Construction and Building Materials 47 (2013) 138–145

Contents lists available at SciVerse ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Physico-mechanical characteristics of blended white cement pastes containing thermally activated ultrafine nano clays

A.E. AL-Salami [a,*], M.S. Morsy [b], S. Taha [a], H. Shoukry [b]

[a] Faculty of Science, King Khalid University, Abha, Saudi Arabia
[b] Specialty Units for Safety & Preservation of Structures, College of Engineering, King Saud University, Riyadh, Saudi Arabia

HIGHLIGHTS

- The effect of nano metakaolin on thermo-mechanical properties of cement has been investigated.
- Nano metakaolin increases compressive strength of hardened cement by 50% at 10% replacement ratio.
- Nano metakaolin increases flexural strength of hardened cement by 36% at 10% replacement ratio.
- Nano metakaolin improves the microstructure of the hardened cement.

ARTICLE INFO

Article history:
Received 19 March 2013
Received in revised form 11 May 2013
Accepted 13 May 2013
Available online 2 June 2013

Keywords:
Nanoclay
Compressive strength
Flexural strength
Microstructure
XRD
DSC
SEM
TEM

ABSTRACT

The aim of this work is to produce highly active and amorphous nano sized pozzolana by means of thermal activation of nano clays and to utilize the thermally activated nano clays as additives in white Portland cement pastes (WPC) to improve their thermo mechanical properties. Nano-kaolin was thermally treated at 750 °C for 2 h to get active activated nano-metakaolin (NMK). The effect of thermal activation on the dehydroxylation of the nano-kaolin was determined by using different techniques such as; X-ray diffraction spectroscopy (XRD) and differential thermal analysis (DTA). The surface morphologies of both nano-kaolin and NMK were studied by transmission electron microscopy (TEM).

NMK were incorporated at a rate of 2%, 4%, 6%, 8%, 10%, 12% and 14% by weight of cement. Hardened blended cement pastes were prepared by using water/cement ratio (W/C) of 0.3 by weight and hydrated for various curing ages 3, 7 and 28 days. In order to study the mechanical and physical characteristics of the hardened cement pastes incorporating NMK, different techniques were used such as compressive and flexural strength testing, differential scanning calorimeter (DSC), X-ray diffraction (XRD) and scanning electron microscope (SEM). The experimental results of this study showed that thermal activation of the nano kaolin leads to transformation of the kaolinite to amorphous phase accompanied with the reduction in grain size. The partial replacement of cement by NMK is helpful in enhancing the compressive and flexural strength of cement products. There was an enhancement of compressive strength by about 50% and flexural strength by 36% at 10% nanoclay. The microstructure of the cement blended with NMK was denser, compact and more uniform than that of the conventional cement.

1. Introduction

Pozzolanas are described as siliceous and aluminous materials, which react with lime to produce cementitious compounds [1]. Clays have been used as pozzolanic materials [2]. The mineralogical composition, particle size distribution, and degree of amorphousness are the main factors affecting the pozzolanic activity of clays [3]. Natural materials like volcanic ash where artificial pozzolans such as clay, shales, bauxite waste have to undergo heat treatment before they become pozzolanic. Metakaolin are obtained from thermal-treated natural kaolin mineral deposits, which have excellent pozzolanic properties mainly because of their chemical composition, amorphous structure, and high specific surface [4]. Portland cement (PC) if fully hydrated produces CH of about 28% of its own weight. The CH (portlandite) liberated by the hydration of PC does not make a significant contribution to strength and can be harmful to concrete durability. Its elimination or reduction by reaction with the pozzolana can result in greatly enhanced durability and strength [5]. Different ways have been carried out for improving the cement paste properties in the past such as the addition of supplementary materials into cement and concrete which has been considered by various researchers all over the world for improving the strength of cement paste and concrete, these supplementary materials including natural pozzolans as well as artificial ones such as fly ash and silica fumes.

* Corresponding author. Tel.: +96 65052896.
E-mail address: aeslami@kku.edu.sa (A.E. AL-Salami).

0950-0618/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.conbuildmat.2013.05.011

The aim of this work is to utilize thermally activated nano-clay to develop the mechanical strength of hardened cement. The current research hypotheses is that, due to its ultra fine size the nano clay particles will distribute and react more efficiently and therefore consume more calcium hydroxide in comparison to traditional pozzolans. The well dispersed nano particles will act as centers of nucleation for hydration products, therefore accelerating the hydration process. The ultra fine particles are also expected to fill the voids between the cement grains and causes packing effect thus densify the cement matrix this in turn enhance strength and improve the microstructure.

2. Experimental

2.1. Materials

The materials used in this investigation were white Portland cement WPC (type I) and nano-clay (NC). The nano-clay used is kaolinite clay with Blaine surface area ≈48 m^2/g supplied by Middle East Mining Investments Company (MEMCO), Cairo, Egypt.

The oxide composition of kaolin and white Portland cement is shown in Table 1.

The nano-clay is characterized by large length to thickness aspect ratio, it is especially favorable in matrix reinforcement, and the mineral platelet thickness is only 1–20 nm, although its dimensions in length and width can be measured in hundreds of nanometers, with a majority of platelets in 200–400 nm range after purification.

