table (1)

2.1.2 Fine Aggregate

The employed fine aggregate in this research is locally available natural siliceous sand was in a regular spherical structure, with a maximum grain size of 1.4 mm, and a specific gravity of 2.5. its particle size distribution lies within the range of fine grading zone according

to the classification of the Egyptian code of practice for design of concrete structure (ECP 203-2007) [10]**.**The grading curve is shown in Figure (1).

2.1.3 Coarse Aggregate

In this research the dolomite aggregate from Attaka was used which are recognized as the best in Egypt .Aggregates size 1 was used that assured Compliance with both: ASTM C33-13 and Egyptian Code: (ECP 203-2007)[10].Coarse grading curve is shown in Figure (2).

2.1.4 Chemical Admixture:

High performance superplasticizer (S.P) (GLENIUM C315)was used which is an aqueous solution of modified Polycarboxylates, obtained from BASF Chemical Company in Egyptmeeting the requirements of (ASTM C494/C494M) [11].The technical data and physical properties of (GLENIUM C315) according to manufacturer are given in the Tables (2) [12].

2.1.5 Nano Powders:

Nano powders are two types:nano Calcium Carbonate and nanoKaoline.

2.1.5.1. Nano Calcium Carbonate:

Limestone (i.e. calcium carbonate ($Caco_3$)), however, has shown an ability to accelerate the hydration process of Portland cement. $CaCO_3$ usually has no chlorides and can readily be found, for instance, in chalk and marble, or produced artificially by cement hydration products form and carbon dioxide [13]. Studies have shown that $CaCO_3$ accelerates the hydration process by acting as a nucleation site on which cement hydration products form. This micro-physical effect results in a higher development rate of mechanical properties [14]. A higher accelerating effect occurs when more $CaCO_3$ is added; however exceeding the optimal amount of $CaCO_3$ (which mainly depends on its particle size) can lead to a reduction in mechanical strength [15].Figure (5) shows the TEM micrograph of $NCaCO_3$with mean size particles 40nmm.

2.1.5.2. Nanokaoline:

Kaoline (K) is one of the recently developed supplementary cementing materials (SCMs). Kaoline differs from other supplementary cementitious materials (SCMs), like fly ash, silica fume, and slag, in that it is not a by-product of an industrial process; it is manufactured for a specific purpose under carefully controlled conditions[16,17].The used material isKaolinewhich extracted from Kaolinitic sandstone of Gabel Gunna, Sinai Peninsula, Egypt). Location of Kaoline of Gabel Gunna is shown in Figure (3). The studied Kaoline raw samples were extracted from Kaolinitic sandstone deposites located at an open quarry (6 km west of Gebel Gunna in the Central Sinai, Egypt). The studied kaolinitic sandstone beds belong to the Naqus Formation of the early Paleozoic age.Kwas obtained fromMiddle East Mining Investments Company in Egypt (Memco) modifiedwith quaternary ammonium salts (sodium calcium aluminum silicate)that is in crystalline state which is characterized by large length according to its thickness ratio. Thermal activation which was performed converted the clay crystalline state to amorphous state; it reduced the grain size of Kaoline. TheKaolinewas exposed to 800 ^{0}c temperature for two hours. Figure (4) shows the TEM micrograph of NKwith mean size particles 24nmm

2.1.6. Silica Fume

Silica fume, also referred to as micro-silica or condensed silica fume, is a by-product material. This by-product is a result of the reduction of high-purity quartz with coal in an electric arc furnace in the manufacture of silicon orferrosilicon alloy. Silica fume rises as an oxidized vapor from the 2000°C (3630°F) furnaces. When it cools it condenses and is collected in huge cloth bags. The condensed silica fume is then processed to remove impurities and to control particle size. Silica Fume obtained by Sika Companyin Egypt.Silica fume meets ASTM C 1240-15 [18].

2.2. Mix Design and preparation of specimens:

Concrete sampleswere prepared according to ECP, NO.203, 2007[10].For all mixes SF was 10% from Cement, Water was 0.39 from (Cement + SF),Chemical Admixture (superplastizer) was 2.5% from (Cement + SF),Sand was 1.65% from (Cement + SF), CoarseAggregates was 2.32 % from (Cement + SF). All mixes were tap water (mixed and cured).

2.2.1. Mix Design

Concretesamples were prepared, mixed, casted, cured and tested in the MaterialLaboratory in the Faculty of Engineering, Cairo University; eleven concrete samplesmixes were designed and shown in Table (4). From the table it can be noticed that MO is the control mix without nanoparticles, while mixtures M1-M6 are mixtures with (5, 6, 7, 8, 9 and 10) % NK by mass replacement of cement. Mixtures M7-M11 issubstituted with (1, 2, 3, 4 and 5) % $CaCO_3$ by mass replacement of cement.

2.2.2. Dispersion Technique of nano-particles:

To achieve perfect dispersion of nano particles to enhance the base matrix, the stirring technique by vane motor is used in this study.Nano particles mixed with half amount of the water and super plasticizer was dispersed by the vane motorshown in Figure (6), the specifications of vane motor is in Table (5).The period of stirring was 4 minutes for NK and 2 minutes for $NCaCO_3$ until the mixture was homogeneous.

