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Influence of Nanoparticles Additions on Fresh Properties and Compressive Strength of Sustainable Self-Compacting HighPerformance Concrete Containing Calcined Pozzolanic Materials

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Abstract.The influence of addition nano ($CaCO_3$ (NC)) on fresh state and compressive strength of blended cement self-compacting highperformance concrete (SCHPC) incorporating calcined kaolin clay (CKC) as pozzolanic materials were studied. Two mixture systems, binary and ternary, were developed in two stages. In the first stage, the control mixture was prepared with only PLC as the binder, While the remaining blends were incorporated binary blending systems (PLC +30%CKC, PLC + 3%NC) in which a percentage of PLC was replaced with CKC, NC (by weight).In the second stage (PLC+30%CKC+3%NC), the ternary blends systems. The results revealed that the use of 30%CKC and 3%NC in binary and ternary blends SCHPC mixes reduced slump flows(D) but increased T_{500} and V-funnel flow time more than the control mixture. In hardened states, the results revealed that the binary blended mixes containing 3%NC enhance the compressive strengths of all ages compared to the other mixtures. In the ternary blends system, the compressive strength was observed to be better than that of the controller mix and binary blends containing 30%CKC for all ages. This study achieved its aims by helping to reduce cement demand, decrease the rate of CO_2 emissions and make SCHPC eco-friendly.

Keywords: Nano calcium carbonate, Calcined kaolin clay, Self-Compacting highperformance Concrete, Fresh Properties, Compressive strength

Introduction

Production of cement among all other constituents of concrete is harmful to the environment because, during the manufacturing of cement, there is a large emission of CO_2, i.e., 7%. One of the major environmental issues facing the concrete industry is carbon dioxide (CO_2) emissions from the manufacture of Portland cement. The emissions of CO_2 in the cement and concrete industry can be controlled by using calcined pozzolanic materials (CPM) as a replacement for cement. Binary and ternary blends system are used in this study to reduce the environmental problems generated by concrete production, improve mechanical properties(compressive strength), preserve natural resources, save production costs, and reduce consumption of cement by using a higher-level replacement of cement. The self-compacting concrete (SCC) can be described as concrete flowing and spreading through congested reinforcements; each corner of concrete blocks is filled and compressed without vibration under its weight [1]. An SCHPC is that concrete that offers excellent performance in terms of filling ability, resistance to segregation, passing ability, and strength. In this study, the main pozzolan used was calcined kaolin clay (CKC) which can be used individually with Portland or blended cement or in different combinations.

Nanotechnology is taken into account as a brand new field of science in materials science and materials engineering. Due to the characteristic properties of nanoparticles, nanotechnology is currently attracting much attention from writers and scientists. The use of extremely tiny particles on the 1-100 nanometer scale is nanotechnology. The nanoparticles are proposed to serve as a cement nucleus accelerating cement hydration and densifying the microstructure of the matrix and interfacial transfer zone (ITZ), thus minimizing concrete permeability [2]. The increase in nano $CaCO_3$ content has contributed to a steady decrease in slumping values and higher V-funnel flow time values for self-compacting mortar [3]. However, it is found based on the literature review that the optimal ratio is between 1% and 4% of cement weight [4]. The need for high fines contributes to a rise in cement content, often between 450 and 500 kg / m3 [5]. Therefore, this study offers an experimental investigation on the impact of utilizing calcined kaolin clay (CKC) and nano $CaCO_3$ (NC) as partial replacements of cement in binary and ternary blends to develop SCHPCs, on rheologic (slump, T_{500}& V-funnel flow time) and compressive strength.

Materials

Cement and calcined kaolin clay: The locally available cement used in all mixtures wasPortland limestone cement (PLC), Which complies with EN 197-1, 2000 [6].Origin of calcined kaolin clay (CKC) or metakaolin (MK) is Iraqi Kaolin clay collected fromDewekhla region, in Al Ramadi desert in West of Baghdad/Iraq. CKC can be prepared by thermal activation of kaolin clay at 800 ºC for 2 h. After that, the CKC was ground by the air blast technique in AL-Zahra′a Shop in Baghdad to obtain reactive material with more fineness. The obtained calcined kaolin clay (CKC) conforms to ASTM C618-03,2005 [7].

Tables 1 and 2, respectively, include PLC and CKC's chemical analysis and physical properties used in this investigation.

Table 1. Chemical compositions and (LOI) of (PLC) and calcined kaolin clay (CKC).

Chemical composition %	Cement	Calcined kaolin clay (CKC)
CaO	62.79	0.84
SiO_2	20.58	54.7
Al_2O_3	5.60	37.4
Fe_2O_3	3.28	1.72
MgO	1.94	0.42
K_2O	0.56	0.54
Na_2O	0.29	0.37
SO_3	2.35	0.13
P_2O_5	-	0.29
TiO_2	-	0.68
LOI	1.94	2.91

Table 2. Physical properties of cement and CKC.

