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FULL LENGTH ARTICLE

Pozzolanic and hydraulic activity of nano-metakaolin

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KEYWORDS

Nano-metakaolin (NMK);
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Abstract Nano-metakaolin (NMK) was prepared by firing of Nano-kaolin (NK) at different temperatures (750–825 °C) for 2 h. The pozzolanic activities of NMK samples were studied using hydrated lime as an activator. The optimum firing temperature of metakaolin (MK) was established from the results of hydration kinetics and differential scanning calorimetry (DSC) and found to be 750 °C; NMK, thus produced, is designated as NMK(750). This was based on the marked consumption of free calcium hydroxide by NMK fired at 750 °C as well as the highest values of chemically combined water at all ages of hydration. Therefore, NMK(750) was used for partial replacement of OPC and studying the physico–mechanical properties of OPC–NMK blended cement pastes. The optimum substitution of OPC by NMK was found to be 8–10%. This was based on the development of compressive strength of the various hardened OPC–NMK blended cement pastes having different NMK contents (0–16%), where the strength increases with NMK content up to 10% and then decreases. In addition, the SEM micrographs obtained for the hardened OPC (93%)–NMK (7%) blended cement paste displayed the formation of amorphous and microcrystalline CSH which fill the pores leading to a more dense structure with higher hydraulic activity as compared to neat OPC paste.

Introduction

The utilization of calcined clay as a pozzolanic material for mortar and concrete has received considerable attention in recent years. The effect of nano-clay on the mechanical properties and microstructure of Portland cement mortar was investigated [1]. The results showed that the compressive strength of the cement mortars with NMK was higher than the plain cement mortar with the same water/binder ratio.

Metakaolin (MK) which is a pozzolanic material, is a thermally activated aluminosilicate material obtained by firing kaolinite clay within the temperature range of 700–800 °C

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Table 1 Mix composition of OPC–NMK(750) dry mixtures.

Sample	OPC	NMK
Mo	100	0
M2	98	2
M4	96	4
M6	94	6
M8	92	8
M10	90	10
M12	88	12
M14	86	14
M16	84	16

[2,3]. It was concluded that the replacement of cement by 5–20% MK increases the compressive strength for concretes and mortars at 28 days [4]. MK has been widely studied due to its high pozzolanic properties [5,6].

By-pass cement kiln dust (CKD) was used as an alkaline activator for burnt clay (B.C.), obtained by firing Libyan clay at 600, 700 and 800 °C, as an artificial pozzolana [7]. The effect of calcination temperature on Belbeis clay and Sammlout limestone as well as hydration characteristics of calcined products was investigated. Three mixes 50/50, 60/40, 70/30 wt.% clay-limestone were calcined at 700, 800, 900, and 1000 °C for 2 h, then hydrated for up to 90 days. The degree of calcination was investigated from the free lime content and the ignition loss for each mixture. Also, the mineralogical composition of the fired mixes was investigated with the aid of X-ray diffractometry. The results revealed that the free lime of each mix increased up to 800 °C then decreased gradually up to 1000 °C. Mix 60/40 clay-limestone fired at 800 °C shows the presence of $Ca(OH)_2$ with quartz. As the firing temperature increased gehlenite appeared and increased up to 1000 °C with the disappearance of free lime. Mix 50/50 gave the highest hydration