2.2.3. Mixing Procedures:

The cement and half amount of water, SF and fine and coarse aggregates needed for each mixture were mixed in a rotary mixer for thirty seconds. The ready mixed liquid (the other half of the water,super plasticizer and the nano particles) that resulted from the nano dispersion technique, was added gradually and mixed for additional three minutes.

2.2.4. Casting and curing procedures:

The mixtures were cast in steel cubes dimensions (15x15x15) cm for compressive strength tests, andcylinders (15x30) cm for splitting tensile strength and permeability tests. Cubes and cylinders were put on a vibratingtable for 1 minute to achieve homogeneity. Samples have been demolded after one day from casting and cured in a tap water. These samples were tested after 3, 7, 28, 60 and 90 days.

2.3. Testing Procedures:

Fresh and hardened concrete samples were carried out for 11 mixes. The testing process is divided into three main phases: mechanical, physical and permeability properties.

2.3.1. Fresh Concrete Tests:

The slump flow test measures the flowability of fresh concrete before it sets. This test was done according to ASTM C 1611. [21].

2.3.2. HardenedConcrete Tests:

Water permeability, physical and mechanical tests were carried out for all mixes.

2.3.2.1. Water Permeability Test (Water penetration test):

This test is carried out according to German Standard DIN 1048[22] on concrete specimens of size 150x150x150 mm, at an age of 28 days.Once the specimen is assembled in the test cell as shown in Figure (7), a water pressure of 700 KPa (7bar) was applied for 24 hours. Water pressure is applied by means of an arrangementconsisting of a water tank connected to an air compressor through a valve, to adjust the pressure. The specimen is adjusted as in Figure (8) and is sealed from the other face. After finishing the test, the volume of accumulated water was recorded from graduated container under each sample. Thespecimens were extracted from permeability machine and Splitting Test was carried out along the middle plane as shown in Figure (9). The specimen issplitted in compression machine by applying concentrated load at two diagonally opposite points slightly away from central axis as shown in Figures (10). While Figure (11) shows the specimen after the Splitting Test and distribution of water penetration depth' h' and its maximum value to be recorded to compensate it in as in the following Equation derived from Darcy's Law:

$K = (Q*\gamma *h) / (t*s*p)$ (cm/sec)……………………….……………Equation (1)[35]

Where:

K: coefficient of permeability in (cm/sec)

Q: quantity of accumulated water in (cm^3)

s: surface area that exposed to water pressure in (cm^2).
t: tested duration time in (sec)
γ: weight of water (kg/cm^3).
h:maximum penetration depth in (cm)
p: hydrostatic pressure in (Kg/cm^2).

2.3.2.2. Mechanical properties Tests:

The mechanical properties of concrete are dependent on many factors such as, characteristic of raw materials used, the curing conditions and the local concrete practice which may vary from place to another.

2.3.2.2.1. Compressive Strength Test

Testing of concrete compressive strength cubes with dimensions150x150x150mm were tested at different ages according to BS EN 12390-3:2009[23]. The machine used in this test is SHIMADZU 500 KN Universal machine in Material laboratory in the Faculty of Engineering, Cairo University.

3.4.3.2. Splitting Tensile Strength Test

Testing of concrete was carried out for all mixes for splitting tensile strength tests. Testing of concretesplitting tensile cylinders with dimensions 300x150mm was tested at different ages (7, 28 and 90 DAYS) according to ASTM C 496/C 496M-04(24)sing the same machine mentioned above.

Table (1): Chemical composition of materials by Weight Percentage

Component	CEM I 52.5	Silica Fume	K	NK	$CaCO_3$	$NCaCO_3$
SiO_2	20.00	90.2	47±1	51.61	0.61	1.239
AL_2O_3	5.50	1.70	37±1	45.07	0.07	0.492
Fe_2O_3	0.50	0.40	0.20	0.27	0.06	0.065
$Mn_2 O_3$	0.00	0.00	0.00	0.00	0.00	0.00
Ca O	63	2.1	0.2	0.60	55.34	92.40
MgO	1	1.7	0.02	0.04	0.12	0.175
P2O3	0.11	0.00	0.00	0.15	<0.01	0.062
K_2O	0.89	0.7	0.04	0.02	0.01	0.028
Na_2O	0.27	0.7	0.15	0.01	<0.01	0.197
TiO_2	0.24	0.00	1.3	1.35	<0.01	0.00
SO_3	3.2	0.5	0.00	0.24	<0.01	0.198
CL	0.00	0.00	0.00	0.04	0.08	0.068
LOI	2	1.18	13.95	0.35	43.48	5.00
ZnO	0.00	0.00	0.00	0.00	0.00	0.004
SrO	0.00	0.00	0.00	0.00	0.00	0.066

Table (2) Technical Data and Physical properties of GLENIUM C315

Form:	Viscous liquid
Appearance:	Light Grey
Specific gravity:	1.10 ± 0.03 g/cm³
pH- value:	6.5 ± 1
Alkali content (%):	≤ 2.00 by mass
Chloride content (%):	≤ 0.10 by mass

Table (3): Physical properties of nano particles

Nano Type	Color	Bulk Density (g/cm^3)	Mean Particle Size (nm)	SurfaceArea (m^2/g)
$NCaCO_3$	White	2.67	40	540
NKaoline	Light Cream	0.19	24	330

