Compressive strength, setting time, and flowability of OPC mortar mixtures modified with a composite of Nano carbon and partially de-aluminated metakaolin

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Abstract
Nano-black carbon (NC) and partially de-aluminated kaolinitic clay (PDK) composite blend was investigated as an additive to mortar fabrication for improving of the compressive strength. PDK was obtained from aluminum sulphate of Egypt (ASCE). PDK was grounded with nano-carbon. PDK achieved a good pozzolanic activity, it reached 120 %. The experimental protocol included chemical and physical properties of the PDK/Nano-carbon (NCPDK) and the produced mortars. The effect of five weight ratios of NCPDK (0, 5, 10, 15 and 20 %) on the properties of the formed OPC mortars was investigated. Each ratio was tested with three contents of Nano-carbon (1, 2 and 3 %) by weight. The accelerating effect of NCPDK was clear on the initial setting time whereas it reduced by about 31 % and the final setting time reduced by 23 % at 10 % NCPDK. The reduction in the initial flowability of OPC mortar reached 2.7 and 6 % for 10 and 20 % replacement respectively of the OPC by NCPDK and After 60 minutes from mixing, the relative flowability loss was 68 % at 10 % NCPDK and 88 % at 0 % replacement. The compressive strength values of the produced mortars ranged between 46.2 and 50.7 MPa (EN 196-1), with a maximum improvement equal to 14.4 % using 10 % NCPDK. There was no significant change in the pH values of the mortar mixtures. According to the obtained results the composite NCPDK can be used as an additive material in mortar fabrication. The structure of the hardened mortar modified with 10% NCPDK was investigated by XRD, FTIR and TGA that assured formation of more CSH. Incorporation of Nano-carbon enhanced the compressive strength.
Key words: nano-carbon, compressive strength, setting time, flowability, dealuminated kaolin, concrete additive
Kulcsszavak: nano-karbon, nyomószilárdság, kötési idő, folyóképesség, dealuminált kaolin, betonadalék

1. Introduction

Meta-kaolinitic clay (MKC) is the reactive phase resulted from heating of kaolinitic clay (KC) at a temperature range of 500 – 750 °C that deteriorate its crystal structure [1]. MKC reacts with sulfuric acid to produce aluminum sulfate solution which is used in the clarification of water. The extraction of aluminum from meta-kaolinitic clay by acid attacking resulted in increasing the silica to alumina ratio, specific surface and the porosity [2]. The accumulation of siliceous solid waste called partially dealuminated metakaolinite clay (PDK), causes negative environmental impacts due to its fine particulates which are easily spread in the surrounding environment [3].

It was reported that the PDK and calcium hydroxide blends using thermal calorimetric experiments, showed considerable cementitious property [4]. The pozzolanic reactivity of the PDK in prepared blends was also confirmed [5]. This reactivity is relatively higher than that of fumed silica and the initial setting duration increased by addition of the nano carbon (NC) and PDK composite denoted (NCPDK). Different ratios of NCPDK were applied to replace certain portion of the normal cement and its effect on consistency, initial and final setting durations of cement and compressive strength of the mortar after the 7 and 28 day were studied.

The rheological characteristics of fresh mortar determine its workability and flowability. The required water for hydration reactions and the physical properties of the hardened mortar depends on the distribution of cement in water. The particle size distribution and mixing intensity affect the rheological properties of the concrete [6]. By application of additive materials to mortar the mechanical properties of mortar/concrete are upgraded such as compressive strength. Referring to the world interest of getting pure and healthy environment and facing the abnormalities in climatic changes, the work for utilization of new nontraditional materials resulted from different industries as a by-product has become necessary. This will improve the environment quality and reduce the negative impacts of the wastes on the public health.

It was known that the manufacturing of traditional Portland cement is highly energy consuming process and significant measures were taken to get cement alternatives. Pozzolana are

known to substitute partially the normal cement in mortar or concrete mixture because it densifies their matrix by closing the pores as well and this enhance the strength growth [7].

ASTM C595, defined pozzolana as a silicate bearing materials which have no binding effect but when they react with lime at normal conditions forming cementing compounds. The majority of pozzolanic materials are a by-product of industrial processes. They are mainly siliceous materials such as fumed silica, flied ash, slag (granulated blast furnace slag of iron smelters), in addition to calcined clays, all of these materials substitute partially the traditional Portland cement.

PDK is an industrial by-product resulted from aluminum sulphate manufacturing. This by-product is a pozzolana has an environmental impact it consists of high silicate and low aluminum content. The pozzolanicity of this by-product was gained as a result of the dehydroxylation process by thermal treatment which removes the OH groups from the tetrahedral silicate and octahedral aluminate sheets of kaolinitic clay changing it to dewatered clay or metakaolin. The sulphuric acid reacts with the calcinated clay extracted aluminum from the structure leaving low aluminum high silicate content by-product. The thermal and acid attack of metakaolin increased the surface area and the porosity yielding amorphous silica [8]. The Brunauer, Emmett and Teller (BET) values that expressing the specific surface area increased as a result of acid attack causing increase of the pore volume and the chemical and physical reactivity such as adsorption and absorption [7].

Carbon black in its pure form is a fine black powder, essentially composed of elemental carbon [9, 10]. It is produced by partial burning and pyrolysis of low-value oil residues at high temperatures under controlled process conditions [11]. Carbon black is mainly used to strengthen rubber in tires, but can also act as a pigment, UV stabilizer, and conductive or insulating agent in a variety of rubber, plastic, ink and coating applications. Apart from tires, other everyday uses of carbon black include hoses, conveyor belts, plastics, printing inks and automotive coat [12].