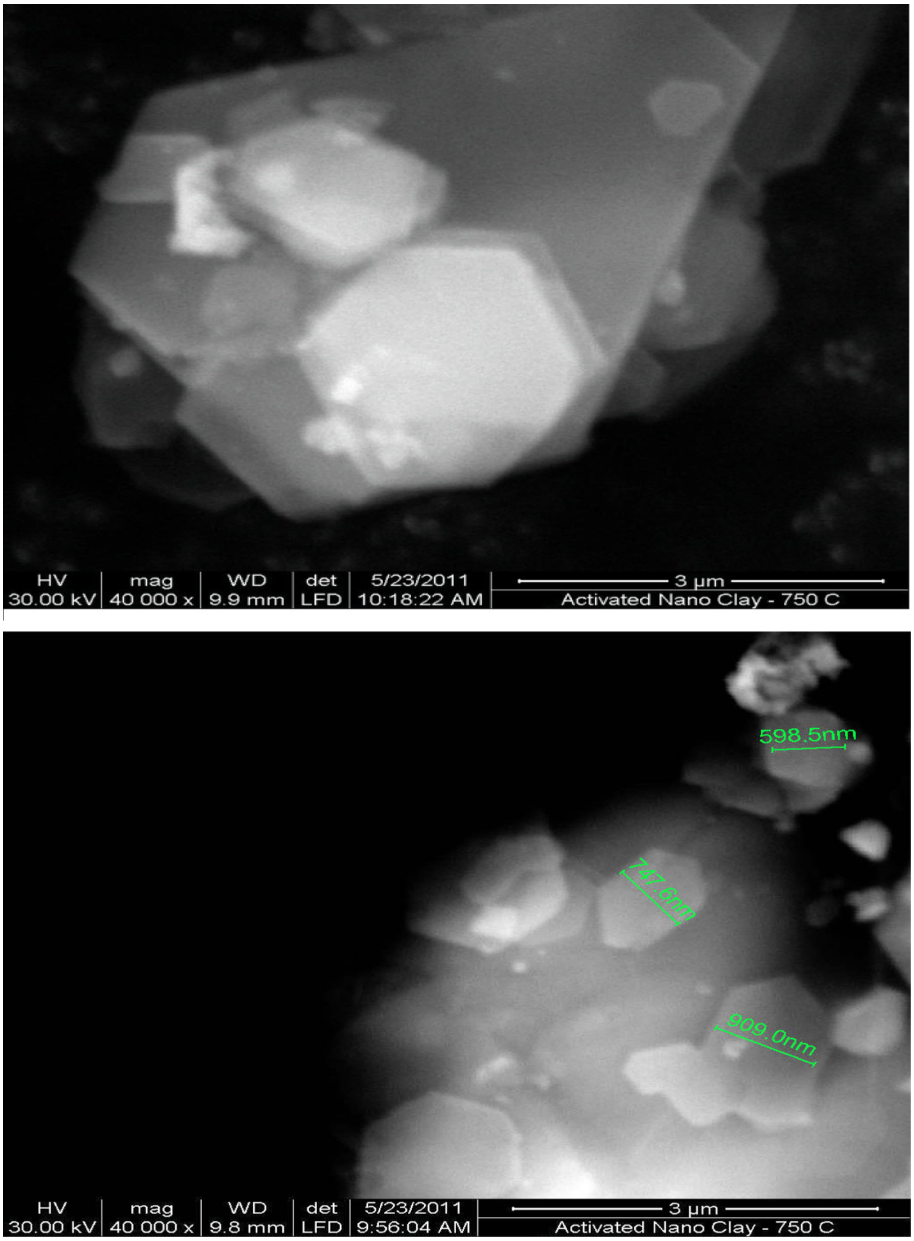

Fig. 1 SEM micrographs of NMK(750).

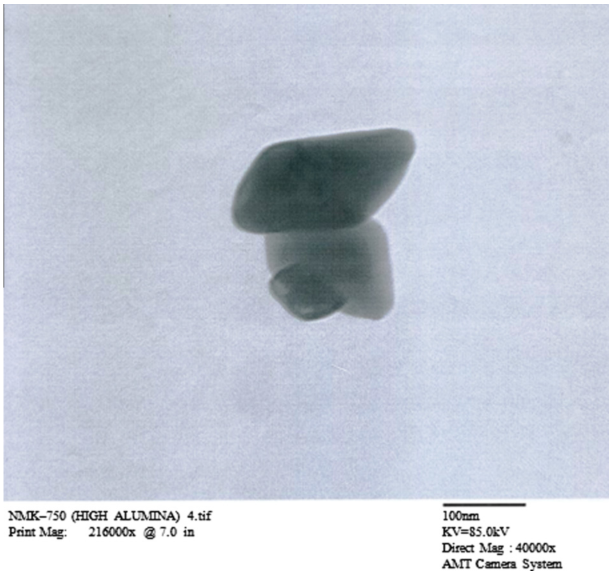

Fig. 2 TEM – micrograph of NMK(750).

kinetics as measured from determination of free lime and combined water contents. As the limestone decreased, the rate of hydration decreased. The suitable firing temperature of the clay-limestone mixes was 800 °C for 2 h [8].

