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COMPARISON BETWEEN THE EFFECT OF ADDITION OF NANO-CALCIUM CARBONATE AND NANO-KAOLINE ON DEVELOPING THE PROPERTIES OF REINFORCED CONCRETE

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The current study is carried out to investigate effect of some nanomaterials on the properties of concrete, experimental program included nanoparticles of both calcium carbonates (CaCO₃) and Kaoline (K) with different percentages. The nano-CaCO₃ was added at percentages 1, 2, 3, 4 and 5% as a partial mass replacement for cement. NK was added at percentages 5, 6, 7, 8, 9 and 10%. The experiment results showed that the addition of these nanomaterials did not reduce the flowability of concrete significantly, but the early compressive strength of concrete was both improved to some extent when the dosage of both was suitable. The optimum amounts of nano calcium carbonates and nanokaolin are 1% and 7% respectively. Results of microstructure analysis were in agreement with the results of strength tests.

Keywords: Nano Calcium Carbonate, nano Kaoline, nano materials.

Introduction

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

Hakamy, et al [1] 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 by 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.

A.S. Prince, et al. [2], showed in their paper; "Experimental Investigation on Concrete Containing Nano Metakaolin" 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 compared between the cost of normal concrete and concrete with nano-metakaolin. From their study, they found that the partial replacement with nano-Kaoline 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], 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 percentages 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 superplasticizers 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], explained in his 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.

Another previous researcher working with Nano Calcium Carbonate was Yamei Cai, et al. [5], who wrote "Effects of Nano-CaCO₃ 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-CaCO₃ (NCaCO₃) were studied through investigations on the setting time and shrinkage. Results showed that Nano-CaCO₃(NCaCO₃) 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 NCaCO₃ 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 Carbonate on 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 attributed to the new surface area associated with the reaction products as they are created in the fresh concrete.

Wei Li, et al. [7], 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], studied "Influence of nano-CaCO₃ on compressive strength and microstructure of high strength concrete with hardening accelerator under different curing temperature". The experiment results showed that adding nano-CaCO₃ did not reduce the flowability 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-CaCO₃ 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-CaCO₃ was too low or too high, but improved at an optimum dosage. This indicated that hardening accelerator Ca (NO₂)₂ and nano-CaCO₃ restricted each other at the developing of early compressive strength of high strength concrete.

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.

Materials and Methods

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:

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.

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 ₂ O ₃	5.50	1.70	37±1	45.07	0.07	0.492
Fe ₂ O 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 ₂ O	0.89	0.7	0.04	0.02	0.01	0.028
Na ₂ O	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

Fine Aggregate: Fine aggregate, used 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.

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.