This study exploited the pozzolanic properties of PDK mixed with Nano-carbon to be used as an additive to mortar replacing a certain proportion of cement ranged between 5 – 20% for improving the compressive strength and the chemical characteristics of the fabricated mortar. The main constituents of PDK are amorphous silica, alumina, and iron oxide; other impurities are reported such as quartz.

2. Materials and experiment

2.1 CEM II 42.5R (EN 197-1)

CEM II 42.5R (EN 197-1) produced by Suez cement company. *Table 1* show the physical properties cement and *Table 2* illustrates the chemical composition of the OPC used.

The properties	Value		Limits
Specific Gravity	2.63		2.50 – 2.75
Bulk density, (kg/m³)	1780		-
The compressive strength for standard mortar (MPa)	2 days	20.8	Not less than 10
	28 days	50.3	Not less than 42.5
Soundness (La Chatelier)	1		Not more than 1
Setting duration (min.)	Initial	135	Not less than 60
	Final	180	-

**ESS 4756-1/ 2013*

*Table 1 The mechanical and physical properties of CEM II 42.5R **
1. táblázat A CEM II 42.5R mechanikai és fizikai tulajdonságai*

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl^-	LOI	Total
%	22.31	5.40	3.1	62.7	1.4	1.95	0.18	0.16	0.03	2.40	99.28

Table 2 The chemical composition of Ordinary Portland Cement (OPC)
2. táblázat A hagyományos portlandcement (OPC) kémiai összetétele

2.2 Partially dealuminated kaolinitic clay (PDK)

2.2.1 The chemical and mineralogical analysis of PDK

PDK resulted from the reaction of calcined kaolin with sulphuric acid during the manufacturing of aluminum sulphate. The calcination of kaolin at 700 – 800 °C results in dehydroxylation and formation of amorphous structure (metakaolin) easily attacked by sulphuric acid forming aluminum sulphate and amorphous rich silica called dealuminated metakaolin. The acid attack causes that the silica is present in a disordered and non-bonded structure. The surface area of the PDK is high due to the acid treatment in addition to the amorphous nature of metakaolin.

Compound	Amount (weight %)
SiO_2	81
SiO_2 (amorphous)	58 = 0.97 Molar
Al_2O_3	6.7 = 0.066 M
SiO_2/Al_2O_3	14.7
Fe_2O_3	0.7
TiO_2	3.6
MgO	0.09
CaO	0.15
Na_2O	0.03
K_2O	0.05
SO_3	1.2
P_2O_5	0.01
SrO	0.05
Cl	0.06
L.O.I	4.8
Total	98.44

Table 3 The chemical analysis of the PDK
3. táblázat A PDK kémiai elemzése

PDK was collected from aluminum Sulphate factory. It was dried at 105 °C for 3 hours to remove moisture. The chemical composition based on the XRF shows that most of the alumina in the waste is present as part of the unreacted meta-

kaolin (*Table 3*). The amorphous silica is about 58% (*Fig. 1*). The XRD pattern displayed the silicate morphism in 20 – 25 2θ complying with that reported in reference [13].

PDK was first washed carefully in compact filter press unit and dried at 120 °C for three hours then XRF analyzed using an AXIOS, analytical 2005, Wave length Dispersive (WD–XRF) Sequential Spectrometer. *Table 3* shows high content of reactive SiO_2 it averaged 58%; reactive silica represents the fraction of silica able to react in the normal environment with alkalies. The averaged value of Al_2O_3 in PDK was 6.7%.

PDK was analyzed by XRD analysis using a Burkur D8 Advanced Computerized X–Ray Diffractometer apparatus to show its constituting phases. *Fig. 1* displays that its main crystalline phases are quartz and anatase. The presence of aluminum oxide and sulfur oxide in the XRF analysis (*Table 3*) indicate the presence of traces of amorphous aluminum sulfate compound.

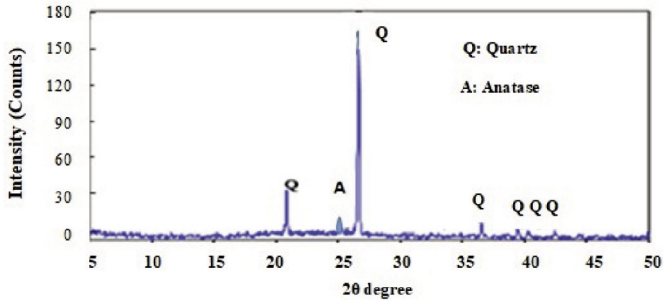

Fig. 1 XRD analysis for PDK
1. ábra A PDK XRD analízise

2.2.2 The grain size-distribution of PDK

The grain size-distribution of the ground PDK by laser granulometry was plotted in *Fig. 2* which shows that the diameter of PDK in cumulative 90% of ~78 μm and 10% of ~ 4.9 μm with an average diameter of ~9.6. BET analysis revealed a high fineness for PDK (20 m^2/g).