The physicochemical, microstructural and thermal characteristics of pozzolanic cement pastes containing burnt clay were studied by Amin et al. [9]. It was concluded that the pozzolanic cement pastes made of OPC-B.C mixes possess a more dense structure than that of the neat OPC paste. The artificial pozzolana (burnt kaolinite clay) was thermally activated by firing at 850 °C for 2 h. The hydration and pozzolanic reactions in cement pastes with different levels of metakaolin replacement were investigated using differential scanning calorimetry (DSC) [10]. The reaction of pozzolana with the lime liberated during the hydration process of Portland cement modifies some properties of cement and resulting concrete. The change occurring in the phase composition and microstructure of pozzolanic cement pastes containing activated kaolinite clay was investigated [11].

The objective of this investigation is to study the pozzolanic activity of nano-metakaolin using hydrated lime as an activator as well as the effect of the partial replacement of OPC by NMK on the compressive strength of the hardened OPC–NMK pastes.

Materials and experimental

Four samples of artificial pozzolana were prepared by firing of Al_2O_3 – rich nano-kaolin (NK), supplied from Middle East Mining Investment Co. (MEMCO), Egypt, at different temperatures of 750, 775, 800 and 825 °C for 2 h. Pozzolanic activity of nano-metakaolin (NMK) samples was studied on 80% NMK – 20% hydrated lime pastes, mixed using absolute ethanol for 1 h in order to attain complete homogeneity of the mix, (water/solid ratio = 1 by mass) at different ages of hydration from 2 h up to 7 days. The phase composition of the hydrated NMK (80%)–CH (20%) pastes was identified using differential scanning calorimetry (DSC).

The microstructure of NMK, obtained by firing of high grade nano-kaolin (untreated) at 750 °C for 2 h, was studied by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Also, the phase composition of NMK was studied by means of X-ray diffraction (XRD).

Different mixtures from OPC and NMK burnt at 750 °C were prepared by the partial substitution of OPC by different percentages of NMK. These mixes are designated as shown in Table 1.

Each dry mixture was mixed with water for paste preparation using water/cement ratio of 0.30 by weight. Mixing of the fresh paste was continuously done for 3 minutes then moulded into one inch cubic moulds. The pastes were first cured at 100% relative humidity (R.H.) for up to 24 h, then demoulded and cured under water up to 28 days of hydration.

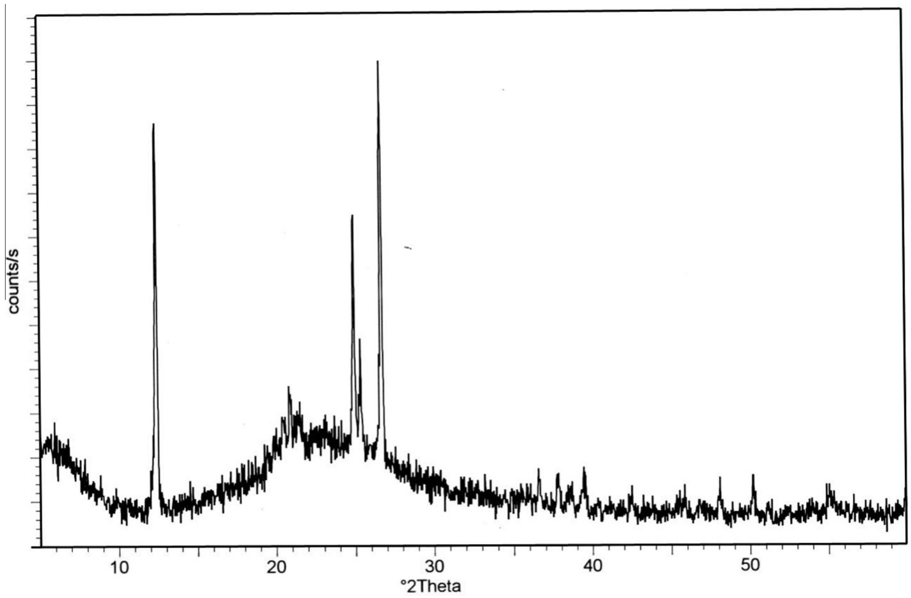

Fig. 3 XRD of NMK(750).