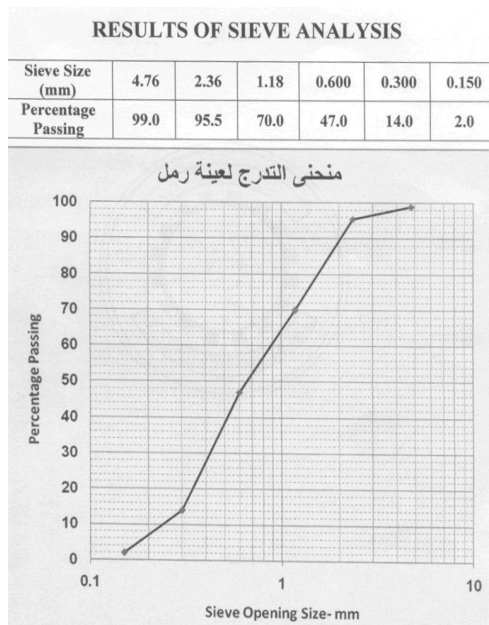


Fig. 1. Fine aggregate grading curve

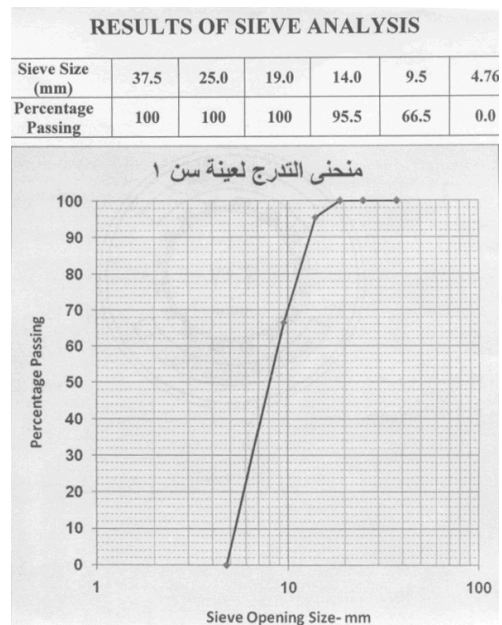


Fig. 2. Coarse aggregate grading curve

Chemical Admixture: High performance super-plasticizer (S.P) (GLENIUM C315) was used which is an aqueous solution of modified Polycarboxylates, obtained from BASF Chemical Company in Egypt meeting the requirements of (ASTM C494/C494M) [11].The technical data and

physical properties of (GLENIUM C315) according to manufacturer are given in the Table 2 [12].

Table 2. Technical Data and Physical properties of GLENIUM C315

Form:	Viscous liquid
Appearance:	Light Grey
Specific gravity:	1.10 ± 0.03 g/cm ³
pH- value:	6.5 ± 1
Alkali content (%):	≤ 2.00 by mass
Chloride content (%):	≤ 0.10 by mass

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

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

Nano Calcium Carbonate: Limestone (i.e. calcium carbonate (CaCO₃)), however, has shown an ability to accelerate the hydration process of Portland cement. CaCO₃ 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 CaCO₃ 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 CaCO₃ is added; however exceeding the optimal amount of CaCO₃ (which mainly depends on its particle size) can lead to a reduction in mechanical strength [15]. Figure 5 shows the TEM micrograph of NCaCO₃ with mean size particles 40nm.

Nano kaoline: 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 is Kaoline, which 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 deposits 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. Kaoline was obtained East Mining Investments Company in Egypt (Memco) modified with 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. The Kaoline was exposed to 800^oC temperature for two hours. Figure 4 shows the TEM micrograph of NK with mean size particles 24nm.

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 or ferrosilicon alloy. Silica fume rises as an oxidized vapor from the 2000^oC (3630^oF) 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 Company in Egypt. Silica fume meets ASTM C 1240-15 [18].

Mix Design and preparation of specimens

Concrete samples were 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 (super-plastizer) was 2.5% from (Cement + SF), Sand was 1.65% from (Cement + SF), Coarse aggregates was 2.32 % from (Cement + SF). All mixes were tap water (mixed and cured).

Concrete samples were prepared, mixed, casted, cured and tested in the Material Laboratory in the Faculty of Engineering, Cairo University; eleven concrete samples mixes 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 is substituted with (1, 2, 3, 4 and 5) % CaCO₃ by mass replacement of cement.

Table 4. Proportions of Concrete Mixes

Mix no	Code of mix	Mix proportion (Kg)						
		Cement	Sand	Water	GL C315	SF	Agg	N
MO	Control	400	726.5	171.5	11	40	1020	0
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	NCaCO ₃ 1%	395.6	726.5	171.5	11	40	1020	4.4
M8	NCaCO ₃ 2%	391.2	726.5	171.5	11	40	1020	8.8
M9	NCaCO ₃ 3%	386.8	726.5	171.5	11	40	1020	13.2
M10	NCaCO ₃ 4%	382.4	726.5	171.5	11	40	1020	17.6
M11	NCaCO ₃ 5%	378	726.5	171.5	11	40	1020	22

M0= Control Mix GL C315 = Glinium SF = Silica Fume N = Nano

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 motor shown 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 NCaCO₃ until the mixture was homogeneous.

Table 5. Specifications of vane motor:

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

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, superplasticizer and the nano particles) that resulted from the nano dispersion technique, was added gradually and mixed for additional three minutes.