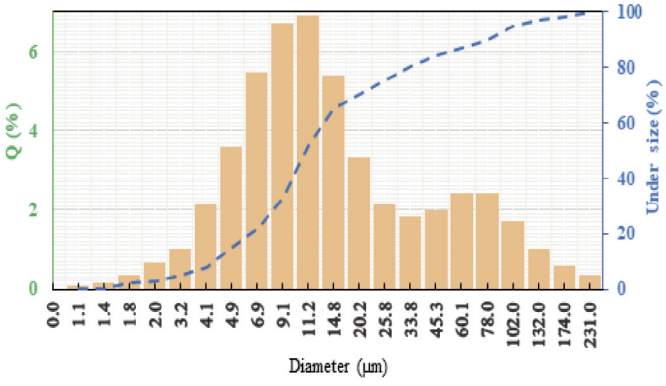

Fig. 2 Grain size distribution of PDK using laser granulometry
2. ábra A PDK lézergranulometriával mért szemcseméret-eloszlása

2.2.3 The pozzolanic testing of PDK

According to ASTM C 618 the pozzolanic materials reacts with portlandite [$Ca(OH)_2$] resulted from the hydration process of OPC and calcium silicate hydrate compound is formed as a cementing material. The pozzolanic reactivity of the samples was determined chemically by mixing of 2 g PDK with 10% lime and 2 drops of water. The free lime of the mixture was measured directly and after 5 days on another sample well covered and stored at 60°C. This chemical method is described in detail elsewhere [14].

Table 4. indicates the pozzolanic activity, specific surface area and the bulk density of PDK. The reactivity test after 5 days recorded 120%.

The parameter	Value
The pozzolanic reactivity	120%
Specific surface area	20 m^2/g
The bulk density	1.35 g/cc

Table 4 The pozzolanic testing of PDK
4. táblázat A PDK puccolán vizsgálata

The surface area was measured by means of BET method which shows the adsorption of nitrogen at liquid nitrogen temperature. The specific density was evaluated using Le Chatelier flask according to ASTM C188-84. The mineralogical composition was monitored by means of X-ray diffraction using an automated diffract meter at a scan range from 10 to 50° (2θ). Positive reaction to pozzolana test (EN 196-4) was given by PDK when blended with CEM I 42.5R. Methylene blue method (UNI EN 933/9) 3.85 g/kg for PDK.

Mixes	NC (g)	PDK (g)	NC/ PDK (%)	NC/OPC (%)	NCPDK / OPC (%)	OPC (%)	Water / binder	Sand / cement
Control 1	0.0	5	0.0	0.0	0.0	100	0.43	2.25
M1	0.0	0.0	0.0	0.0	5	95		
M2	0.05	4.95	1.01	0.0005		95		
M3	0.10	4.90	2.04	0.001	5	95		
M4	0.15	4.85	3.03	0.0015		95		
M5	0.0	10	0.0	0.0	10	90		
M6	0.05	9.95	0.5	0.0005		90		
M7	0.10	9.90	1.01	0.001	10	90		
M8	0.15	9.85	1.52	0.0015		90		
M9	0.0	15	0.0		15	85		
M10	0.05	14.95	0.33	0.0005		85		
M11	0.10	14.90	0.67	0.001	15	85		
M12	0.15	14.85	1.01	0.0015		85		
M13	0.0	20	0.0	0.0	20	80		
M14	0.05	19.95	0.25	0.0005		80		
M15	0.10	19.90	0.50	0.001	20	80		
M16	0.15	19.85	0.76	0.0015		80		

w/b = water/OPC+ weight of NCPDK

Table 5 The mix ratios of mortars ingredients
5. táblázat A habarcs összetevőinek keverési arányai

2.2.4 Thermogravimetry and differential scanning calorimetry of PDK (TG/DSC)

The thermal behavior of the starting PDK is presented in the *Fig. 3*. The main changes revealed by TG and DSC analysis are as follows: The DSC line indicates the removal of absorption

water or free water as demonstrated in the small band at 186.6 °C (water absorbed in pores and on the surface = 1.73%). The thermal degradation occurs between 186.6 and 550 °C is associated with the presence of silicate and the chemical dewatering within the structure. The remaining weight loss at between 550 and 1000 °C can be attributed to more bound water which results from silanol or aluminol. The results show that approximately 6.93% measured over the temperature range of ambient to 988 °C.

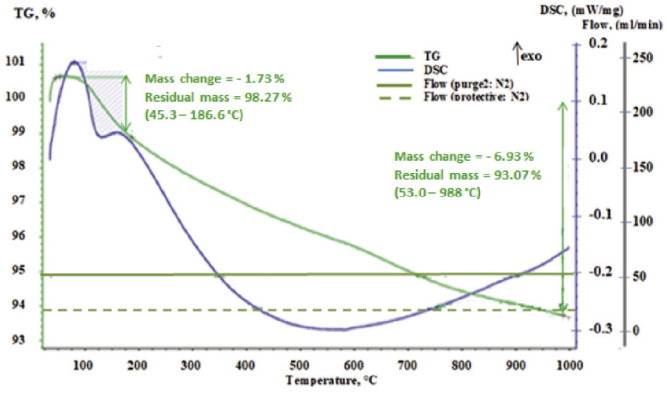

Fig. 3 Thermogravimetry and differential scanning calorimetry of PDK (TG/DSC)
3. ábra A PDK termogravimetriája és differenciális pásztázó kalorimetriája (TG/DSC)

2.3 The fine aggregate

Using sand as a fine aggregate in both mortar and concrete mixtures. Sand tests were carried out according to the standard specifications (EN 1097, EN 933). *Table 6* shows the physical properties of the sand used. *Fig. 4* shows the gradation of sand. The results showed that the specifications of the sand used matched the Egyptian Code for the Design and Implementation of Concrete Structures No. 203 of 2018.