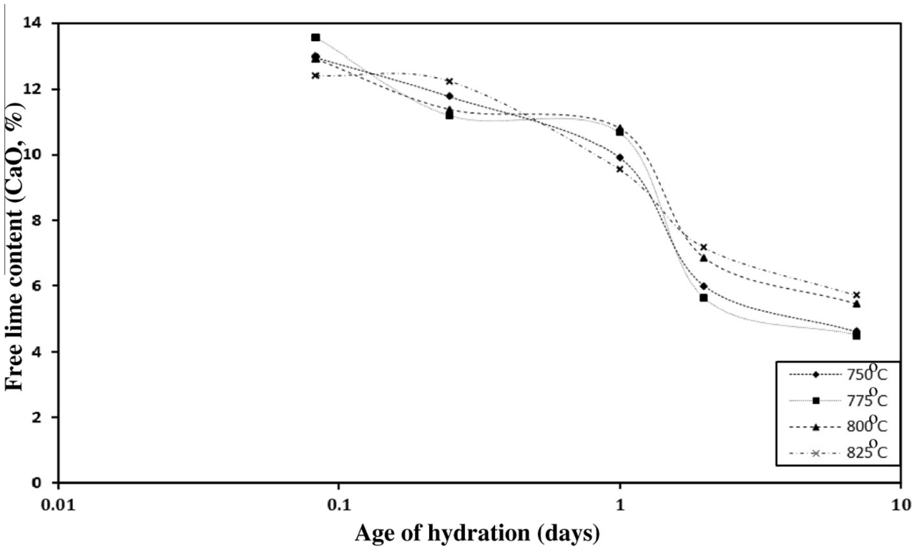

Fig. 4 Free lime contents of NMK (80%)–CH (20%) pastes versus age of hydration using NMK fired at different temperatures (water/solid = 1).

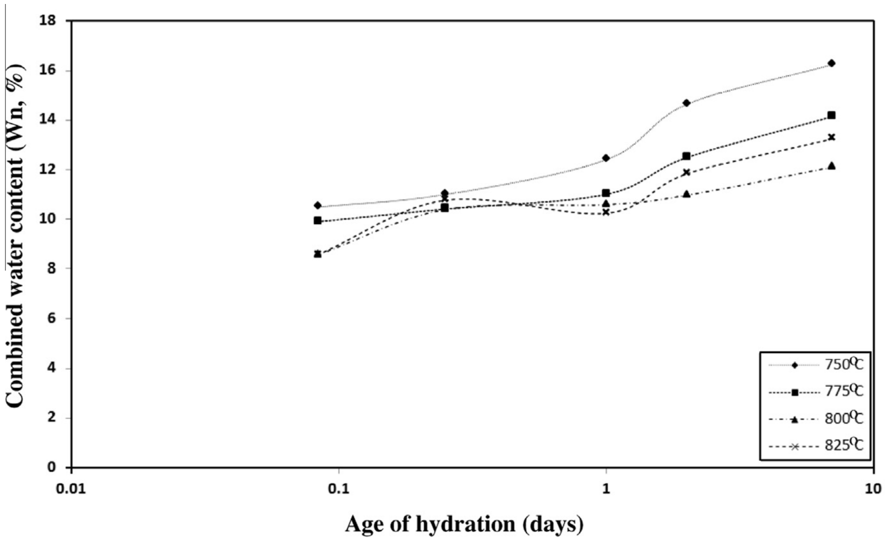

Fig. 5 Combined water contents of NMK (80%)–CH (20%) pastes versus age of hydration using NMK fired at different temperatures (water/solid = 1).

