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Case study

Effects of calcined halloysite nano-clay on the mechanical properties and microstructure of low-clinker cement mortar

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ABSTRACT

This paper explores the effects of calcined halloysite nano-clay (CHNC) on the physico-mechanical properties and microstructure of high volume slag (HVS) cement mortar. The principal objective of this research is to constitute a low-clinker cement mortar with high mechanical properties. Ordinary Portland cement clinker blended with 70% of ground granulated blast furnace slag (GBFS) was partially substituted with CHNC in ratios of 0%, 1%, 2%, 3%, 4%, 5% and 6% by weight. The results showed that the early age and long-term mechanical strengths of the slag cement mortars were significantly improved by the presence of CHNC. The slag cement containing 5 mass % of CHNC possessed the highest improvement of the mechanical properties and microstructure of hardened cement pastes and mortars. It was suggested that the higher pozzolanic activity of CHNC particles and the nucleation of calcium hydrosilicate (C–S–H) caused the enhanced strength development.

1. Introduction

Today, the term « durability » exceeds its initial meaning of life expectancy of buildings. It is now reverting to the current objective that asks construction activity to focus on preserving the planet. For the construction activity, concrete remains the basic material and its use always requires cement as a binder for the growing urbanization which generates ever more important cement needs.

In 2015, world cement production was about 4.6 billion tones, which represented an average annual growth rate of 7% compared to the year 2010 which had recorded a production of 3.3 billion tones (U.S geological survey minerals organism) [1]. The production of this construction material, indispensable for the manufacture of concrete, is not only consuming limestone, clay and fuel, but also is responsible for around 5% of total global industrial and energy CO2 emissions (OECD/IEA and World Business Council for Sustainable Development, 2009) [2].

In this regard, the manufacture of Portland cement is highly carbon dioxide emissive operation due to the chemical transformation process of limestone and various other raw materials into clinker and the combustion of fuels in the kiln. Indeed, the production of one metric ton clinker involves the emission of 0.51 ton CO_2 from the calcination process of calcium carbonate ($CaCO_3$) and 0.40 ton CO_2 from burning fuel. (Hendrik G et al, 2011) [3]. These numbers reveal the necessity and urgency to act on the manufacturing process of this building material in accordance with the international agreements on climate change, which have fixed as a main objective, the reduction of greenhouse gas emissions and in particular carbon dioxide.

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In order to achieve these goals which remain the most important objective, the countries that have ratified these agreements, have implemented measures that include the development of cements with the lowest possible environmental impact by using mineral additions as a partial replacement of Portland clinker. Blast furnace slag is the most known and the most reliable clinker additive product. Cements and concretes containing high contents of slag have been used in large projects situated in severe environments, and they have often revealed increased mechanical properties, better abrasion resistance and also ameliorated the long term engineering properties of concrete.

One of the major disadvantages of cement containing high volumes of slag is the slower initial strength development of concretes. However, recent researches have shown that the addition of a small amount of nanomaterials can have a significant beneficial impact on the early mechanical strengths development of the cement mortars and concretes containing high volume of slag, potentially resolving this obstacle to reducing carbon dioxide emissions in the cement industry. The available literature related to the incorporation of nanomaterials into cement partially replaced with Ground blast furnace slag (GBFS) can be summarized as following (Zhang et al. 2012) [4] : reported 14%, 39%, 30%, 17% and 23% enhancement in the 1, 3, 7, 28 and 91 days compressive strength of mortars containing 50% GBFS with the inclusion of 2% nano-silica, by weight of cementitious materials. Authors investigated also the effect of nano-silica on the early age, up to 30 h, hydration kinetics of cement replaced with 50% GBFS. They reported that the addition of nano-silica accelerated the hydration reaction. Ali Nazari et al. (2011) [5–9] studied the effect of different nano particles (SiO2, TiO2, Al2O3, ZrO2 and ZnO2) on split tensile strength, thermal behaviour, pore structure, and microstructure of concrete with partial replacement of cement with GBFS. The results showed that the inclusion of these nanoparticles increased the split tensile strength and improved the pore structure of concrete specimens. Mohamed Heikal et al. [10] reported that cement containing 45% GBFS modified with 3% and 4% of nano-silica possessed an optimum improvement of mechanical properties, hydration kinetics and microstructure of hardened cement pastes and mortars. Mingle Liu et al. [11] studied the synergistic effect of nano-silica and GBFS on the performance of cement pastes and mortars, the results revealed that the addition of nano-silica to the cement containing GBFS increased significantly the 28 days compressive strength, reduced the porosity and increased the density of the cement matrix.