The mixtures were cast in steel cubes dimensions (15x15x15) cm for compressive strength tests, and cylinders (15x30) cm for splitting tensile strength and permeability tests. Cubes and cylinders were put on a vibrating table 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.

Testing Procedures of 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.

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].

Hardened Concrete Tests

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

Water Permeability Test was 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 6, a water pressure of 700 KPa (7bar) was applied for 24 hours. Water pressure is applied by means of an arrangement consisting of a water tank connected to an air compressor through a valve, to adjust the pressure. The specimen is adjusted as in Figure 7 and is sealed from the other face. After finishing the test, the volume of accumulated water was recorded from graduated container under each sample. The specimens were extracted from permeability machine and Splitting Test was carried out along the middle plane as shown in Figure 8. The specimen is split 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:

$$K = \frac{(Q * \gamma * h)}{(t * s * p)} \left(\frac{cm}{sec} \right) \quad (1) [35]$$

Where:

K: coefficient of permeability in (cm/sec)

Q: quantity of accumulated water in (cm³)

s: surface area that exposed to water pressure in (cm²).

t: tested duration time in (sec)

γ : unit weight of water (kg/cm³).

h: maximum penetration depth in (cm)

p: hydrostatic pressure in (Kg/cm²).

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.

Compressive strength test was carried out on cubes with dimensions 150x150x150mm 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.

Splitting tensile strength test was carried out for all mixes for splitting tensile strength tests, cylinders with dimensions 300x150mm was tested at different ages (7, 28 and 90 days) according to ASTM C 496/C 496M-04 [24] using the same machine mentioned above.