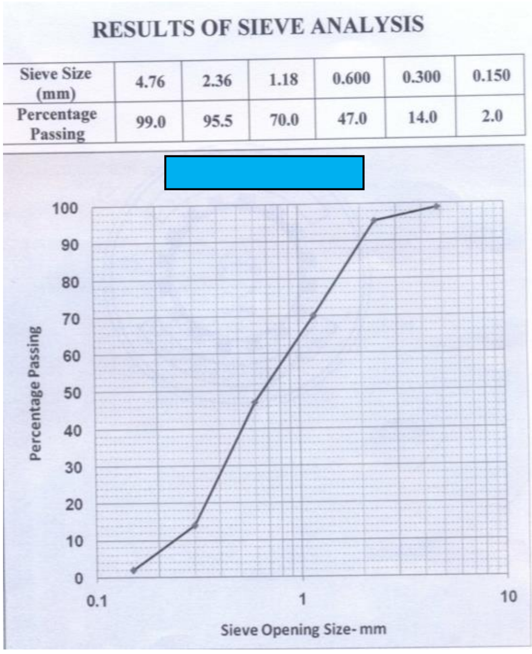
Table (4): Proportions of Concrete Samples (on weight basis)

Mix No	Code of mix	Mix proportion of concrete (Kg)						
		Cement	Sand	Water	GL C315	SF	Agg	N
MO	Control	400	726.5	171.5	11	40	1020	22
M1	NK 5%	378	726.5	171.5	11	40	1020	22
M2	NK 6%	373	726.5	171.5	11	40	1020	27
M3	NK 7%	368	726.5	171.5	11	40	1020	32
M4	NK 8%	364	726.5	171.5	11	40	1020	36
M5	NK 9%	360	726.5	171.5	11	40	1020	40
M6	NK 10%	356	726.5	171.5	11	40	1020	44
M7	NCaCO31%	395.6	726.5	171.5	11	40	1020	4.4
M8	NCaCO32%	391.2	726.5	171.5	11	40	1020	8.8
M9	NCaCO33%	386.8	726.5	171.5	11	40	1020	13.2
M10	NCaCO34%	382.4	726.5	171.5	11	40	1020	17.6
M11	NCaCO35%	378	726.5	171.5	11	40	1020	22

MO= Control MixGLC315 = GliniumSF = Silica FumeN = Nano

Table (5): Specifications of vane motor:

Speed range (rpm)	Up to 40000
Frequency (Hz)	50-60
Power consumption (watt)	810



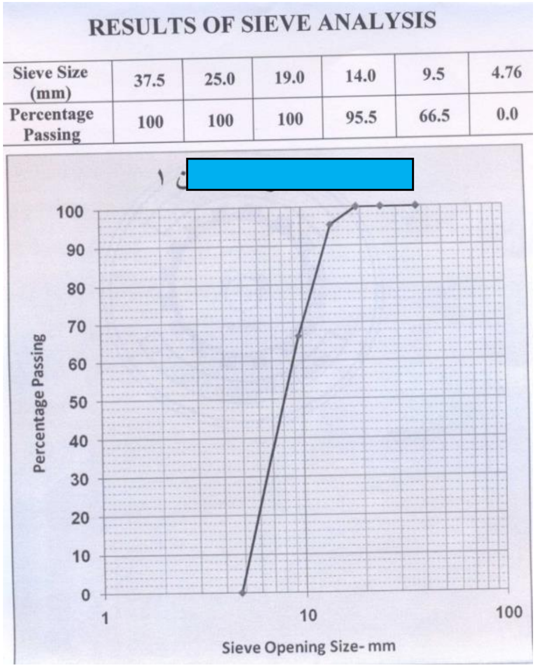


Figure (1) Fine aggregate grading curve   Figure (2) Coarse aggregate grading curve