They reported also that the cement paste containing 30% of GBFS and 3% of nano-silica possessed the highest compressive strength (5942 MPa). M. S. Amin et al. [12] investigated the effect of addition of magnetite nanoparticles on the hydration and mechanical properties of high slag cement (HSC) paste (25% OPC and 75% GBFS). The results of compressive strength showed that the hardened pastes made from HSC admixed with different amounts of magnetic fluid had higher compressive strength values than those of the neat HSC cement pastes at almost all ages of hydration. Taijiro et al. [13] reported that the micro-hardness and modulus of elasticity of cement containing 50% of slag were remarkably improved, in the early stage of the hydration by the addition of nano-CaCO3. V. Nagendra et al. [14] investigated the compressive strength of concrete with GBFS as partial replacement of cement with percentage varying from 10% to 40%. The optimum strength obtained was at 20% replacement. SiO2 nanoparticles were partially added to concrete with the optimum content of GBFS. They reported that samples containing 20% GBFS and 4% nano-silica as a partial replacement of cement possessed the highest strengths. Mohamed Heikal et al. [15] studied the effect of nano-silica on the mechanical properties of composite cement pastes and mortars containing GBFS subjected to seawater attack. The results indicated that nano-silica improved the compressive and flexural strengths of specimens subjected to seawater up to 12 months.In other research Mohamed Heikal et al. [16] studied the effect of nano-clay on the hydration process and compressive strength of OPC containing 40% of GBFS, the results revealed that the inclusion of 6% mass nano-clay activated the hydration reaction and increased the compressive strength for specimen hydrated at 1, 3, 28 and 90 days. As can be seen from the previous literature, various oxides nanoparticles have been introduced into cement containing GBFS; however there is little information on nano-clays and their effect on the hydration kinetics and the mechanical properties of cement containing GBFS.

Recently the use of nano-clays in cement based materials to increase the engineering properties and the performance of cement and concretes is getting increasing concentration due to their low cost and the availability in comparison with the other nanoparticles. Based on their morphology and chemical composition, nano-clays can be divided into various groups: kaolinite, bentonite, hectorite, montmorillonite, halloysite, and organically-modified nano-clays (organo-clays) (Taghiyari HR. 2011) [17]. Halloysite nano-clay is one of the new generations of processed clay that has been extremely ignored in the application of nano-clays in cement based materials. Halloysite nano-clay (Al2Si2O5 (OH) 4) has a tube like morphology; it consists of two layers of aluminosilicates in 1:1 Al: Si ratio (Marini J et al. 2014) [18].

Recently a few studies have revealed that the introduction of this nano-clay into cement composites can improve their engineering properties due to its chemical composition and physical properties (N. Farzadnia., 2013) [19]. Using Halloysite nano-clay in cement paste has been studied in few researches as mentioned above, but incorporating this nano-clay in cement containing high volume of slag has not been addressed in any work. Consequently this study aims to investigate the effect of calcined halloysite nano-clay on the hydration, the physico-mechanical properties and the microstructure of cement pastes and mortars containing 70% GBFS.

2. Experimental procedure

2.1. Raw materials

Ordinary Portland clinker (PC) and gypsum provided from (Lafarge Cement Company. Algeria) were ground in laboratory ball mill to produce Ordinary Portland Cement (OPC). Ground blast furnace slag (GBFS) provided by the Algerian Iron and

Steel Complex El-Hadjar was also finely ground to attain a surface area of 4000 cm2/g. The chemical analysis obtained by X-ray fluorescence (XRF) spectrometry and the physical characteristics of PC, gypsum and GBFS are listed in Table 1.

The clinker mineral contents deducted by Bogue calculation are also listed in Table 1. Grain size distributions determined by laser granulometer (MASTERSISER 2000) of OPC and GBFS are shown in Fig. 1.

The nano-clay, used in this research, is Halloysite Nano-Clay (HNC) manufactured by Sigma-Aldrich USA with Linear formula of $H4Al2O9Si2.2H2O$ and molecular weight of 294.19 g/mol. The chemical composition, physical properties, X-ray diffraction (XRD) spectra and scanning electron micrograph (SEM) of HNC are shown in Table 2, Figs. 2 and 3 respectively. Silica sand with normalized grain size distributions, according to EN-196-1(2013), was used for mortar preparation.

2.2. Thermal treatment of halloysite nano-clay

The thermal treatment of halloysite nano-clay was performed by calcination of halloysite nano-clay (HNC) for 2 h, at temperatures between 650 °C and 800 °C.

The Pozzolanic activity of the different calcined HNC (650 °C, 700 °C, 750 °C and 800 °C) was evaluated by measuring the quantity of lime fixed by 1 g of calcined HNC samples for 30 days at ordinary temperature according to the following method (EN 196-5(2013)) :

1) The sample (2 g) was mixed with 100 ml of lime solution (1.1 g/l CaO) in a plastic Erlenmeyer and sealed. The solution was kept for the first 24 h in a thermostat at 45 °C.
2) At the end of the period, the 50 ml of the solution was taken and titrated with a solution of hydrochloric acid (HCl) (0.05 N) in the presence of phenolphthalein as an indicator.
3) The volume of 50 ml of lime was added to the cylinder and the operation was repeated as before every 2 days for 30 days.
4) The results were expressed by fixed CaO in milligrams per gram of pozzolanic additive.
5) The quantity of lime fixed for 30 days per 1 g of CHNC was calculated as follow:

$$Qcao = \frac{\left(16*V0 - \left(\sum_{i}^{14} Vi - 2*V15\right)*NHCL*meq*gCaO*1000\right)}{2} \tag{1}$$

where:

V_0: medium volume of HCl required for neutralizing 50 ml of lime solution.