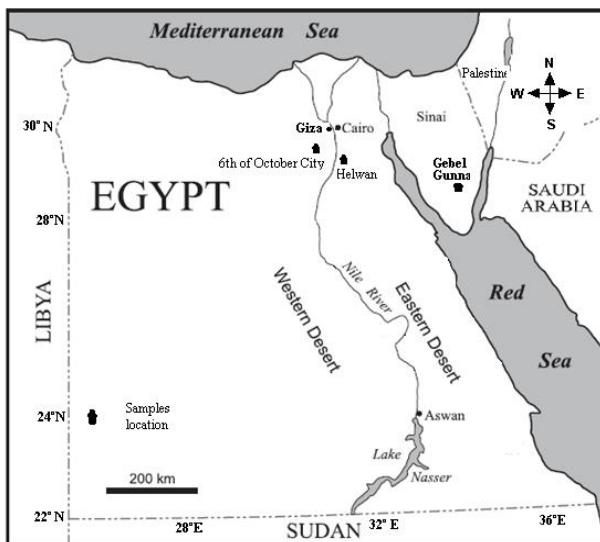


Fig. 3. Location of Kaoline in Egypt

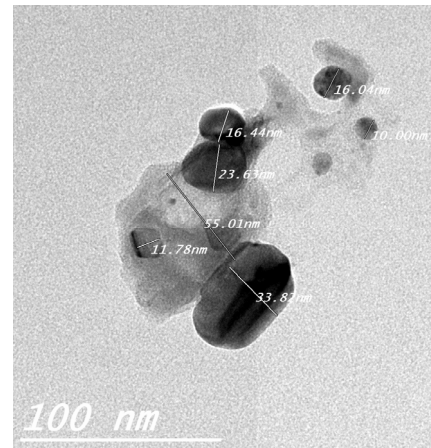


Fig. 4. TEM micrograph of NK mean size particles 24nm

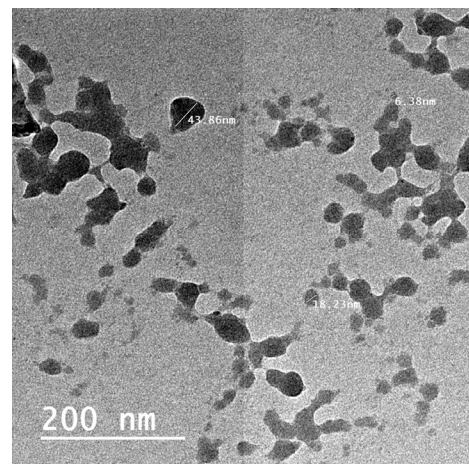


Fig. 5. TEM micrograph for nano-CaCO₃ mean size particles 40nm



Fig. 6. Water permeability equipment



Fig. 7. Adjusting the specimen



Fig. 8. Specimen extracted from permeability equipment

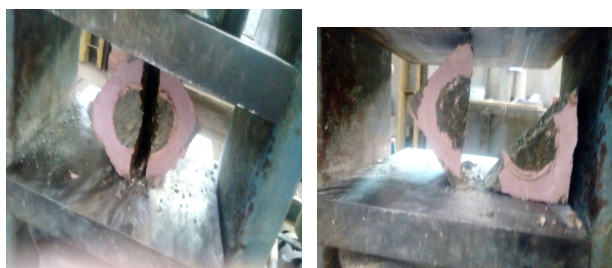


Fig. 9. Specimen after Splitting Test



Fig. 10. Water penetration depth

Analysis and Discussion of Test Results

Fresh concrete results

Tables 6, 7 show slump flow test results for adding NK and nano CaCO₃ to mixtures respectively.

Table 6. Slump Flow test results for NK Samples

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

Table 6 showed that slump flow increased with adding NK until NK reaches 7%, then decreased by increasing percentage of NK. Table 7 showed that slump flow increased with increasing percentage of NCaCO₃.

Table 7. Slump Flow test results for Nano CaCO₃ Samples

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

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 13.8×10^{-10} cm/sec. The concrete samples with Nano CaCO₃ 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% NCaCO₃ gives coefficient of permeability less than samples with 7%NK.

Table 8

K (cm/sec)	Penetration/cm	Type	Mix. ID
13.8E-10	4.8	MO	M1
3.50E-10	2	NCa CO ₃ 1%	M2
4.70E-10	2.5	NCA CO ₃ 2%	M3
5.10E-10	2.5	NCa CO ₃ 3%	M4
5.80E-10	2.7	NCa CO ₃ 4%	M5
7.70E-10	2.8	NCa CO ₃ 5%	M6
7.80E-10	3.8	NK 5%	M7
6.50E-10	3.2	NK 6%	M8
6.50E-10	3	NK 7%	M9
6.50E-10	3	NK 8%	M10
7.10E-10	3.5	NK 9%	M11
7.20E-10	3.6	NK 10%	M12

Compressive Strength

The effect of adding NK on compressive strength

The effect of using NK with cement replacement ratios of (5, 6, 7, 8, 9 and 10%) on compressive strength at ages (3, 7, 28, 60 and 90 days) with constant w/c ratio and superplasticizer percentage

are presented in Table 9. NK 7% mixtures recorded the highest values for compressive strength at 3, 7 and 28 days, which were 29, 38, 55 MPa. Also, Figure 11 recorded compressive strength results for mixtures containing NK. 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 gel material besides, nano particles act as a filler.

Table 9. Compressive strength results for mixtures containing NK

Compressive Strength (Mpa)			Mixture
28 DAYS	7 DAYS	3 DAYS	ID
37.66	24.42	24.62	Control
42.57	30.79	25.47	NK 5%
46.97	35.31	28.50	NK 6%
55.27	37.95	28.68	NK 7%
47.97	26.30	18.44	NK 8%
39.17	28.34	20.50	NK 9%
41.57	24.84	19.32	NK 10%