Parameters	The results	The limits ECCS203-2018 Egyptian standard
The specific gravity	2.60	-
The bulk density (ton/m³)	1.60	-
Dust and clay	1.20	Not more than 2.5

Table 6 The physical properties of sand
6. táblázat A homok fizikai tulajdonságai

2.4 Nano carbon

The used Carbon black is a specific kind of the basic carbon which is obtained as colloid particles from incomplete combustion or thermal decomposition of the liquid or gaseous hydrocarbons under controlled conditions. This material can be observed as a fine black powder similar to the materials obtained from the combustion of the hydrocarbons, coal or exhaust soot. Carbon black contains more than 95% of amorphous carbon and a small percentage of oxygen, hydrogen, nitrogen, and others [15, 16].

The addition of nano-carbon black (NC) was made on OPC content weight basis; NC/OPC ratios considered were as follows: 0.0, 0.0005, 0.001 and 0.0015%. The NCPDK mix design/m³ is shown in *Table 5*. The replacement of OPC was made by addition of 5, 10, 15, and 20% NCPDK in cement paste and the mortar mixes. The w/b ratio required to attain the standard consistency of the reference OPC paste was determined using Vicat apparatus according to ASTM C187-92. The initial and final setting times were measured according to ASTM C191-92. The same methods were utilized to investigate the effect of NCPDK on the water demand and the setting behavior of the pastes. The mixing procedures were carried out according to ISO 9597 (1989) and ASTM C305-82.

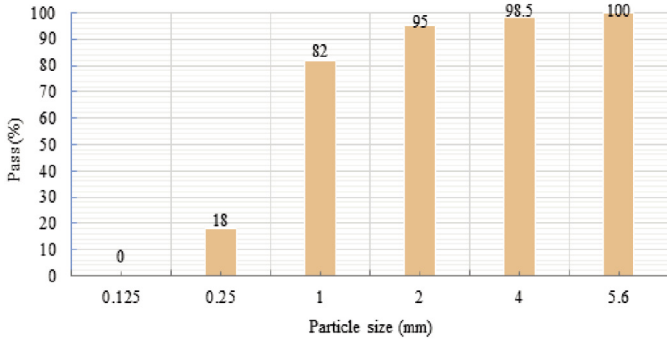

Fig. 4 Graduation of sand
4. ábra A homok szemcsemérete

2.5 The chemical additives

In order to achieve good mixing of the mortar mixtures, a water reducing agent, Master Reobuild 3045, was added, which conforms to ASTM 494 Type G.

2.6 The mixture properties

2.6.1 The pH of mortar slurry

The pH of the mortar slurry was performed as follows by adding 20 g of cement to 100 ml of distilled water (w/b = 5) in glass bottles (ASTM F710-05). The NCPDK was added to the cement as a replacement material with 0, 5, 10, 15 and 20%. The components were mixed manually and the change in the pH- values was recorded by means of a digital pH meter after 0, 30, 60, 90 and 120 minutes.

2.6.2 Flowability testing

The Mortar Flow Table Apparatus (MFTA) was done for determining the flowability and the rate of flowability changing of the OPC and OPC/NCPDK mortars. The MFTA are described in ASTM C230/C230M–14. After mixing; the flowability of the mortar was measured using MFTA, according to the ASTM C109-99. To test the rate of flowability changing during the fresh state of mortar mixes, the flow diameters were determined at different durations from mixing: 0, 30, 60, 90 and 120 min.

The flowability was determined as the ratio between the diameter of the resulting form and that of the original mix:

$$\text{Flowability} = \frac{df - di}{di} \times 100 \quad (1)$$

Where, d_f is the final diameter (mm) and di is the initial diameter (mm).

Casting and compaction of the specimens used in the determination of the compressive and the direct tensile strengths respectively were based on ASTM C109-99. Mixing, casting,

curing, and testing were carried out at normal conditions. The prepared cubic mortars and briquette specimens were covered with plastic for 24 hours, demolded and then immersed in water until testing. The compressive strengths were determined at ages of 7 and 28 days according to ASTM C109-99, the specimens prepared to test the direct tensile strength were tested at the age of 56 days according to ASTM C307-99.

2.6.3 Initial and final setting duration

The initial and final setting tests were done as explained in IS 4031-Part 5. Standard Vicat needle was used in assessing its penetration in a fresh mix. Three specimens were tested each time and the average values were recorded.

2.6.4 Compressive strength testing

The mechanical characteristics of tested mortar specimens fabricated with NCPDK are expressed in compressive strengths**.** According to EN 206, NCPDK can be used as a pozzolanic material. The efficiency of NCPDK as a replacement of portion of OPC has been verified in concrete blends. In all trials the addition were done on dry basis with reference to the sum of cement and additive (c+a).

Superplasticizer was used with an average of 1.6%. The density in the fresh state (EN 12350-6) is 2360 kg/cubic meter; and cubic compressive strength was done according to (EN 12390-3). The samples were immersed in water for 24 hrs, the measurements were done according to the Egyptian specifications ESS 1658-1991.