V_i: volume of HCl solution obtained by titration of the solution containing 2 g of CHNC

N HCl: normality of HCl solution: N HC l = 0.05 N.

Meq.g. CaO: equal mass gram of CaO = 0.028

The phase composition of the different calcined HNC (650 °C, 700 °C, 750 °C and 800 °C) was studied by means of X-ray diffraction (XRD) analysis.

Table 1
Chemical and mineral composition, physical properties of cementitious materials.

	Clinker	Gypsum	GBFS
Chemical composition (%)			
SiO2	22.17	8.95	41.75
Al2O3	5.07	2.66	11.19
FeO3	3.34	0.89	1.43
CaO	66.04	31.09	44.05
MgO	1.56	2.38	7.92
K2O	1.56	0.43	0.42
Na2O	0.67	0.00	1.00
SO3	0.18	36.54	0.42
Cl-	1.19	0.00	0.00
L.O.I	0.01	–	–
Mineral composition (%)			
C3S	61.04	–	–
C2S	17.54	–	–
C3A	7.78	–	–
C4AF	10.16	–	–
Free lime	0.01	–	–
Glass content	–	–	97.9

Physical properties	OPC	GBFS
Blaine fineness (cm^2/g)	3800	4000
Specific gravity	3.15	2.98

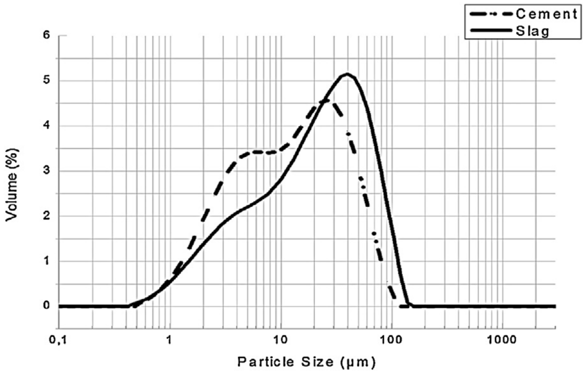


Fig. 1. Grain size distribution of OPC and slag.

Table 2
Physical properties of halloysite nano-clay.

Physical properties	
Appearance (Color)	white
Appearance (form)	powder
Surface area	65 m^2/g
diameter	30-70 nanometers
length	1-3 microns
Pore volume	1.26-1.34 ml/gm.
PH	4.5-7

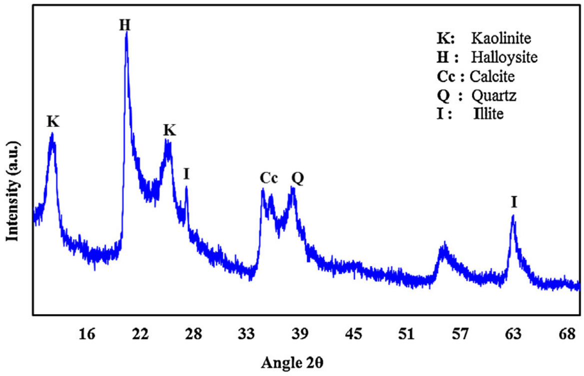


Fig. 2. X-ray diffraction pattern of halloysite nano-clay.

2.3. Mixtures proportions

Seven different cementitious materials were formulated. The first sample was formulated from 30% OPC and 70% GBFS to produce high volume slag cement (HVSC) (as a reference). The remaining six samples were formulated by partial substituting of HVSC by CHNC at different amounts ranging from 1% to 6% with a step of 1%, by weight. OPC, GBFS and CHNC were then mechanically mixed for 3 min in steel ball mill to attain complete homogeneity. The mixtures proportions are given in Table 3.

2.4. Mixing method

Paste: pastes were prepared by mixing the different dry cementitious materials with water of consistency Table 4 according to the procedure reported in EN196-3 (2013). Molded in micro cubic molds (3 cm) for 24 h, de-molded, then immersed in water at 20 °C for 2, 7, 28 and 90 days. After the predetermined curing time, small portions were cut from the cubes and conserved in acetone in order to stop the hydration process according to the procedure described by (M. A. Abd- El. Aziz, et al. 2012) [20]. The dried samples were ground. Powder passing a 63 μm sieve was used to estimate the free lime

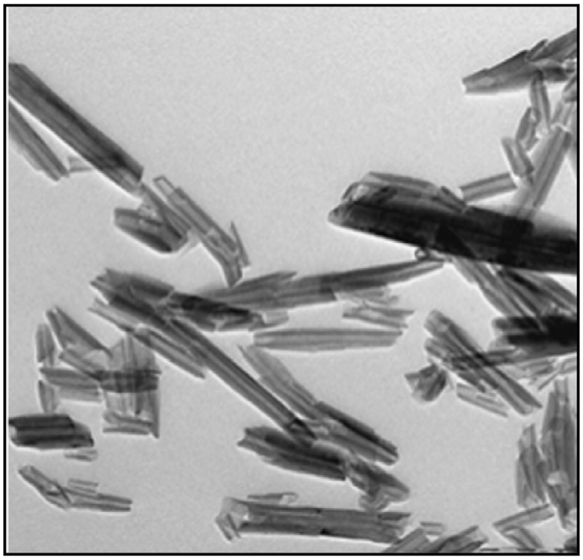


Fig. 3. TEM Image of 50 nm diameter halloysite nano tubules (TEM image provided by the supplier Sigma-Aldrich-USA).