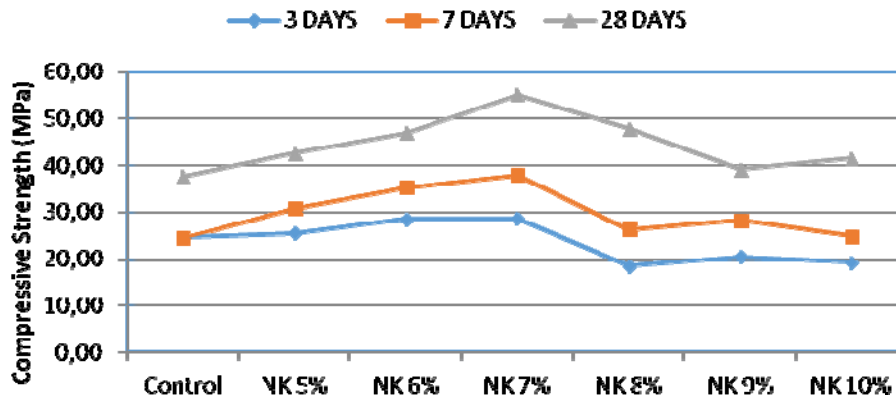


Fig. 11. Development of compressive strength for control mix and mixes with different % of NK

The effect of adding NCaCO₃ on compressive strength

The effect of using Nano CaCO₃ with cement replacement ratios of (1, 2, 3, 4 and 5%) on compressive strength at ages (3, 7, 28, 60 and 90 days) with constant w/c ratio and superplasticizer percentage are presented in Table 10. Figure 12 shows also that CaCO₃ 1% mixture recorded the highest values for the compressive strength as achieved 33, 60, 62 MPa at 3, 7, and 28 Days, respectively. The percentage of increase in compressive strength were 36, 60 and 32 % over the control mix at the previous ages, respectively. NCaCO₃ had a strong acceleration effect on the early-age hardening process. Hence, nano-CaCO₃ addition can be considered as a setting

and hardening accelerator. Results showed that when adding 1% NCaCO₃ compressive strength reached 60 MPa.

Table 10. Compressive strength results for mixtures containing Nano CaCO₃ in comparison with control mix

Compressive Strength (Mpa)			Mixture
28 DAYS	7 DAYS	3 DAYS	ID
37.66	24.42	24.62	Control
59.57	33.20	29.35	NCa CO ₃ 1%
41.88	37.41	30.15	NCa CO ₃ 2%
44.33	34.14	27.75	NCa CO ₃ 3%
38.79	35.74	18.02	NCa CO ₃ 4%
31.51	28.77	19.58	NCa CO ₃ 5%

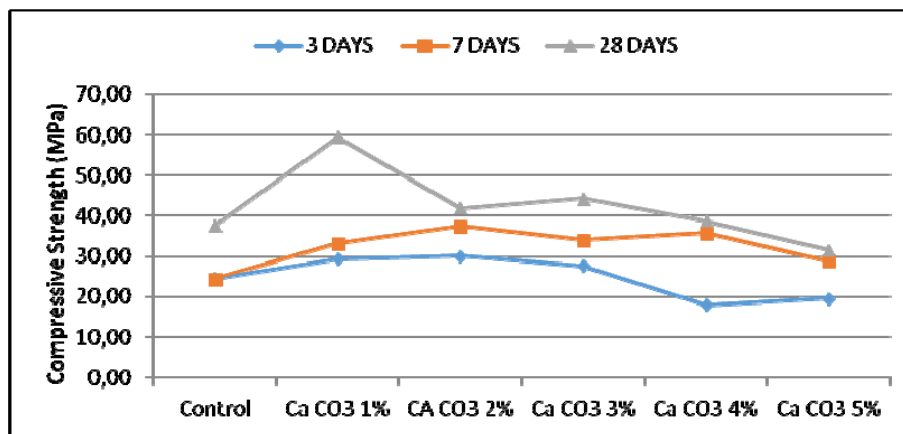


Fig. 12. Development of compressive strength for control mixand mixes with different % of NCaCO₃

The effect of adding NK and NCaCO₃ on Splitting Tensile strength

The effect of using NCaCO₃ 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 11 , Figure 13 and Figure 14 respectively. It can be seen that the splitting tensile strength consistently increased with age for both nano CaCO₃ mixture and NK mixtures. The maximum splitting tensile strength occurred at 1% nano CaCO₃ as partial replacement of cement weight, while NK 7% showed high splitting tensile strength.