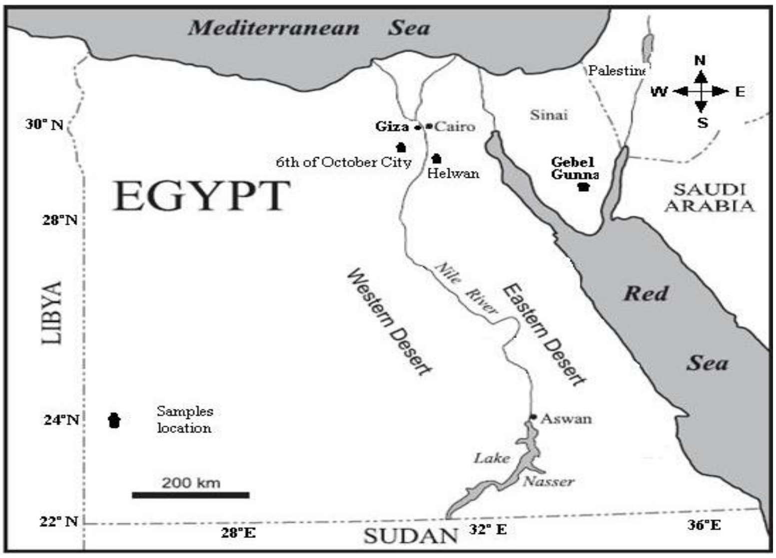


Figure (3): Location of Kaoline in Egypt

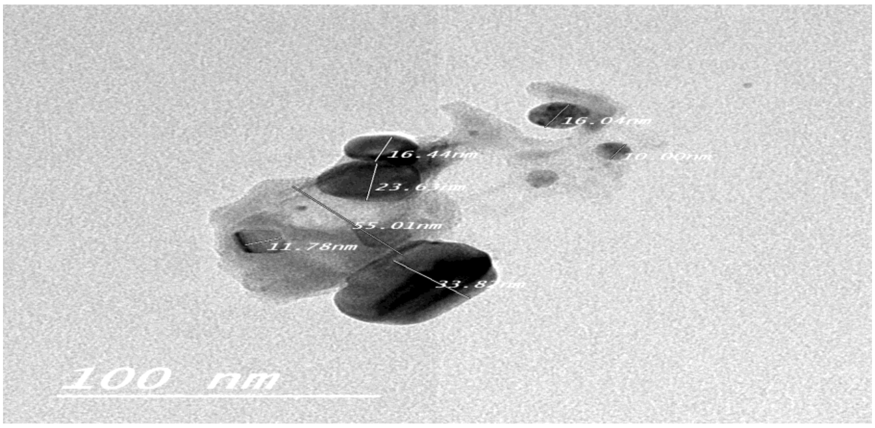


Figure (4): TEM micrograph of NK mean size particles 24nmm

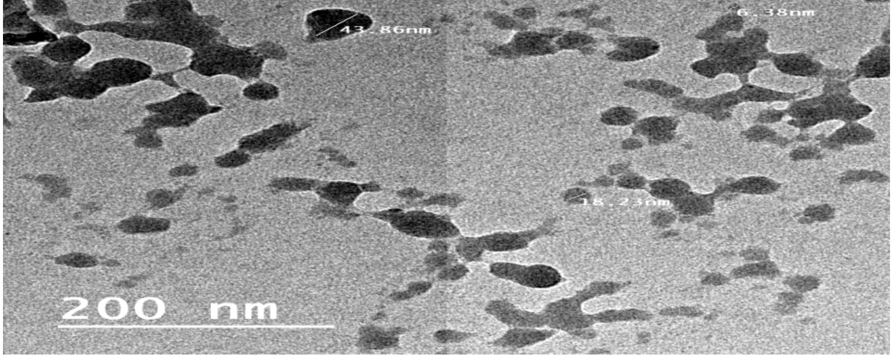


Figure (5): TEM micrograph for nano-CaCO3 mean size particles 40nmm

Figure (6): Van Motor

Figure (7) Water Permeability Equipment

Figure (8) adjusting the specimen

Figure (9) Specimen extracted from Permeability Equipment

Figure (10) specimen after Splitting Test

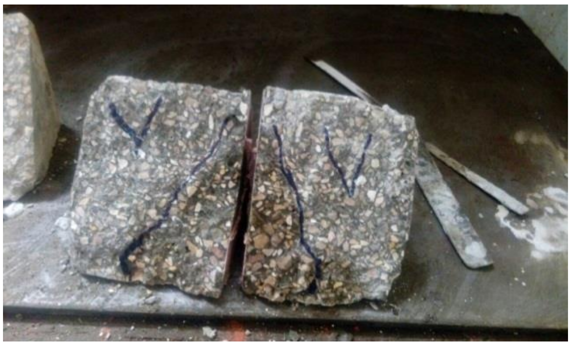


Figure (11) water penetration depth

3-Analysis and Discussion of Test Results

3.1. Fresh concrete results

Tables (6), (7) show slump flow test results for adding NK and nano $CaCO_3$ to mixtures respectively.

Table (6) Slump Flow test results for NK Samples

Mixture I.D.	Slump Flow (mm)
Control	610
NK 5%	610
NK 6%	640
NK 7%	680
NK 8%	650
NK 9%	640
NK 10%	620

Table (6) showed that slump flow increased with adding NK until NK reaches 7% , then deceased by increasing percentage of NK. Table (7) showed that slump flow increased with increasing percentage of $NCaCO_3$.

Table (7) Slump Flow test results for Nano CaCO3 Samples

Mixture I.D.	Flow (mm)
Control	610
NCa CO3 1%	620
NCa CO3 2%	650
NCa CO3 3%	670
NCaCO3 4%	675
NCaCO3 5%	680

3.2. Water Permeability Test Results

Table (8) shows the water permeability test results after 28 days curing. Obviously, it can be seen that concrete without nanoparticles (Control) had water penetration depth 4.8 cm and coefficient of permeability was about 1.38×10^{-9} cm/sec. The concrete samples with Nano $CaCO_3$ have less water penetration depth. The coefficient of permeability of those samples was improved compared with the value of control one. Sample with 1% improved nearly to quarter compared with the value of control one.The concrete samples with NK have less water penetration depth. The coefficient of permeability of those samples was improved to be half compared with the control one. Most improved samples were that of percentage (7% and 8%).Samples with 1% $NCaCO_3$ gives coefficient of permeability less than samples with 7%NK.