Table 3
Mixture proportions.

Mix designation	HVSC (%)	CHNC (%)
HVS0	100	0
HVS1	99	1
HVS2	98	2
HVS3	97	3
HVS4	96	4
HVS5	95	5
HVS6	94	6

Table 4
Cement pastes proportions.

Mix designation	HVSC (g)	CHNC (g)	Water (g)
HVS0	450,0	0,0	112.50
HVS1	445.5	4.5	113.40
HVS2	441,0	9,0	114.75
HVS3	436.5	13.5	116.10
HVS4	432,0	18,0	117,00
HVS5	427.5	22.5	118.35
HVS6	423,0	27,0	119.70

content (FL%) and to perform X-ray diffraction (XRD) analyses. Small cubes of (1cm3) were also cut from the selected samples for the scanning electron microscope (SEM) investigation.

Mortar: standards mortars containing one part by mass of dry cementitious materials and three parts by mass of standard sand with a water-binder ratio of 0.50 were prepared according to the normalized formulation and procedures reported in EN 196-1 (2013).

The mixture proportions of fresh mortars are listed in Table 5. Prismatic test specimens (40mm*40mm*160 mm) in size, were prepared and cured for 2, 7, 28 and 90 days at 20 °C and RH < 95%.

2.5. Characterization

2.5.1. Determination of water standard consistency

The standard consistency of cement paste was measured according to standard norm EN196-3 (2013). This test is conducted to define the percentage of water introduced in cement to penetrate the Vicat plunger up to a depth of 33–35 mm from top of the Vicat mold.

Table 5
Standards mortars proportions.

Mix designation	HVS (g)	CHNC (g)	Water (g)	Sand (g)
HVS0	450.0	0.0	225.0	1350.0
HVS1	445.5	4.5	225.0	1350.0
HVS2	436.0	9.0	225.0	1350.0
HVS3	436.5	13.5	225.0	1350.0
HVS4	432.0	18.0	225.0	1350.0
HVS5	427.5	22.5	225.0	1350.0
HVS6	423.0	27.0	225.0	1350.0

2.5.2. Determination of initial and final setting time

Setting time was measured using Vicat apparatus according to standard norm EN 196-3 (2013). Initial setting time is that time period between the time water is added to cement and time at which a needle (Φ 1.13 mm) stops to penetrate the cement paste, placed in the Vicat's mold at a distance of 5 mm to 7 mm from the bottom of the mold.

Final setting time is that time period between the time water is added to cement and the time at which a needle (Φ 1.13 mm) cannot penetrate more than 0.5 mm from the summit of the mold.

2.5.3. Determination of the chemically combined water (W_n, %)

The hydration degree of cement pastes was evaluated by the determination of the mass loss in samples after being subjected to heating at 1000 °C. The sample must be previously dried to ensure the disappearance of the free water present in the pore of the material. The mass loss corresponding to the chemically combined water content (W_n) was calculated using the following equation.

$$W_n\% = \frac{(W_1 - W_2)}{W_2} \tag{2}$$

where

W_1 is the mass of the dried sample before ignition (g).

W_2 is the mass of the dried sample after ignition (g).

2.5.4. Determination of free line content (FL%)

The degree of cement hydration was followed by the estimation of free lime content. This test is carried out by boiling titration in an anhydrous glycerol alcohol mixture using an alcoholic solution titrated of ammonium acetate in the presence of phenolphthalein, according to the modalities of PT 207 CERHIL 1970 method, and standard norm EN 2-1-015-1984.

2.5.5. Flexural strength

The flexural strength was carried out on prismatic test specimens 40 mm × 40 mm × 160 mm in size at 2, 7 and 28 days using central point loading under a load control rate of 50 ± 10 N/s until fracture according to standard norm EN 196-1 (2013).

2.5.6. Compressive strength

The compressive strength was carried out on the prism halves after the test of flexural strength at 2, 7 and 28 days using a uniaxial hydraulic compression machine under a load control rate of 2400 ± 200 N/s over the entire load application until fracture according to standard norm EN 196-1 (2013).

2.5.7. X-ray diffraction analysis

The phase composition of the formed hydrates was investigated for some selected hydrated cement pastes at 2, 7 and 28 days using a Phillips diffractometer PW1730 with an X-ray source of Cu Kα radiation.

2.5.8. Microstructure examination

Changes, occurring in the microstructure, were identified for some selected hydrated cement pastes at 28 days using a Philips ESEM XL30 scanning electron microscope.

3. Results and discussions

3.1. Pozzolanic activity of CHNC

The X-ray diffraction patterns shown in Fig. 4 of uncalcined HNC exhibited peaks attributed to crystalline phases such as kaolinite, halloysite, calcite, quartz and illite, while diffractgrams of calcined halloysite nano clay at 650°, 700°, 750° and 800 °C showed that the calcination caused an important loss of crystallinity.