2.2. Samples preparations and testing

The blended cement paste samples were prepared by partial replacement of cement with different NMK ratios ranging from 2% up to 14%. All pastes were prepared with the same W/C ratio 0.3. Table 2 gives the mix design.

The ingredients were homogenized on an electric mixer to assure complete homogeneity. Two groups of cement samples were casted for tests, the first group was casted as cubes 5 × 5 × 5 cm for compressive strength test, and the second group was casted as prisms 4 × 4 × 16 cm for flexural strength. The molds filled with cement paste were vibrated for one minute to remove any air bubbles. The samples were kept in molds at 100% relative humidity for 24 h, and then cured in water for 28 days. After the designated periods of curing (3, 7 and 28 days) the compressive strength test was carried out on four specimens following the procedure described by ASTM-C109M (2007) [6]. Compressive strength measurements were carried out using five tones German pressing machine with a loading rate of 100 kg/min. The flexural strength test was done in accordance with ASTM-C348 [7]. Differential thermal analysis was conducted using Shimadzu DSC-50 thermal analyzer at a heating rate of 20 °C/min. The samples chamber was purged with nitrogen at a flow rate of 30 cc/min. The scanning electron microscope (FEI-Inspect S) was used for identification of the changes occurred in the microstructure of the formed and/or decomposed phases. The resolution of SEM was 4 nm.

3. Results and discussion

3.1. Thermal activation of nano kaolin

The XRD pattern of the nano kaolin clay was illustrated in Fig. 1.

As clear, the pattern interpretation led to identification of the following mineral phases; *kaolinite*, *illite* and *quartz*. The sharp intense peaks indicate the crystalline nature of nano kaolin. In order to be transformed into amorphous nano metakaolin (NMK), the

Table 1
Chemical composition of starting raw materials (mass%).

Oxide composition (wt.%)	WPC	NC
SiO_2	20.65	47.688
AL_2O_3	3.96	32.432
Fe_2O_3	0.18	0.183
CaO	68.30	0.317
MgO	0.58	0.029
SO_3	2.69	0.039
L.O.I.	3.49	13.47
Na_2O	0.12	0.144
K_2O	0.02	0.042
Total	99.97	99.99

Table 2
Mix design of the test specimens.

Test specimens	WPC (%)	NMK ratio (%)	W/C ratio (%)
Plain	100	0	0.3
M1	98	2	
M2	96	4	
M3	94	6	
M4	92	8	
M5	90	10	
M6	88	12	
M7	86	14	

nano kaolin has to be thermally treated at high temperature for this purpose the DTA analysis was performed for the nano kaolin to specify the decomposition/calcinations temperature as illustrated in Fig. 2.

As evident, the nano kaolin exhibited a peak at 570 °C corresponding to its dehydroxylation (*i.e.* the conversion of kaolinite, $2SiO_2{\cdot}Al_2O_3{\cdot}2H_2O$, into metakaolin.

The nano Kaolin was thermally treated at 750 °C for 2 h to assure complete decomposition and to get active amorphous nano metakaolin (NMK). The ingredients were homogenized on a roller in a porcelain ball mill with four balls for 1 h to assure complete homogeneity.

Fig. 3 shows the XRD pattern of nano metakaolin. (*i.e.* after calcinations at 750 °C for 2 h). The pattern indicated that, the kaolinite phase transformed into amorphous phase.

Fig. 4 shows the TEM images of inactivated and activated nano clay particles. As shown by TEM images, The thermal activation of the nano kaolin leads, by dehydroxylation, to breakdown or partial breakdown of the crystal lattice structure forming a transition phase with high reactivity. Also the thermal activation was accompanied with the reduction in grain size with ill-defined edges which suggesting some amorphous character and result in increasing the pozzolanic reactivity of NMK [8].

3.2. NMK-blended Cement pastes

NMK were incorporated at a rate of 2%, 4%, 6%, 8%, 10%, 12% and 14% by weight of cement. Hardened blended cement pastes were prepared by using water/cement ratio (W/C) of 0.3 by weight and hydrated for various curing ages 3, 7 and 28 days.

3.2.1. Compressive strength

The compressive strength of NMK-modified cement pastes as a function of NMK ratios at different ages of curing is shown in Fig. 5.

It is evident that the compressive strength of the cement pastes increases with NMK loading and a maximum value was reached at about 10%. This represents an increase of nearly 48% at 28 days of curing from the unmodified cement paste; this is a significant enhancement in the compressive strength. The reasons for compressive strength increase of the nano modified cement pastes up to 10% cement replacement of NMK may be due to its high silica content, ultra fineness and specific surface area. Basically, the NMK enhances the strength of hardened cement mortar by two mechanisms. The first mechanism is the packing effect of NMK as filler into interstitial spaces inside the skeleton of hardened microstructure of cement paste and thus increasing its density as well as the strength. The second mechanism is the pozzolanic effect. The thermal treatment of nano-kaolin produces anhydrous alumino-silicate ($Al_2O_3{\cdot}2SiO_2$) which is mainly amorphous material and behaves as a highly reactive artificial pozzolan. The reaction of alumino-silicate in NMK with free lime liberated during cement hydration was leads to addition bond strength and solid volume; resulting in higher strength of hardened cement pastes