Table 11. Splitting tensile strength results for mixtures containing nano material

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

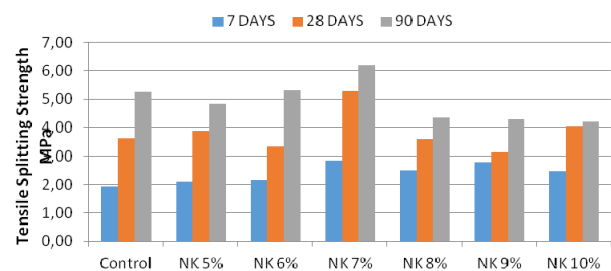


Fig. 13. Splitting tensile strength results for mixtures containing nk at different ages

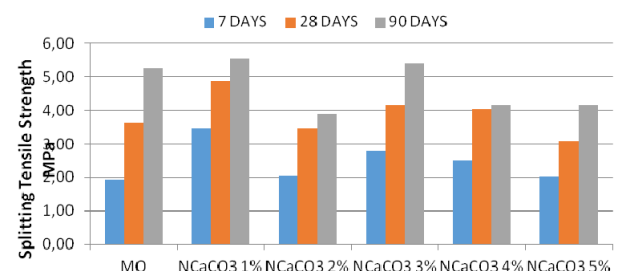


Fig. 14. Splitting Tensile Strength results for mixtures containing NCaCO₃ at different ages

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 (15) shows the SEM photograph of Control mix without nano particles. Figure (16) 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 (15) that calcium-silicate-hydrate (C-S-H) gel existed in the form 'stand-alone' clusters, lapped and jointed together by many needle hydrates.

Figure (16) 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 (16), 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.

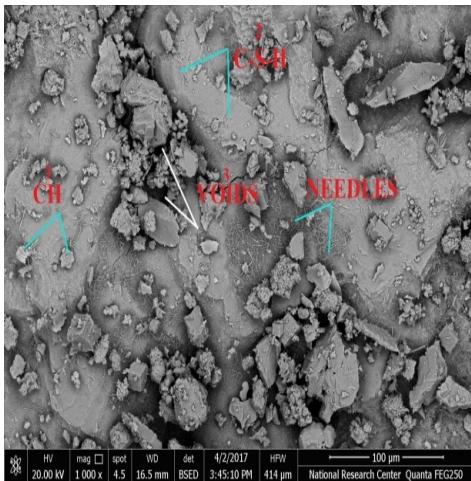
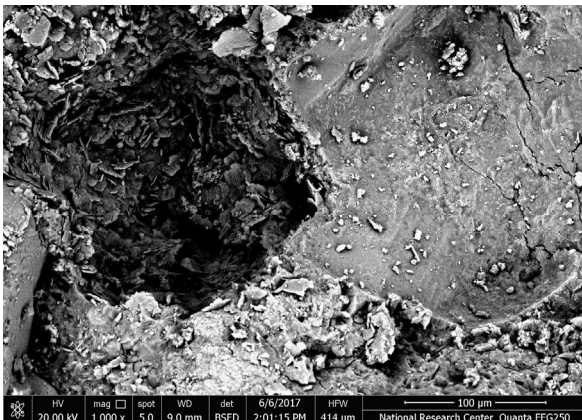
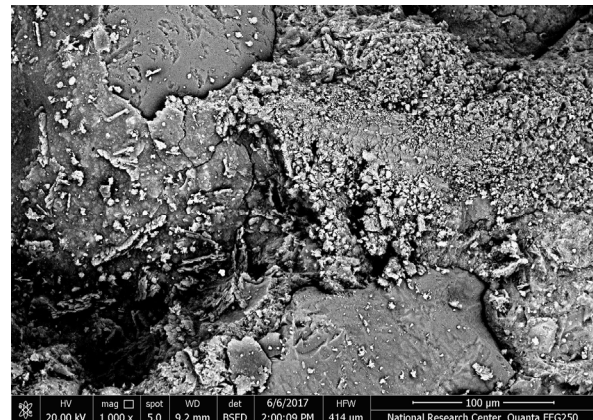