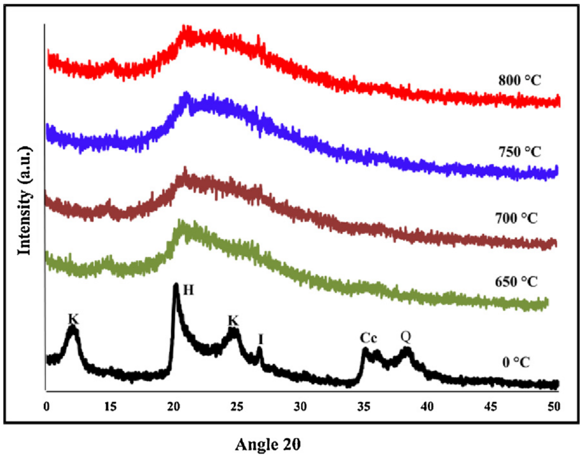


Fig. 4. X-ray diffraction patterns of calcined HNC at different temperatures.

The crystalline phase's peaks of uncalcined (HNC) disappeared at these temperatures and transformed to amorphous phases, except illite peak (2-Theta 26.8°) was not affected by the thermal treatment. Calcination results in deshydroxylation and destruction of the initial crystal structure of halloysite clay.

In order to determine the maximum calcination temperature of HNC, the quantities of calcium consumption by 1 g (Fig. 5) of calcined HNC was determined. The results revealed a diminution in the content of CaO% in the lime solution with all calcined HNC. The (750 °C) nano-clay possessed the highest calcium consumption (252 mg CaO/g), which indicated the strong pozzolanic activity of this sample. The optimum heating temperature for HNC was found 750 °C. Based on these results the HVS cement was partially replaced with different amounts of 750 °C halloysite nano-clay (CHNC).

3.2. Water of consistency

The variations of the required water of standard consistency of HVSC-CHNC pastes (HVS0, HVS1, HVS2, HVS3, HVS4, HVS5 and HVS6) are graphically illustrated in Fig. 6. It was observed that the addition of CHNC to the plain HVSC increased the water demand with increasing the CHNC content. The inclusion of 6% of CHNC to the net HVS cement increased the water/cement ratio from 0.25 to 0.267 to achieve a constant consistency. The high surface area and particle size of CHNC optimized at nano scale increased the required water for standard consistency. This quantity of water is consumed by CHNC.

3.3. Setting time

The variations of the initial and final setting time of HVSC-CHNC pastes as a function of CHNC content are graphically represented in Fig. 7. Results revealed reduction of initial and final setting time of HVS cement with increasing the CHNC content. The addition of CHNC affected significantly the setting time compared to the net HVS cements. Results showed a diminution of initial and final setting times of 40 min and 71 min respectively with the addition of 6% of CHNC, compared to the reference cement. The ultra-high fineness and reactivity of CHNC particles contribute significantly to the acceleration of hydration process and also advance the pozzolanic reaction. (Kawashima et al., 2013) [21].

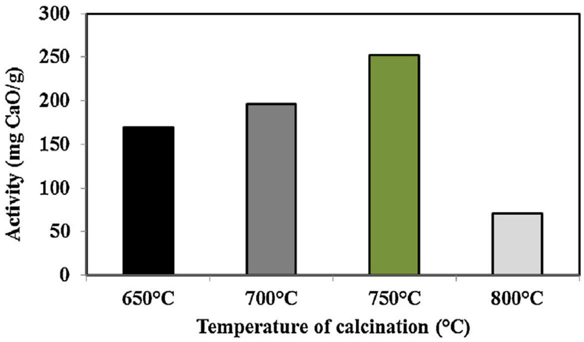


Fig. 5. The pozzolanic activity of calcined HNC at different temperatures.

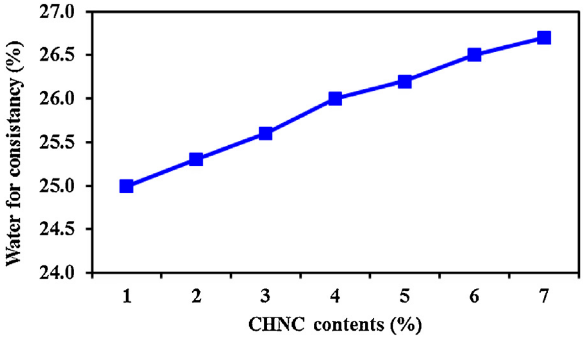


Fig. 6. Water of standard consistency of HVS cement pastes as a function of CHNC contents.

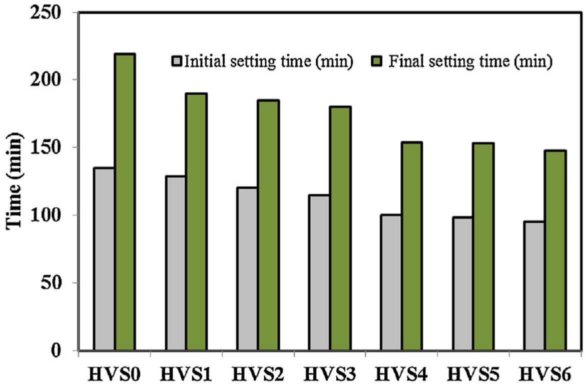


Fig. 7. Initial and final setting time of HVS cement pastes as a function of CHNC contents.