2.6.5 The mortar mixes preparation and testing

Five mixtures of cement mortar were carried out using five different substitution ratios in the NCPDK mixture of cement to test the compressive strength at the age of seven days for determination of the pozzolanic activity of the mixes, and based on the results, the best substitution ratios were chosen for the test at an age of 28 days. The standard ASTM C1240 was taken into account in determining the basic mixing ratios for cement mortar, where the compressive strength of the mortar was measured at the age of 7 days using the average value of three cubes with dimensions of 70 × 70 × 70 mm using NCPDK mixture substitution ratios of cement (5, 10, 15 and 20% which contain 1, 2 and 3% C for each ratio, respectively) and compared with the control mix that does not contain NCPDK.

2.6.6 Preparing samples and curing

The prepared mortar mixtures were poured into the steel moulds. The mortar mixtures were poured into the moulds in three layers and each layer was compacted using a steel rod. After 24 hours, the mortar specimens were removed from the moulds and cured in water at room temperature until testing.

3. Results and discussion

3.1 The flow of the modified mortars with NCPDK

The initial flowability and the rate of flowabilities loss containing different contents of the NCPDK were tested. The OPC mortar mixes prepared with different ratios of NCPDK were assessed. *Fig. 5* displayed the effect of NCPDK on the flowability of OPC mortars. It is clear from the figure that the incorporation of NCPDK had only a slight effect on the initial flowability of the OPC mortar. The reduction in the initial flowability of OPC mortar reached 2.7 and 6% for 10 and 20% replacement of the OPC by NCPDK. The fineness of PDK and Nano carbon increase the water demand causing reduction of flowability.

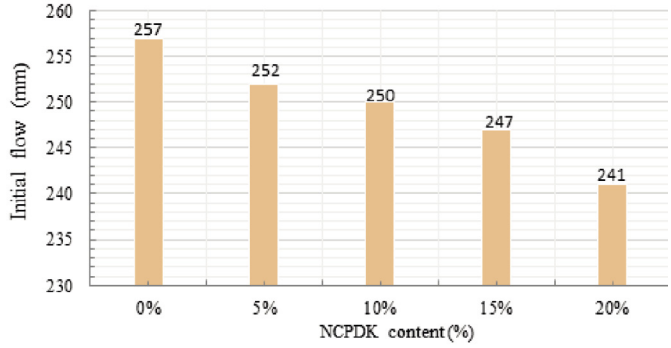

Fig. 5 Flowability of OPC mortar containing different contents of NCPDK
5. ábra Különböző NCPDK-tartalmú OPC habarcsok folyóképessége

The loss rate of flowability of OPC mortar OPC/NCPDK mortars was determined by measuring the instant flowability at different periods of time from mixing namely 0, 30, 60, 90 and 120 min. The relative flowability (instant flowability/ initial flowability) versus time are illustrated in *Fig. 6*. It was found that the relative flowability of the NCPDK modified samples is reducing with increasing time. The flowability loss is decreasing with increasing of as the NCPDK content at a constant time. After 60 minutes from mixing, the relative flowability was 68% at 10% replacement of NCPDK while the OPC mortar was 88 (*Fig. 6*).

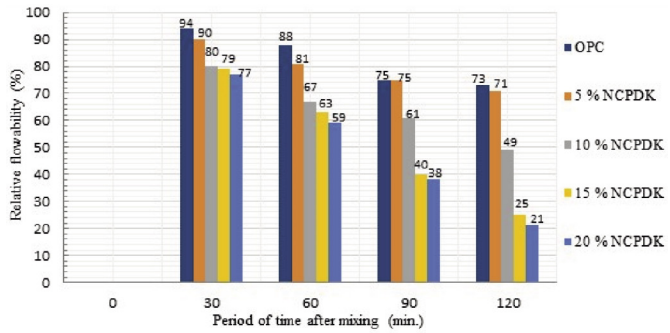

Fig. 6 Flowability loss of OPC mortars containing different contents of NCPDK
6. ábra Különböző NCPDK-tartalmú OPC habarcsok átfolyóképességi vesztesége

3.2 Strength characteristics

The compressive strengths of the twelve mixtures and the control mixture were measured at an age of 7 and 28 days using the average value of three specimens according to the standard specification EN196-1.The mechanical properties of the modified mortar with NCPDK are expressed in terms of compressive and tensile strengths as illustrated in *Fig. 7*. It was found that the compressive strength delayed in the 7 days, but it developed in the 28th day. The 28-days compressive strength of the OPC mortar increases with increasing the replacement ratio of the CPDK in the OPC mix. It achieved a peak value at 10% DK beyond which the compressive strength started to

Design mixes	Cem. (g)	NC/PDK (%)	NCPDK/ OPC (%)	Sand (g)	Flow (mm)	Water (g)	Compressive Strength (MPa)		Increase of compressive strength (%)	Effect of Nano-carbon on compressive strength (%)
							7 days	28 days	28 days	28 days
Control	100	0.0	0.0	225	257	44	36.3	44.3	-	-
M1	95	-	5	225	252	44	34.3	46.2	+4.3	-
M2		1			252		35.4	46.3	+4.5	+0.2
M3	95	2	5	225	252	44	35.6	46.6	+5.2	+0.9
M4		3			252		35.8	46.8	+5.6	+1.3
M5	90	-	-	225	250	44	33.7	50.0	+12.9	-
M6		1		225	250		34.7	50.2	+13.3	+0.4
M7	90	2	10		250	44	35.1	50.5	+14.0	+0.7
M8		3			250		35.8	50.7	+14.4	+1.5
M9	85	-	-	225	247	44	33.6	49.2	+11.0	-
M10		1		225	247		33.5	49.3	+11.3	+0.3
M11	85	2	15		247	44	33.8	49.5	+11.7	+0.7
M12		3			247		34.2	49.7	+12	+1.0
M13	80	-	-	225	241	44	34.0	48.7	+9.9	-
M14		1		225	241		34.2	48.9	+10.3	+0.4
M15	80	2	20		241	44	34.4	49.0	+10.6	+0.7
M16		3			241		35.5	49.2	+11.0	+1.1