Compressive strength tests were carried out on the hardened OPC–NMK blended cement pastes after 3, 7 and 28 days of hydration.

At each time interval, the hydration of the hardened pozzolanic cement pastes was stopped using the methods described in an earlier publication [12]. The samples were then dried at 100 °C for three hours and maintained in a desiccator until further investigation. Then, free lime and combined (non-evaporable) water contents were determined using the ground dried samples according to the methods reported in earlier investigations [13,14].

The morphology and microstructure of the hardened neat ordinary Portland cement (OPC) paste and OPC–NMK blended cement pastes; made by substitution of OPC by 7% of NMK by using an initial water/solid ratio 0.30; were studied using scanning electron microscopy (SEM).

Results and discussion

Morphology and microstructure of NMK

The microstructure of nano-metakaolin (NMK), obtained by firing of high grade nano-kaolin at 750 °C for 2 h, was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The SEM micrographs shown in Fig. 1 displayed the presence of NMK particles (< 1 μm) having an almost hexagonal shape with varying crystal sizes ranging from 50 to 950 nm with the predominance of NMK particles having sizes of 50–200 nm (Fig. 1). The TEM micrograph shown in Fig. 2 indicated three dispersed particles of NMK having sizes of 50–200 nm. The XRD pattern shown in Fig. 3

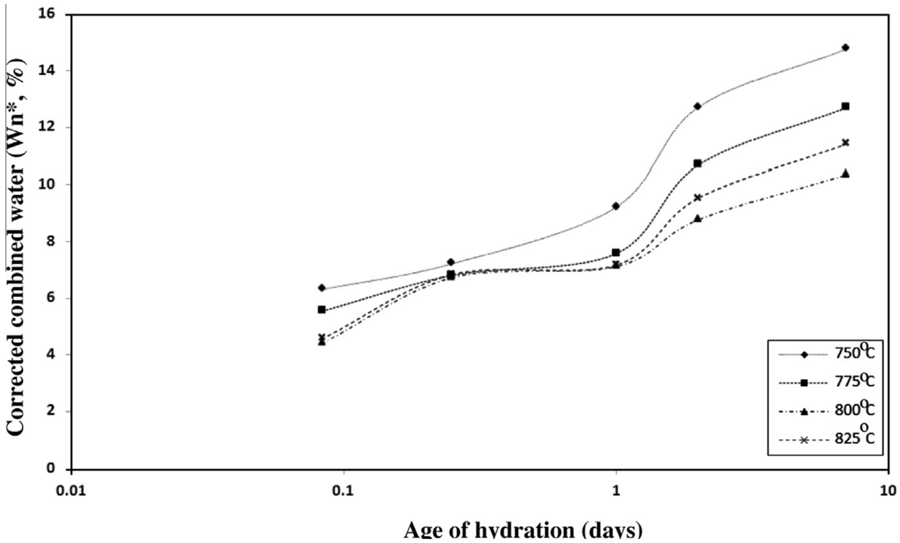

Fig. 6 Combined water contents of NMK (80%)–CH (20%) pastes versus age of hydration using NMK fired at different temperatures as corrected for hydration products (water/solid = 1).