3.4. Chemically combined water (Wn, %)

The hydration degree of samples was followed by the estimation of the amount of chemically combined water (Wn, %) in HVSC-CHNC cement paste at different hydration times up to 90 days. Fig. 8 represented the variations of combined water content of hydrated cement pastes up to 90 days as a function of CHNC contents (%).

It was noted that, (Wn, %) values increased with increasing age of hydration for all samples. This is due to the continuous hydration process of cement phases.

The results showed also that the (Wn, %) increased with increasing the CHNC content. This is due to the high surface area and the pozzolanic reaction of CHNC which react with the portlandite liberated from hydration process of clinker phases leading to the formation of more hydrated products with higher water content (Qing Y et al. 2007) [23].

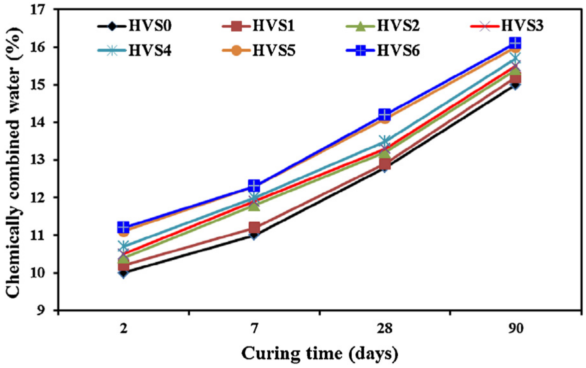


Fig. 8. Combined water contents of HVS cement pastes as a function of CHNC contents.

3.5. Free lime content (%)

The pozzolanic reaction of CHNC was followed by quantification the free lime content (FL%) of HVSC-CHNC cement pastes at different hydration times up to 90 days. Fig. 9 represented the variations of FL% of the hydrated cement pastes up to 90 day as a function of CHNC%. It was observed that, FL% values decreased during hydration process for all samples, this due to the pozzolanic reaction of both slag and CHNC with the free lime liberated by clinker hydration (M.Aiu. 2006) [22].

The results revealed also that the free lime content decreased with increasing the CHNC content. This is due to the strong and the higher pozzolanic affinity of CHNC which reacts with the portlandite to form more hydrated products mainly C-S-H.

3.6. Mechanical strength

The effects of different contents of CHNC on the compressive and flexural strengths of HVS cement mortar at ages of 2, 7 and 28 days are shown in Figs. 10 and 11, respectively. Results revealed that the compressive and flexural strengths of HVS cement mortars containing CHNC are both higher than those of plain HVS cement mortars at all ages of curing. Samples containing 5 wt% CHNC possessed the highest mechanical strength, while the incorporation of more than this content decreased their mechanical strengths.

This may be due to the diminution of CaO quantity when GBFS is used. Thus, the amount of crystalline portlandite is reduced and the amount of CHNC assist to formation C–S–H gel is decreased (Nazari Ali et al.) [5]. The mechanical strengths of the other samples (HVS1, HVS2, HVS3, HVS4 and HVS5) gradually enhanced with enhancing CHNC content.

The HVS5 mortar possessed about 105%, 29.70%, 36.21% higher compressive strengths at 2, 7, 28 days, respectively and exhibited also about 73.71, 16%, 16.40% higher flexural strength at 2, 7, 28 days, respectively than the neat HVS cement mortar. These results revealed the effectiveness of CHNC in increasing the early age and long-term mechanical strengths.

This is attributed to the effect of CHNC particles optimized at nano scale, which acts as an activator to accelerate the pozzolanic reaction and also as nucleating sites to generate more additional contents of hydrated products of second generation such as calcium hydrosilicate or calcium hydroaluminate (C-S-H or C-A-H), or even a mixture of the two hydrated products (C-A-S-H) leading to filling up the voids between the cement particles and consequently the formation of compact, dense, refined and homogeneous microstructure (S.S. Shebl. 2011, K. Liao. 2004, M. Heikal .2013) [24,25,10].

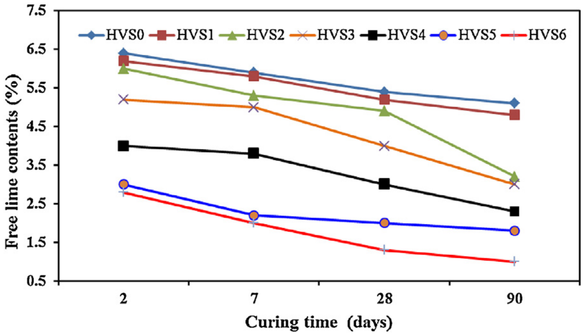


Fig. 9. Free lime of HVS cement pastes as a function of CHNC contents.

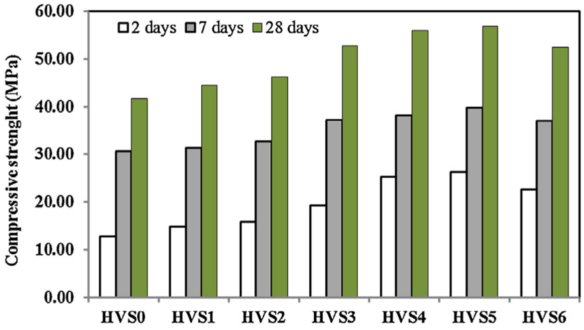


Fig. 10. Compressive strength of HVS cement mortars.