Table (8) Water Permeability Test Results after 28 Days

Mix. ID	Type	Penetration/cm	K (cm/sec)
M1	MO	4.8	1.38E-09
M2	NCa CO3 1%	2	3.50E-10
M3	NCA CO3 2%	2.5	4.70E-10
M4	NCa CO3 3%	2.5	5.10E-10
M5	NCa CO3 4%	2.7	5.80E-10
M6	NCa CO3 5%	2.8	7.70E-10
M7	NK 5%	3.8	7.80E-10
M8	NK 6%	3.2	6.50E-10
M9	NK 7%	3	6.50E-10
M10	NK 8%	3	6.50E-10
M11	NK 9%	3.5	7.10E-10
M12	NK 10%	3.6	7.20E-10

3.3. Compressive Strength

3.3.1. The effect of adding NK on compressive strength:

Figure (12) shows that when adding NK with different percentages as partially replacement ofcement, compressive strength was enhanced at all ages compared to the control Mix. NK 7% mixtures recorded the highest values for compressive strength at 3, 7and 28 days which were 29, 38, 55 MPa..The increase in compressive strength is due to efficiency of nano particles in activating pozzolanic reaction, consuming calcium hydroxide forming additional (C-S-H) which is a gelly material besides nano particles act as afiller.

3.3.2. The effect of adding $NCaCO_3$ on compressive strength:

Figure (13) shows that $CaCO_3$ 1% mixture recorded the highest values for the compressive strength as achieved33, 60, 62 MPa at 3, 7, and 28 Days, respectively.The percentage of increase in compressive strength were 36, 60 and 32.00 % over the control mix at the previous ages, respectively.$NCaCO_3$had a strong acceleration effect on the early-age hardening process. Hence, nano-$CaCO_3$ addition can be considered as a setting and hardening accelerator.Results showed that when adding 7% NK Compressive strength reached 55 MPa(550 kg/cm^2) after 28 days and when adding 1% $NCaCO_3$ reached 62 MPa (605 kg/cm^2).

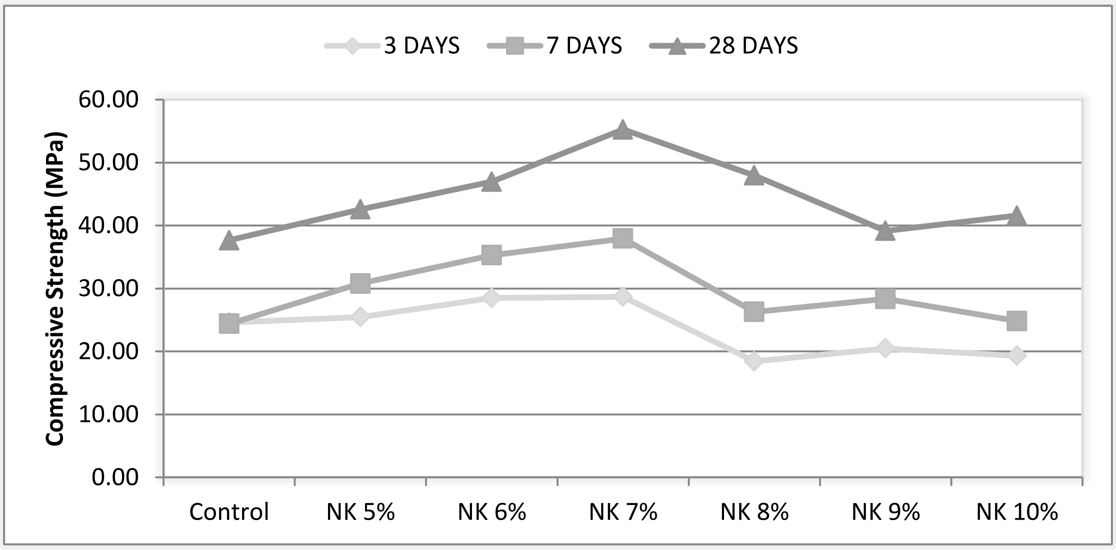


Figure (12): Development of compressive strength for control mix and mixes with different % of NK

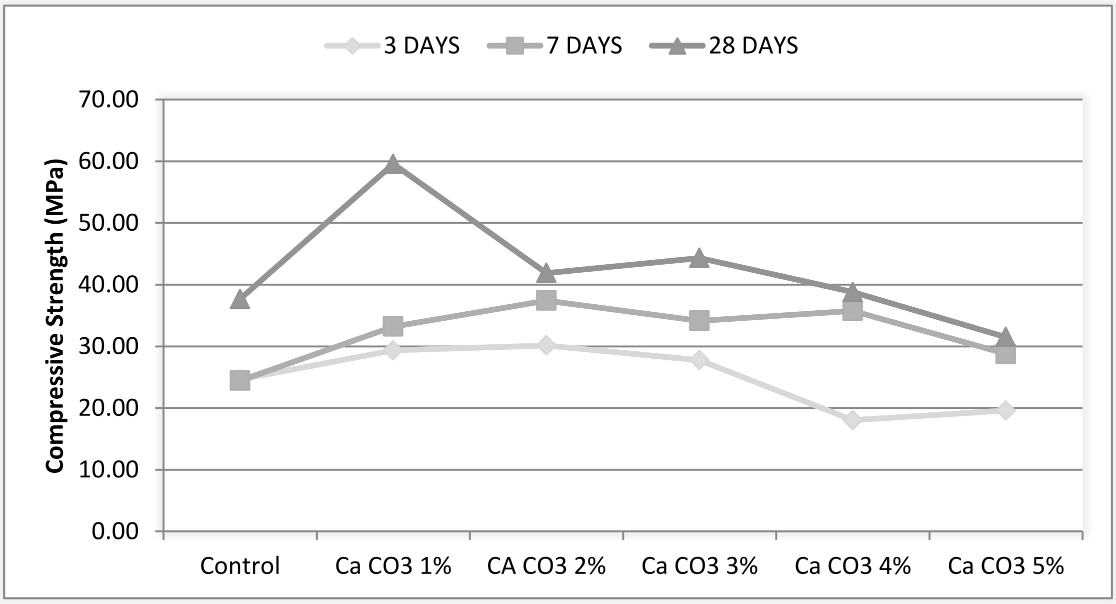


Figure (13): Development of compressive strength for control mixand mixes with different % of NCaCO3