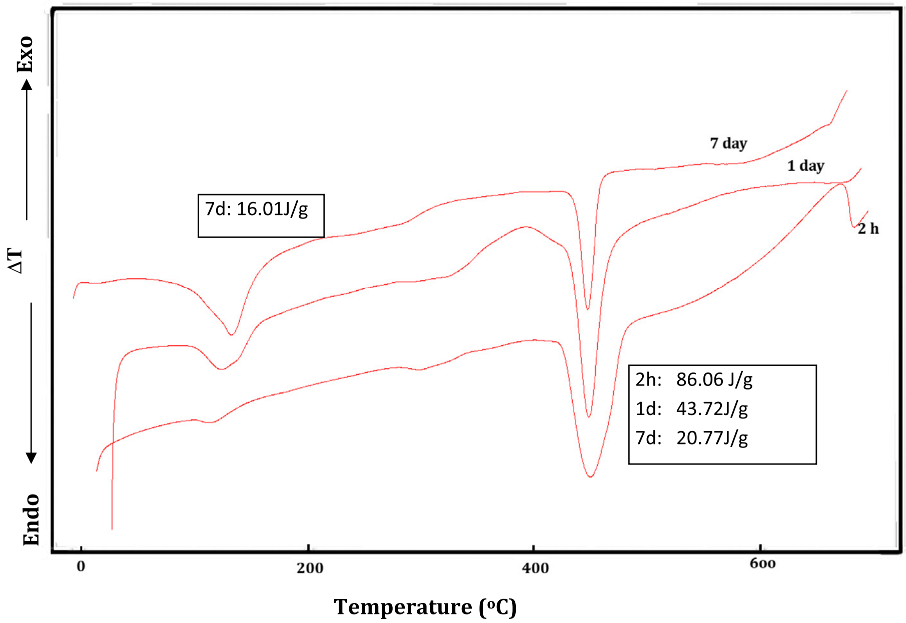

Fig. 7 Pozzolanic activity of NMK, prepared by firing of alumina – rich kaolin at 750 °C, for NMK (80%)–CH (20%) paste (water/solid = 1).

indicates the presence of mainly alumina and silica in the NMK prepared.

Pozzolanic activity of NMK

Kinetics of hydration

Pozzolanic activity of NMK samples, prepared by firing of Al_2O_3 – rich nano-kaolin (NK) at different temperatures of 750, 775, 800 and 825 °C for 2 h, was studied on 80% NMK – 20% hydrated lime pastes (water/solid = 1) from 2 h up to 7 days. The results of hydration kinetics are graphically represented in Figs. 4–6. The results of Figs. 4–6 indicated that NMK prepared by firing at 750 °C has the highest pozzolanic activity as compared to NMK prepared by firing at the other temperatures (775, 800 and 825 °C); therefore it is recommended for the improvement of high performance concrete. The higher reactivity of NMK(750) is due to the relatively lowest values of free calcium hydroxide (CH) contents of NMK(750) –CH samples at almost all ages of hydration as consumed by NMK–CH hydration. In addition, the relatively highest values of combined water contents (Wn & Wn^*) of NMK(750)–CH samples at all ages of hydration give an additional evidence for the optimum firing temperature (750 °C) required for the activation of nano-kaolin to produce NMK with

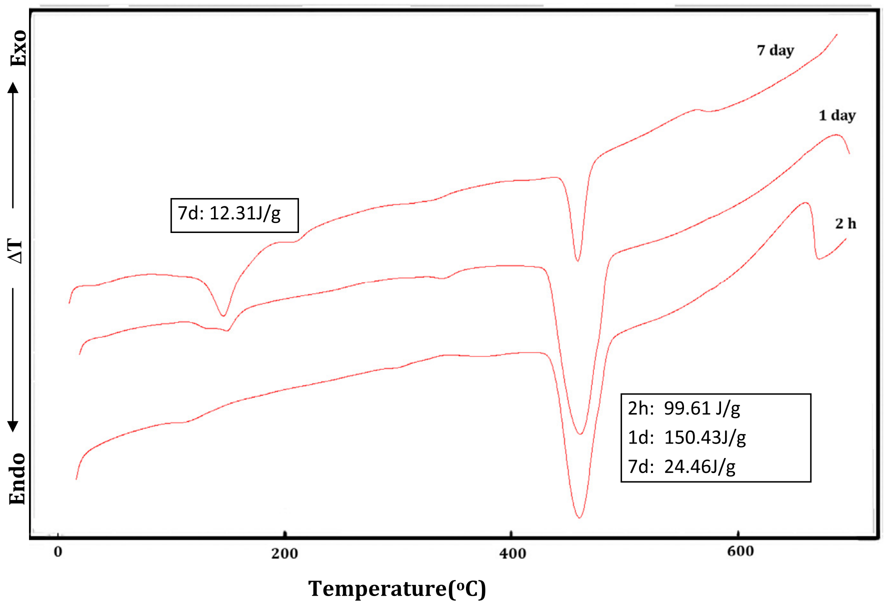

Fig. 8 Pozzolanic activity of NMK, prepared by firing of alumina – rich kaolin at 800 °C, for NMK (80%)–CH (20%) paste (water/solid = 1).