Property	Cement	CKC
Fineness [m^2/kg]	314	1640
Specific gravity	3.12	2.59
Median particle size [μm]	16.8	14.3
Color	Grey	Off-White

Fine Aggregate: Locally available natural sand from the Al-Akhaider region was used. The results found that the used fine aggregate is located within the third gradient zone and conforms to IQS 45,1984 [8].Where it had (Fineness Modulus, absorption, SO_3 content and specific gravity) (2.5, 0.94%, 0.309% & 2.65).

Coarse Aggregate: The single maximum size of the coarse aggregate used is 10 mm, and all results show that the coarse aggregate (CA) grading and sulfate content met the requirements of IQS 45, 1984 [8].Where (SO_3 content, specific gravity, and absorption) were as follows (0.03%, 2.58 & 0.5%).

Chemical admixture: A modified polycarboxylic ether-based Superplasticizer (SP), commercially known as Glenium 54, was used to produce the required flowing ability. It is available Whitish to straw-colored liquid form. It is chloride-free and has a relative density equal to 1.07.

Nano Calcium Carbonate powder: The nano calcium carbonate ($CaCO_3$) used in this study as nanoparticles was imported from Sky spring. Nanoscale Calcium Carbonate Particles are typically less than 100 nanometers (nm). It is the powder form.The properties of the nano calcium carbonate (NC) are taken from the manufacture described in Table 3.

Table 3. Nano Calcium Carbonate ($CaCO_3$) Properties

Property	Result
Colour	White
density [g/cm3]	2.5
size[nm]	< 100
Specific area [m2/g]	≥20
pH	8.5-9.7
Whiteness %	≥93
Moisture content %	≤0.9
Loss on ignition%	44±1
$CaCO_3$content %	≥96
MgO content %	≤0.8
Alumina+Iron oxide %	≤0.3
The insoluble matter with acid%	≤0.3
Activation rate %	≥95

Experimental works

Mixed Design: In this paper, as partial cement replacements, CKC and nanoparticles minimize the quantity of cement used and keep the constant adhesive volume. A total of 4 mixtures of self-compacting highperformance concrete (SCHPC) were designed and cast at 0.38 water to binder ratio (w/b), 485 kg/m3 total binder content.

Several experimental combinations were performed to decide the amount of SP needed to provide the SCHPC requirements required in compliance with EFNARC,2005 [9]. Where the superplasticizer dosages (1.7%and 2%) by mass. The experiment is divided into two stages. In the first stage, the control mixture was prepared with the only PLC as the binder, While the remaining blends were incorporated binary blending systems (PLC + CKC, PLC + NC) in which a percentage of PLC was replaced with 30%CKC, 3% NC (by weight).In the second stage, the ternary blends systems (PLC+CKC+NC), the replacement ratios for CKC were 30% with 3% of NC as partial replacement of cement (by weight). The mixture proportions SCHPC mixes used in this phase are summarized in Table 4.

Table 4. The mixture proportions of SCHPC mixes [kg/m^3].

Mix	C	W/B	CKC	NC	S	G	SP %
Control-PLC	485	0.38	-	-	850	862	1.7
30%CKC	339.5	0.38	145.5	-	850	862	2
3%NC	470.45	0.38	-	14.55	850	862	1.7
30%CKC3%NC	324.95	0.38	145.5	14.55	850	862	2

Where (C: cement), (W: water), (B: binder),(CKC: calcined kaolin clay), (S: sand), (G: gravel), (NC: nano (CaCO3)) and(SP: superplasticizer).

Results and discussion

Fresh properties: The fresh properties of SCHPC were tested in this experimental study using slump flow (D (mm), T_{500} (s)), and V-funnel flow time tests. The slump flow test (D (mm)) is used to evaluate the flowability of concrete mixes. This test is an important test considered a primary test to see whether the specification meets the fresh concrete consistency. T_{500} slump flow time (s) and V-funnel time (s) are used to measure the viscosity of fresh concrete mixtures.Table 5 indicates the result of fresh properties for all mixtures.

Table 5. Fresh properties results.