3.4.The effect of adding NK and NCaCO3 on Splitting Tensile strength:

The effect of using NCaC O_3 with (1, 2, 3, 4 and 5%) and NK with (5, 6, 7, 8, 9 and 10%) on splitting tensile strength at ages (7, 28 and 90 Days) with constant w/c ratio and super plasticizer percentages are clarified at Table (9) , Figure (14) and Figure (15) respectively.It can be seen that the splitting tensile strength consistently increased with age for both nano$CaCO_3$ mixture and NK mixtures. The maximum splitting tensile strength occurred at 1% nano$CaCO_3$ as partial replacement of cement weight, while NK 7% showed high splitting tensile strength.

Table (9) Splitting Tensile Strength results for mixtures containing Nano material

Mixture ID	Tensile Strength (Mpa.) at diff. ages		
	7 DAYS	28 DAYS	90 DAYS
Control	1.92	3.64	5.28
$NCaCO_3$ 1%	3.47	4.86	5.55
$NCaCO_3$ 2%	2.04	3.47	3.88
$NCaCO_3$ 3%	2.78	4.16	5.40
$NCaCO_3$ 4%	2.50	4.03	4.16
$NCaCO_3$ 5%	2.04	3.08	4.16
NK 5%	2.10	3.89	4.83
NK 6%	2.17	3.33	5.32
NK 7%	2.83	5.29	6.21
NK 8%	2.50	3.60	4.37
NK 9%	2.78	3.13	4.3
NK 10%	2.47	4.03	4.2

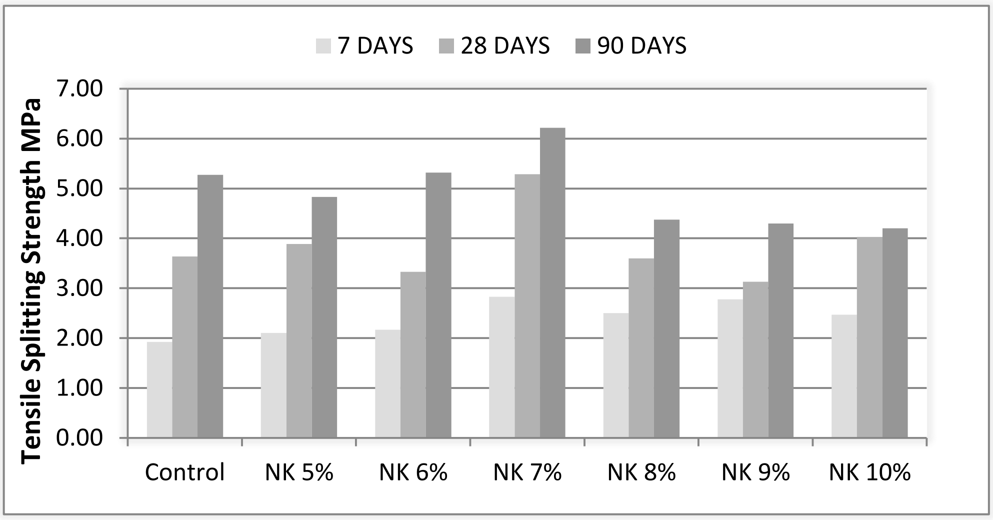


Figure (14) Splitting Tensile Strength results for mixtures containing NK at different ages