Table 7 The mixing ratios and compressive strengths for the mortar mixtures
7. táblázat A habarcskeverékek keverési arányai és nyomószilárdsága

decrease with increasing the NCPDK content. The compressive strength of the OPC mortar specimens made with either 5, 10, 15, and 20% NCPDK (containing 3% of Nano-carbon) are higher than that of pure OPC mortar specimens by about 8.0, 17.0, 15.8 and 4.5%, respectively (*Table 7*, *Fig. 7*). The results show that 3% of Nano-carbon achieved higher strength than 1 and 2%. This behavior attributed to filling concrete pores which causes an increase in the compressive strength. This perfectly lines up with the study conducted by [17].

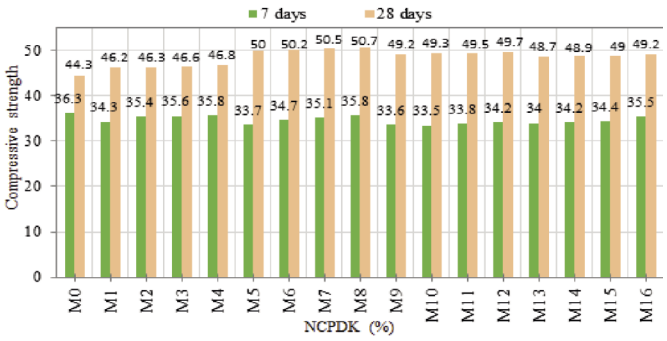

Fig. 7 The compressive strength of cement mortars containing different contents of NCPDK after 7 and 28 days
7. ábra Különböző NCPDK-tartalmú cementhabarcsok nyomószilárdsága 7 és 28 nap után

3.3 The pH change as a result of adding the NCPDK to the cement mixture

As the alkalinity of the mortar medium is of great importance in preserving the mortar from deterioration when the alkalinity decreases below (pH = 11.5), which leads to stresses within the mortar leading to the formation of cracks in it [18]. Therefore, it was necessary to test the effect of replacing a percentage of cement by NCPDK on the pH-value of the cement slurry.

Fig. 8 shows the results of the pH measurements, where a slight decrease in the pH value as a result of the presence of CPDK in the cement mix. It also shows the decrease in alkalinity arising with the increase of NCPDK (15%) due to the presence of a percentage of SO_3 as the pH decreased to 12.4.

Mix No.	OPC (g)	NCPDK (%)	Duration (min)				
			0	30	60	90	120
1	100	0	12.75	12.7	12.64	12.6	12.6
2	95	5	12.7	12.65	12.62	12.6	12.6
3	90	10	12.65	12.62	12.6	12.6	12.6
4	85	15	12.6	12.55	12.5	12.5	12.5
5	80	20	12.54	12.5	12.45	12.42	12.4

Table 8 Effect of NCPDK on the pH values of cement mixes
8. táblázat Az NCPDK hatása a cementkeverékek pH-értékeire

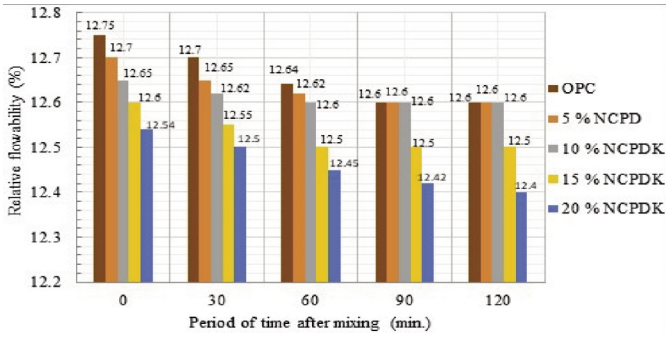

Fig. 8 The pH expressing the alkalinity of the mortar mixtures containing different contents of NCPDK
8. ábra A különböző NCPDK-tartalmú habarcskeverékek lúgosságát kifejező pH-érték

3.4 The paste consistency

Fig. 9 shows the effect of addition of NCPDK on the water/binder ratio (w/b) ratio required for the standard consistency of the replaced OPC. It was found that the w/b ratio increases with increasing the NCPDK ratio.