Mix designation	Fresh Properties		
	Flow time[second]	Slump flow [mm]	V-funnel[second]
Control-PLC	2.7	780	6.8
30%CKC	5.2	665	10.7
3%NC	3	760	7.3
30%CKC3%NC	5.5	610	11.8

The slump flow of SCHPCs mixtures had been in the range of 780-610 mm, flow times (T_{500}) in the range of 5.5-2.7 s, and the V-funnel times (s) in the range of 11.8-6. 8s. The slump flow diameters for control-PLC mix is confirmed with class three (SF3), for 30%CKCis confirmed with class two (SF2), 3%NC is confirmed with class three (SF3), and 30%CKC3%NC is confirmed with class one (SF1).Thus, all the mixes are considered good consistency and workability from the filling point of view. On the other hand, one thing was noticeable in all SCHPC blends: while adding the CKC and NC replacement ratio, the slump values are steadily decreasing. This is in line with the provisions of [10, 11, 12, and 13]. It may be attributed to the fact that the calcined pozzolanic materials and nanoparticles' fineness/ higher surface areas are higher than of cement. Slump flow times (T_{500}) of all SCHPCs mixtures confirmed with class two (SF2).Funnel flow times (s) for 30%CKC3%NC and 30%CKC were confirmed with class two (SF2), but the Control-PLC mix and 3%NC were confirmed with class one (SF1). These results are conforming to acceptable criteria for SCC reported by EFNARC, 2005[9].The lowest T_{500mm} and V-funnel times of 2.7 s and 6.8 s were measured for the control mixture, respectively, while the mixture with 30%CKC+3%NC had the highest flow time of 5.5 s and 11.8 s for V-funnel times.

The cause may be due to the shape and size of the long, hexagonal plates of particles of calcined kaolin clay that create obstacles in the fresh mix and increase friction between the particles, as well as the fine particle size of CKC and nanoparticles (NC), which have much higher surface areas absorbing water, leaving less free water to contribute to flowability. The water demand is therefore higher. Other researchers have shown the same findings [12, 14, 15]

Compressive strength: Compressive strength has been an established measure that represents one of the important mechanical properties of concrete, which could provide an overall image of the quality of concrete.

According to BS 12390, 2009 [16], the compressive strength test was carried out. In each test, an average of three 100 mm cube specimens were tested for SCHPC mixes at 7 and 28 days of age using a compression machine with a 2000 kN load capacity.The compressive strength result of SCHPCs mixes is shown in Table 6.

Table 6. The compressive strength results

Ages[days]	Compressive strength [MPa]			
	Control-PLC	30%CKC	3%NC	30%CKC3%NC
7	39.7	35.4	52.7	45.7
28	48.6	44.2	64.3	54.2

The higher replacement of CKC with cement contributes to a reduction in compressive strength. The highest reduction incompressive strength was noted for 30%CKC replacement in 7 and 28 daysrelative to other mixtures. This can be due to the pozzolanic, or the micro-filling effect of CKC with ($Ca(OH)_2$)in the presence of water. On the other hand, CKC was unable to compensate for the decrease in compressive strength due to the low cement content, meaning that the calcined pozzolanic did not show an immediate increase in strength during the early ages of curing.The substitution of cement with 3%NC is observed to increase the compressive strength for all ages in the binary blended SCHPC mixture. As a result, 3% of NC demonstrated the highest compressive strength (early and long term) at all ages relative to other replacement contents. This is attributed to the $CaCO_3$ nanoparticles with a strong acceleration effect at the early ages of the hydration process and react with tricalcium silicate (C_3S) and tricalcium aluminate (C_3A) to produce C-S-H and calcium carboaluminates. In addition, due to the high specific surface area and the NC particles' fineness, the compressive strength increases, thus affecting the hydration process more significantly.Similar findings were in agreement with previous studies of nanoparticle concrete mixes [14, 17].In terms of compressive strength, the performance of ternary blends in mixes includes 30%CKC with 3%NC, which is better than the performance of the control-PLC mix and binary blends containing 30%CKC at 7 and 28 days of age. These results can be attributed to (i) accelerating early cement hydration (mainly at early ages), because NC possesses nanoparticles, it acts as nucleation sites C-S-H can be deposited and achieving an immediate filler effect, (ii) the nano $CaCO_3$ reaction with the aluminate phase that results from the higher volume of the hydration product. The pattern was consistent with previous studies of pozzolanic materials and nanoparticle concrete mixes [18, 3].

Conclusions

- Self-compacting highperformance concrete can be successfully produced with binary and ternary binder combinations incorporating calcined kaolin clay and nano $CaCO_3$.
- For fresh properties, in the binary blend mixes, the value of the slump flow diameter decreases, the T_{500}, and V-funnel flow time increases compared to reference mixtures.Generally, including CKC in the system made the concretes more viscous.Owing to the addition of 30%CKC and 3%NC, the ternary blends of mixtures had a comparatively greater effect than the effect on binary mixtures. The value of the slump flow decreases further, while T_{500} and V funnel increase more than the binary and reference mixtures.

- For compressive strength, the binary blended SCHPC mixes containing 3%NC enhance the compressive strengths of all ages (early and long term). Due to the high pozzolanic activity of NC in the short term, the greatest effect on strength development was achieved at the early curing ages. Nevertheless, with 30%CKC, the highest reduction was noted in compressive strength in comparison to other mixes. The compressive strength is observed to be better for ternary mixes containing (30%CKC with 3 %NC) than control-PLC mix and binary blends containing 30%CKC for all ages.

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