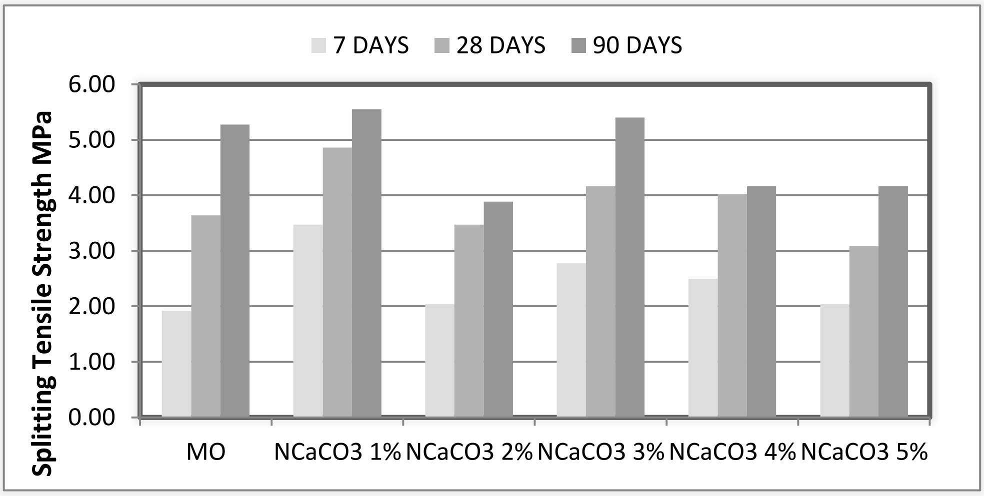
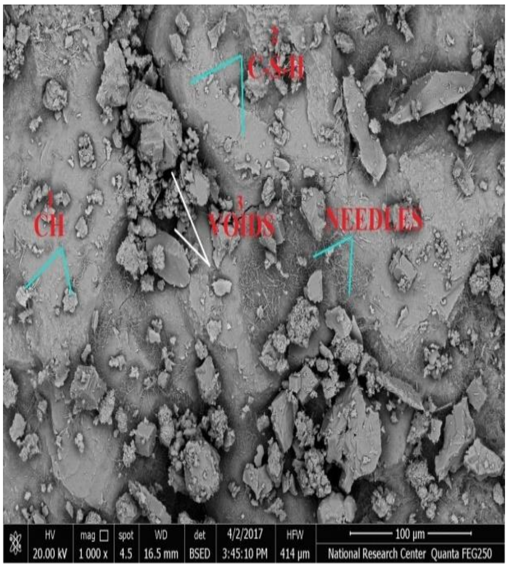


Figure (15) Splitting Tensile Strength results for mixtures containing NCaCO3 at different ages

3.5 Scanning Electron Microscope (SEM)

Studies of the microstructure of cement paste and concrete have been largely done using electron microscopy[25].The scanning electron microscopy uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The information from scanning electron microscopy included external morphology and crystalline structure. Figure (16) shows the SEM photograph of Control mix without nano particles. Figure (17) show SEM photograph of concrete mix that replaced cement with 7% nanoKaoline. These figures give good comparison between sample with nanoKaoline and without it. It was found in Figure (16) that calcium-silicate-hydrate (C-S-H) gel existed in the form 'stand-alone' clusters, lapped and jointed together by many needle hydrates. Figure (17) shows the microstructure of concrete mix with nanoKaoline which was different from the control mix. The texture of hydrate products was denser and compact[26].The dense and compact structure of concrete mix will result in better mechanical properties and strengthen the structure. As we can see in Figure (16) there is a lot of crystal in the structure. Different with Figure (17), the photograph show compact structure by adding nanoKaoline. It is because, the role of NK were not only acting as nano filler but also as an activator to promote hydration.



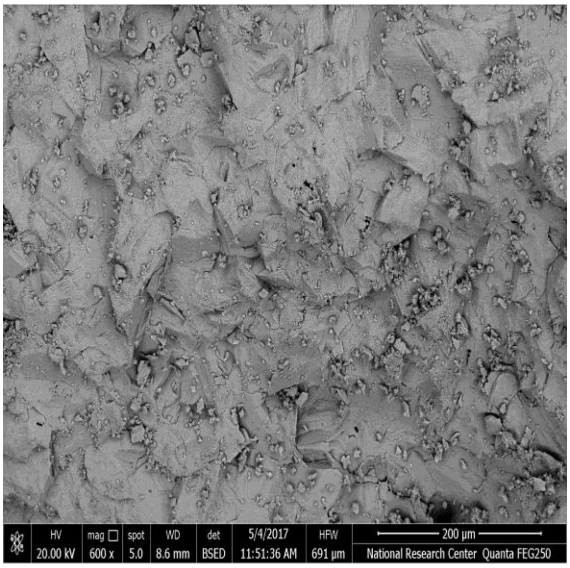
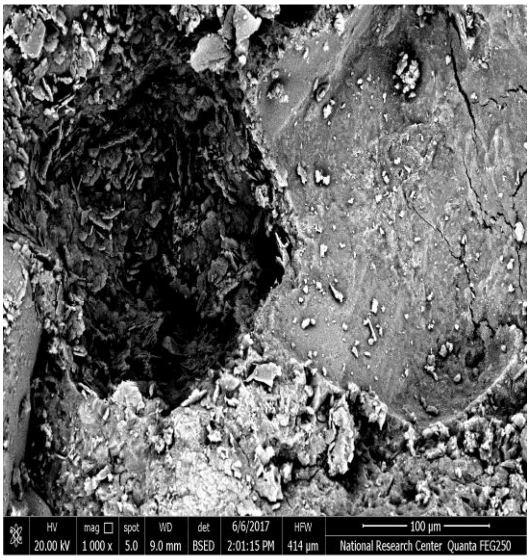


Figure (16): SEM without nano particles Figure (17): SEM with concrete mix (NK7%)

Figure (18) shows the microstructure of concrete mix with 1% Nano Calcium Carbonate.The improvement of strength is essentially due to the formation of calcium carbaluminateshydrate as in Figure (18-a), which may be contributed to overall increase in the rate of hydration. Also, the increased binding capacity of carboaluminates is likely due to its compact structure as described by Bonavetti et al.[27] Silica Calcium Hydrates (CSH) according to Figure (18-b) shows how the filler has been dispersed in the concrete. SEM confirms that the concrete becomes more heterogeneous when the amount of filler is optimum.The relatively lower compressive strength results for mixtures with high nano-$CaCO_3$ content can be ascribed to several factors including dilution, filler and agglomeration effects.The dilution effect, due to partially replacing cement by an inert material, results in fewer hydration products being formed and, consecquantly, a weakermicrostructure (Bonavitti et al., 2003)[27]. Adding nano-$CaCO_3$ will fill space and obstruct the formation of more hydration products [27]. Also, the agglomeration of nanoparticles will create weak zones in the microstructure [27]. This agglomeration effect was confirmed by scanning electron microscopy (SEM) results shown as in Figure (19) due to adding 3% (nano-$CaCO_3$).