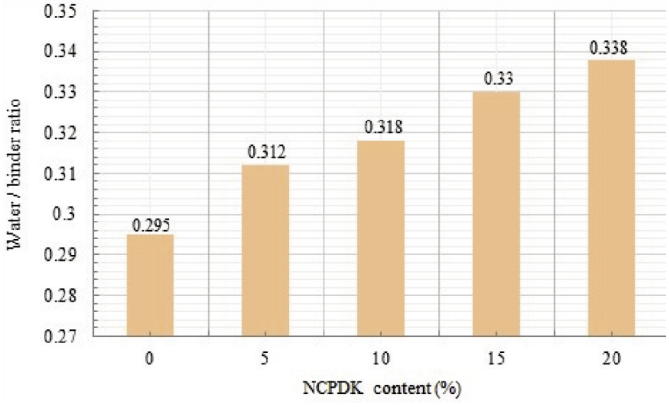

Fig. 9 Effect of NCPDK on the w/b ratio required for standard consistency of OPC pastes
9. ábra Az NCPDK hatása az OPC paszták standard konzisztenciájához szükséges w/b arányra

3.5 Setting duration for the mortar containing NCPDK

The setting time of OPC depends on the phase composition, the concentration of the liquid phase and the pH-value; the amount of alkali and soluble alumina play dominant role in the process. Setting is accelerated by soluble alumina; it is retarded by calcium hydroxide, iron hydroxide, and sulfates. Relative setting delay was noticed due to the presence of Nano carbon particles in NCPDK. *Fig. 10* shows the results of the initial and final setting times of the blends with normal consistency with the NCPDK at different replacement of cement. The setting durations of the fabricated paste without replacement was found to slightly higher than those containing NCPDK and both setting times decrease at higher replacement ratios up to 20%. This means that NCPDK has accelerated the effect especially for the initial setting, i.e. setting time is inversely proportion with the quantity of NCPDK. The initial setting times of the OPC paste without replacement was found to be 122 min. While at replacement ratio of 5% CPDK caused a slight decrease of both setting times and is followed by a steady increase at higher replacement ratios up to 20%. However the reduction of final setting time was referred to the high pozzolana reactivity of NCPDK and high surface areas of NCPDK determined as B.E.T that accelerate hydration of OPC and setting.

The initial setting duration decreased by the added NCPGK, from 118.6 min. at zero addition to 81.7 min at 10%. The final setting duration decreased from 158 min at zero addition down to 121.3 min at 10% addition. Further increasing of NCPDK addition to 15% decrease the initial setting duration to 63.5 min. and the final setting duration to 88.2 min. The accelerating effect of NCPDK was clear on the initial setting time whereas it reduced by about 31% and the final setting time reduced by 23% at the 10% NCPDK. The setting time for the paste fabricated with CPDK/Cement is within the reported range for the normal portland cement mixture (equal or greater than 45 min. and final setting equal or less than 10 hrs.) as recommended by ASTM C 305-82 and ISO 9597(1989).

The pozzolana properties of NCPDK cause increasing of rate and heat of hydration of cement in the fabricated concrete. The specific surface area (BET) active silica and alumina content yield alkali that activates acceleration of hydration process of cement. The addition of NCPDK increases the water requirement due to the fine grained NCPDK. The active hydration, the binding of lime reaction and hydroxide species release heat. The aluminum ions convert to aluminate which react with lime forming hydrated calcium aluminate of weak binding which react with lime sulphate forming ettringite. The presence of lime and active silica hydrated calcium silicate polymer chain. The aluminum content in NCPDK is in the form of metakaolin which has alumina encourage the hydration products and so accelerate hydration and setting duration.

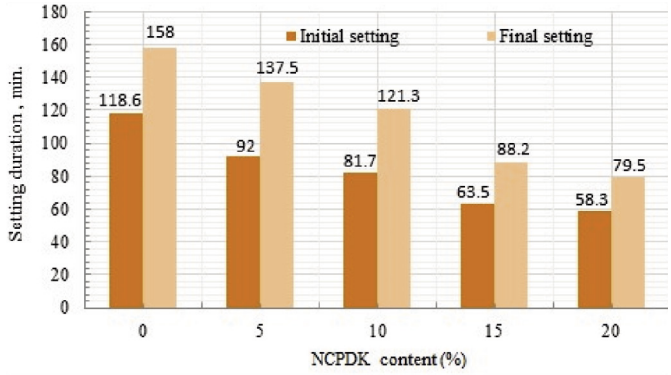

Fig. 10 Effect of NCPDK on the initial and final setting duration of OPC pastes
10. ábra Az NCPDK hatása az OPC paszták kezdeti és végső kötési idejére

3.6 The mineralogical composition of mortar containing 0, 10, 15% of NCPDK

Fig. 11 shows that the XRD for the mixes containing 10 and 15% of NCPDK and the control mix (OPC) after 28 days. It was found that increasing of NCPDK resulted in increasing of calcium silicate hydrate (CSH) and reduction of portlandite ($Ca(OH_2)$).

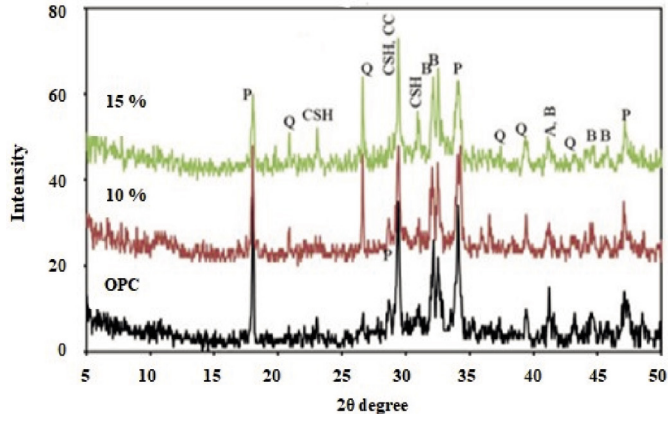

Fig. 11 The XRD analysis for the mortars containing 0, 10, 15% of NCPDK
11. ábra A 0, 10, 15% NCPDK-t tartalmazó habarcsok XRD elemzése