Fig. 15. SEM without nano particles

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 carbo aluminates hydrate as in Figure (17-a), which may be contributed to overall increase in the rate of hydration. Also, the increased binding capacity of carbo aluminates is likely due to its compact structure as described by Bonavetti et al [27].



a



b

Fig. 17. SEM concrete (1% NCaCO₃): a) SEM formation of Carboaluminate, b) SEM Formation of C-S-H

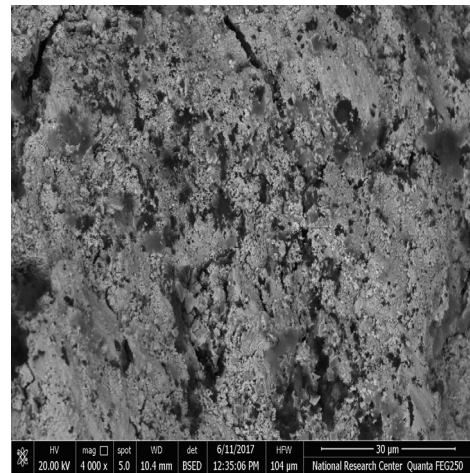


Fig. 16. SEM with concrete mix (NK7%)

Silica Calcium Hydrates (CSH) according to Figure 17-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-CaCO₃ 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, consequently, a weaker microstructure (Bonavitti et al., 2003) [27]. Adding nano-CaCO₃ will fill space and obstruct the formation of more hydration products. 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 18 due to adding 3% (nano-CaCO₃).

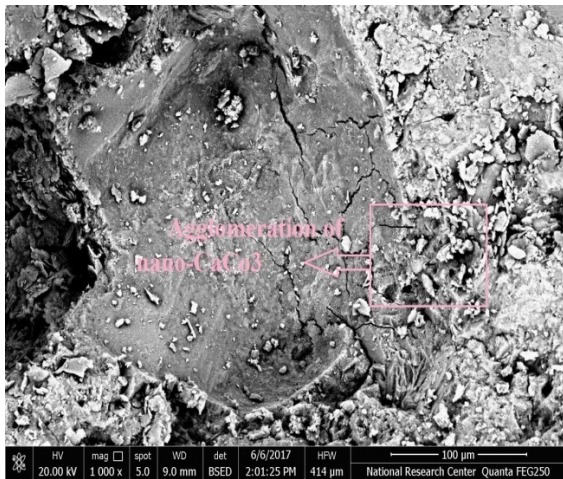


Fig. 18. SEM of agglomeration of nano-CaCO₃ 3%

Conclusions

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

- 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-CaCO₃ 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 CH leading 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].

- Flowability 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 result showed 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% NCaCO₃ 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 observation showed that adding small amounts of NCaCO₃ 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% Nano Kaoline.

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Сравнение влияния действия нанокarbonата кальция и нанокаолина на свойства железобетона

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Данное исследование было проведено с целью установления влияния действия некоторых наноматериалов на свойства бетона, экспериментальная часть включала использование наночастиц карбоната кальция (CaCO_3) и нанокаолина (К) в различных концентрациях. Нанокarbonат кальция вводили в состав в концентрации 1, 2, 3, 4 и 5 %, частично заменяя цемент. Количество нанокаолина составляло 5, 6, 7, 8, 9, 10 %. Результаты экспериментального исследования показали, что при введении этих материалов подвижность бетонной смеси значительно не снижалась, а прочность на сжатие на ранних сроках при определенных концентрациях повышалась. Оптимальное содержание нанокarbonата кальция и нанокаолина составило 1 и 7 % соответственно. Была выявлена прямая зависимость между результатами микроанализа материалов и их испытаниями на прочность.

Ключевые слова: нанокarbonат кальция, нанокаолин, наноматериалы.

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