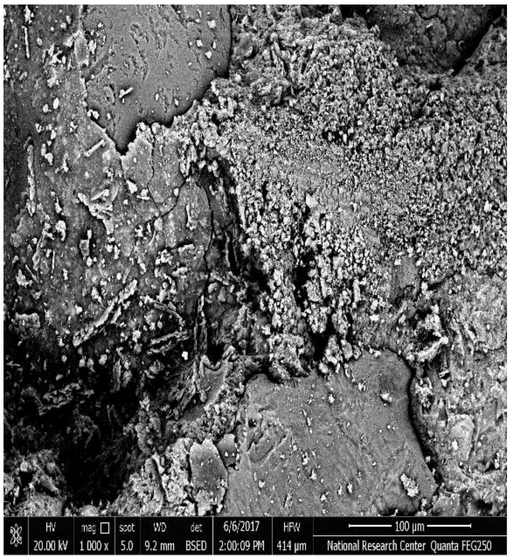


Figure (18-a): SEM formation of Carboaluminate   Figure (18-b): SEM Formation of C-S-H

Figure (18): SEM concrete (1% NCaCO3)

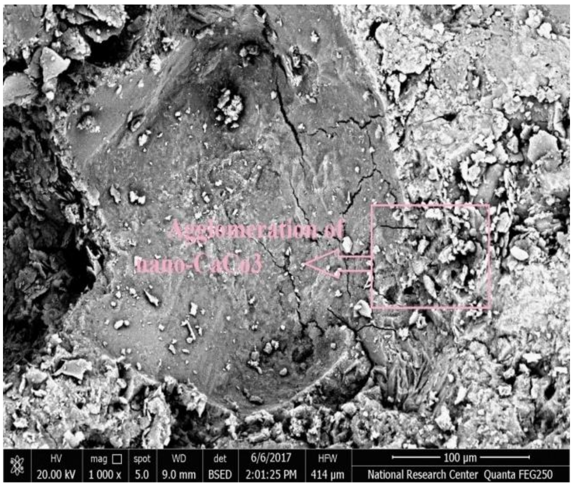


Figure (19) SEM of agglomeration of nano-CaCO3 3%

4- Conclusions:

From the conducted with the materials used in this study; the following conclusions can be drawn:

- The nano particles improve the features of mixtures by promoting pozzolanic reaction, packing the voids, consuming Calcium hydroxide and forming additional calcium silicate hydrate (C-S-H) which participates in increasing strength.
- When the nano particle size decreases, the pozzolanic reaction increases leading to high compressive strength.
- Adding nano-CaCO3 resulted in higher flowability of HPC mixtures compared to that of the control mixture and exhibited better workability than that induced by other accelerating mixtures.

- The addition of nano-CaCO3 had a strong acceleration effect on the early-age hardening process. Hence, nano-CaCO3 addition can be considered as a setting and hardening accelerator.
- Adding nano-$CaCO_3$ can impart two key effects: (i) it can enhance the packing density of the granular skeleton, and consequently few hydration products are needed to gain strength (28),(ii) CaCO3 acts as crystallization nucleus for the precipitation of CHleading to an acceleration of the hydration of cement grains. These simultaneous effects result in a higher early strength.
- High dosages of Nano calcium carbonate content is not the more the better. The best dosage is about 1.0%. High dosage of nano-CaCO3 addition (i.e. > 1.0%) will diminish the 28-d compressive strength achieved. This result agrees with Guhua Li, Bo Gao(29).
- Flowabilty of concrete mixtures increased with using NK up to 7% as replacement ratio. Whereas after 7%, a reduction in flowability was recorded.
- Inclusion of NK in concrete mixtures enhanced the compressive strength at both early and later ages when compared to the control mix. The resultshowed that 6% replacement ratio of cement recorded the best enhancement. 66% increase in compressive strength was recorded at 60 days for the above mentioned mix above the control mix.
- For splitting tensile strength, mixture containing 7% NK and mixture containing 1% $NCaCO_3$showed the best enhancement among the conducted mixes at all ages compared to were recorded at 7, 28, 90 days age respectively.
- The SEM observations confirmed that NK was not only acting as a filler , but also as an activator to promote hydration process and provided more dense structure, with decrease of calcium hydroxide CH ratio and increase in calcium silicate hydrate C-S-H which is responsible for increasing strength.
- The microstructure analysis conducted on NK mixtures demonstrated that the enhancing in mechanical properties is primarily due to its high packing efficiency in filling voids.
- SEM observationshowed that adding small amounts of $NCaCO_3$increasing compressive strength while adding dosages > 1% reduced compressive strength.
- From performance and economic points of view, adding 1% nano-CaCO3 can provide an efficient improvement for concrete properties, then 7% NanoKaoline.

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