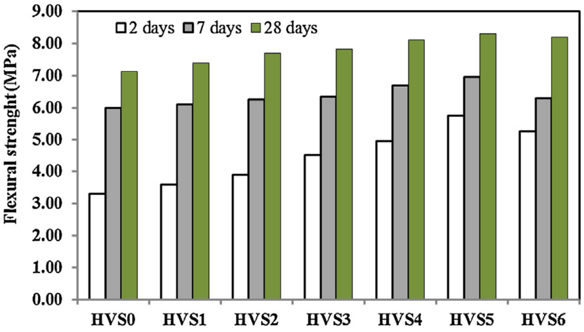


Fig. 11. Flexural strength of HVS cement mortars as a function of CHNC contents.

3.7. X-ray diffraction analysis

Figs. 12 and 13 represented the X-ray diffractgrams of control HVS0 and HVS0 samples hydrated at 2, 7 and 28 days. The principal compounds identified for both samples are calcium hydrosilicate (C–S–H) and portlandite (CH), in addition to the remaining unhydrated parts of β C_2S and C3S grains.

The intensity of CH peaks decreased with increasing the age of the hydration, whereas the peaks corresponding to CSH increased with hydration age. This is due to the continuous hydration process of cement containing pozzolanic materials as GBFS and CHNC, which react with the liberated portlandite produced by hydration reaction of cement clinker phases.

It was observed from Figs. 12 and 13, Control samples exhibited higher intensity of portlandite peaks and lower (CSH) peaks compared to that of HVS_5 at all hydration ages.

The inclusion of 5% CHNC decreased considerably the intensity of portlandite peak. This peak disappeared completely at 28 days of hydration. These results confirm the strong and rapid pozzolanic reaction of CHNC with portlandite in comparison with GBFS, leading to the continuously production of hydrated products mainly as CSH at early stages of hydration.

3.8. SEM

Observations obtained by means of scanning electron microscopy (Figs. 14 and 15) illustrated the microstructural and morphological changes attributed to the inclusion of 5% CHNC to the reference pastes samples (HVS0) hydrated at 28 days.

It was observed that the reference sample possessed inhomogeneous microstructure Fig. 14(a), with the presence of voids and unreacted angular slag particles (light grey) Fig. 14(b). The HVS samples, containing 5% wt of CHNC, show more homogeneous and refined micro-structure Fig. 15(a) compared to the reference sample Fig. 14(a). This microstructure is characterized by the presence of dense, compact and amorphous C-S-H gel structure Fig. 15(b).

It is important to notice that no portlandite hexagonal crystals or unreacted slag particles were observed in this microstructural analysis. These results confirm the strong pozzolanic reactivity of CHNC leading to the production of more hydrated silicate calcium C-S-H (secondary C-S-H generation), the main product responsible for the creation of compact, dense, refined and homogeneous microstructure.

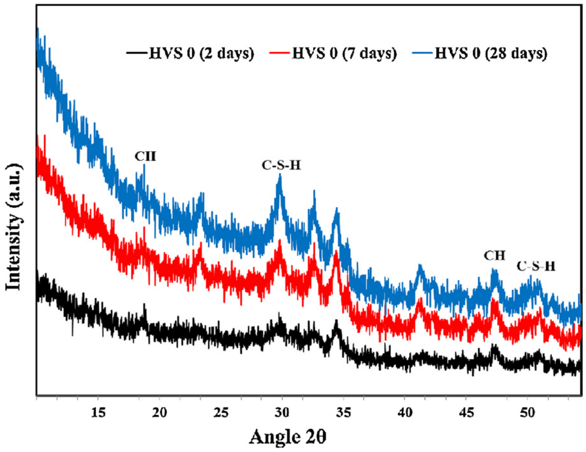


Fig. 12. X-ray diffraction patterns of HVS0 at 2, 7 and 28 days of hydration.