3.7 The thermal properties of cement mixes containing NCPDK (TGA/DTGA)

Fig. 12 shows the appearance of a band before reaching 100 °C it is related to humidity. The thermal absorption band in the thermal range 100 - 200 °C resulting from the presence of hydrated calcium silicate compound. The thermal absorption band in the thermal range 450 - 500°C is due to the removal of the hydroxyl anion of calcium hydroxide. The thermal absorption band at 700°C is due to the formation of calcium carbonate compound as a result of the carbonation of lime with carbon dioxide. It is noted that replacing cement with NCPDK at rates of 5, 10, 15 and 20% increases the formation of CSH compound at the expense of lime. These results are in agreement with previous research studies [19-21].

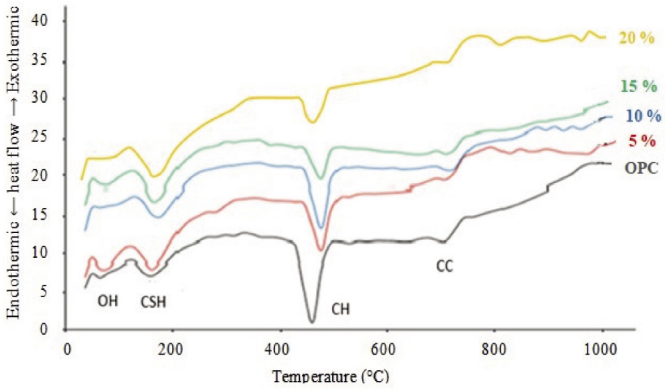

Fig. 12 The thermal analysis of NCPDK-containing cement mixes (TGA/DTA)
12. ábra NCPDK-tartalmú cementkeverékek (TGA/DTA) termikus analízise

3.8 Infrared spectrum analysis (FTIR)

This analysis was carried out to identify the structural state after replacement with NCPDK at 5, 10, 15 and 20% of cement and after 28 days of immersion in water. *Fig. 13* represents the infrared pattern of the reaction products with water after 28 days in the positive range 400-4000 cm^{-1}. The band at 3645 cm^{-1} is due to the tension fluctuation of the OH group of portlandite $Ca(OH)_2$. At 1461 cm^{-1} the band is due to the presence of calcite resulted from the interaction of lime with calcium dioxide. The band in the range 900 - 1000 cm^{-1} indicates the presence of the structure of amorphous calcium silicate. These bands agree with the interpretation of reported in the references [22-24].

The density of the band at 970 cm^{-1} in the aqueous mixtures of NCPDK/OPC increases with increasing of NCPDK up to 15% of the cement. This behavior indicates an increase in the formation of aqueous calcium silicate compound. The density of the band begins to decrease with an increase in NCPDK of more than 15% this is due to the decrease in pozzolanic reactivity.

From the previous experiments conducted on (NCPDK/OPC) mixture, which contains increasing percentages of NCPDK, the manufactured product (5-20% NCPDK/OPC) and after 28 days of curing, to study the behavior of Nano-carbon /partially dealuminated kaolinitic clay as an additive, using DTA /IR shows the following:

NCPDK behaves with cement as a pozzolanic material by interacting with calcium hydroxide resulting from the interaction of cement with water (hydration) forming more (C-S-H) according to the American standard specifications ASTM C618.

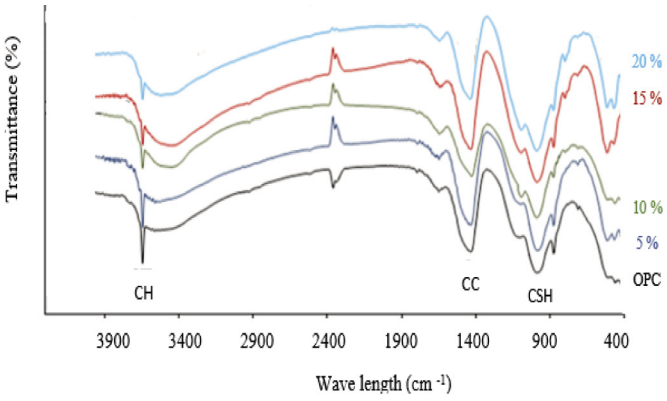

Fig. 13 FTIR analysis of cement mixes containing NCPDK with different substitution ratios
13. ábra Különböző helyettesítési arányú NCPDK-t tartalmazó cementkeverékek FTIR elemzése

Further researches shall be done to investigate the durability of the mortar modified with a composite of Nano-carbon and dealuminated calcined kaolin.

4. Conclusions

- Based on the obtained results it was found that the 10 and 15% replacement ratio of NCPDK achieved 14.4 and 12% respectively improvement in the compressive strength at an age of 28 days compared with the control mix.
- Adding a NC to PDK increased the compressive strength with an average ratio of 1.5% at 10% NCPDK.
- Using of NCPDK with ratios of 5, 10, 15 and 20% resulted in delayed the compressive strength at an age of 7 days compared with the control mix.
- The high surface area of PDK and nano-carbon causes relative reduction of setting duration.
- No significant reduction in the pH of mortar for all mixes.
- The loss rate of flowability Of OPC modified with NCPDK was reported.
- 10% of replacement of OPC with NCPDK is optimum ratio for improving the compressive strength of mortar.

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