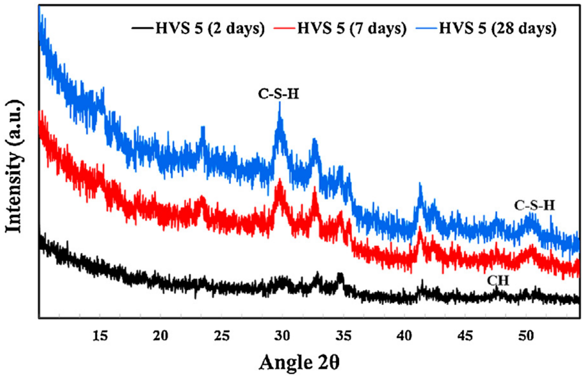
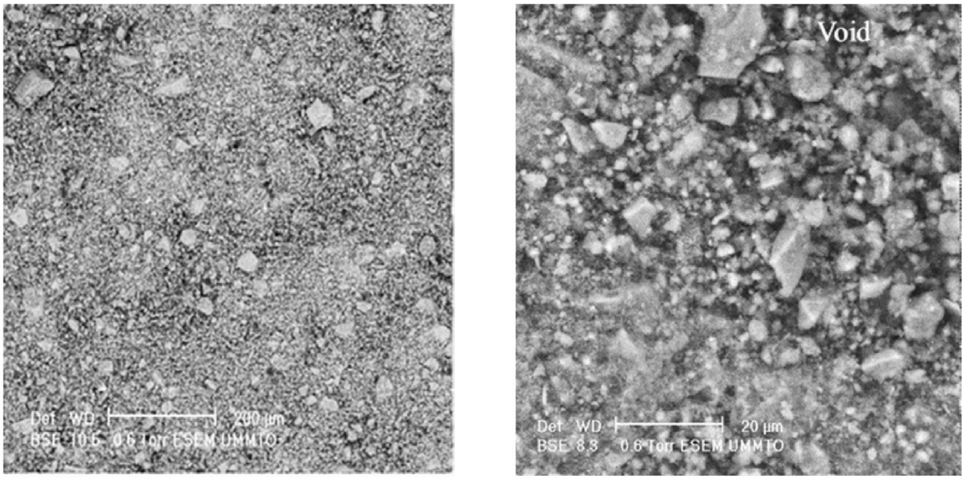


Fig. 13. X-ray diffraction patterns of HVS5 at 2, 7 and 28 days of hydration.

4. Conclusions

Based on the experimental results concerning the effects of the inclusion of calcined HNC into ordinary Portland cement clinker partially substituted by 70% of GBFS, it can be concluded that:

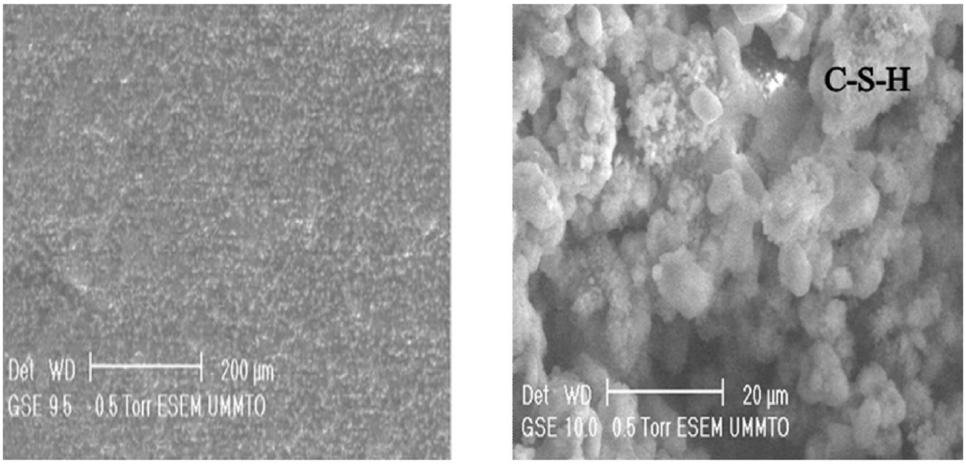
1) The water for standard consistency percentage increased with increasing the CHNC contents, due to the high specific surface of this nano-clay.
2) Calcined HNC significantly reduced the initial and final setting time of HVS cement pastes.
3) The free lime contents decreased with increasing the CHNC contents, due to the strong pozzolanic reaction of this nano-clay with the lime liberated from clinker hydration, which generates more hydrated products mainly C-S-H.
4) The chemically combined water contents revealed the positive effect of the addition of CHNC on the hydration process of the HVS cement pastes.
5) The early mechanical strengths of HVS cement mortars were considerably increased by the addition of CHNC. Mortars containing 5% CHNC as partial replacement of HVS cement exhibited about 105% and 73, 71% improvements of the 2 days compressive and flexural strengths respectively as compared to the plain HVS cement mortars.
6) The addition of 5% of CHNC increased the 7 and 28 days compressive strength of HVS mortar by about 29.70% and 36.21% respectively. However, the increments were about 16% and 16.40% at 7 and 28 days flexural strength of HVS mortar respectively.
7) The XRD analysis results showed that the addition of 5% of CHNC to the plain HVS cement paste reduced significantly the picks corresponding to the portlandite at all ages of hydration leading to the formation of additional hydrated products mainly C-S-H, which explained the improvement of the mechanical strengths.



a. Heterogeneous microstructure

b. Presence of voids and unreacted slag particles

Fig. 14. (a)–(b). Microstructure of the reference HVS0 cement pastes hydrated at 28 days.
a.Heterogeneous microstructureb. b.Presence of voids and unreacted slag particles.



a. Homogeneous microstructure

b. Presence of densified and spherical C-S-H morphology

Fig. 15. (a)–(b). Microstructure of HVS5 cement pastes hydrated at 28 days.
a. Homogeneous microstructure. b. Presence of densified and spherical C-S-H morphology.

8) The SEM examination showed that the incorporation of CHNC greatly refined the microstructure of the hardened HVS cement paste at 28 days of hydration.
9) The addition of clay at nano scale modifies the nanostructure of hardened cement paste and leads the creation of new macro materials more compact and more resistant.

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