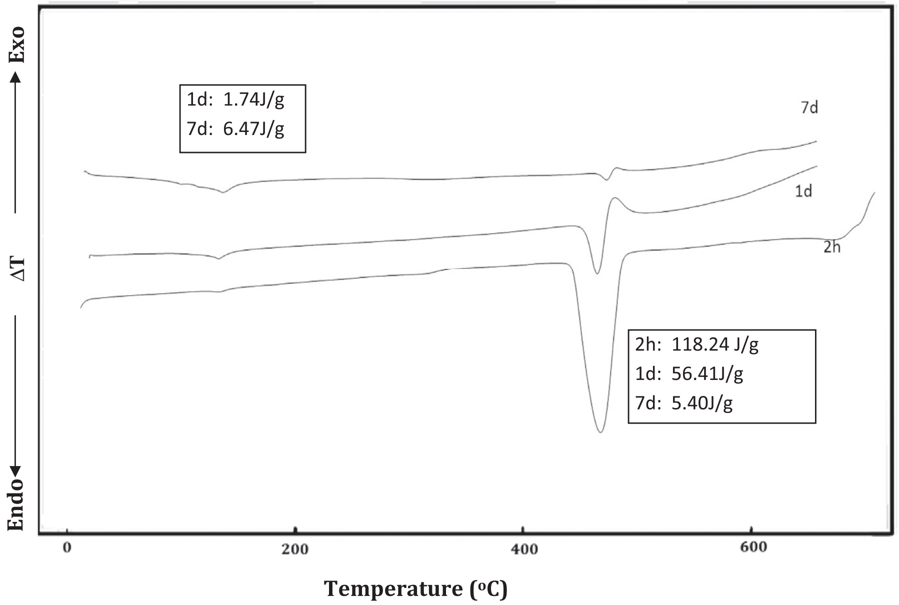

Fig. 9 Pozzolanic activity of NMK, prepared by firing of alumina – rich kaolin at 825 °C, for NMK (80%)–CH (20%) paste (water/solid = 1).

the highest pozzolanic reactivity. The Wn – values represent the chemically combined water contents of all hydration products including the free calcium hydroxide; while the Wn^* – values represent the chemically combined water corrected for the hydration products themselves after subtracting the water content corresponding to the free calcium hydroxide present.

Differential scanning calorimetry (DSC)

The results of DSC studies of hydrated NMK (80%)–CH (20%) pastes made by using NMK fired at 750, 800 and 825 °C are shown in Figs. 7–9, respectively. The results of Figs. 7–9, indicate two main endothermic peak characteristic for calcium silicate hydrates (C–S–H) and calcium hydroxide (CH); these endotherms are located at the temperature ranges of 155–175 °C and 460–490 °C for C–S–H and CH phases, respectively [15].

These DSC thermograms indicated that the reactivity of nano-kaolin (NK) burnt at 750 °C is higher than those burnt at 800 °C and 825 °C. This is clearly understood from the amount of heat required for the decomposition of the C–S–H and CH phases as shown in Table 2.

Evidently, the intensity of the endothermic peak characterizing the free CH phase decreases with age of hydration while the

Table 2 Characteristics of the DSC thermograms for NMK–CH pastes (NMK 750, NMK 800 and NMK 825).

Age	C–S–H phase		CH phase	
	Decomposition temperature (°C)	Heat (J/g)	Decomposition temperature (°C)	Heat (J/g)
NMK (750 °C)–CH				
2 h			455–484	86.06
1 day			460–475	43.72
7 day	155–175	16.01	471–482	20
NMK (800 °C)–CH				
2 h			464–490	99.61
1 day			462–487	150.43
7 day	158–171	12.31	471–482	24.46
NMK(825 °C)–CH				
2 h			460–485	118.24
1 day		1.74	460–480	56.41
7 day	150–170	6.47	475–490	5.4

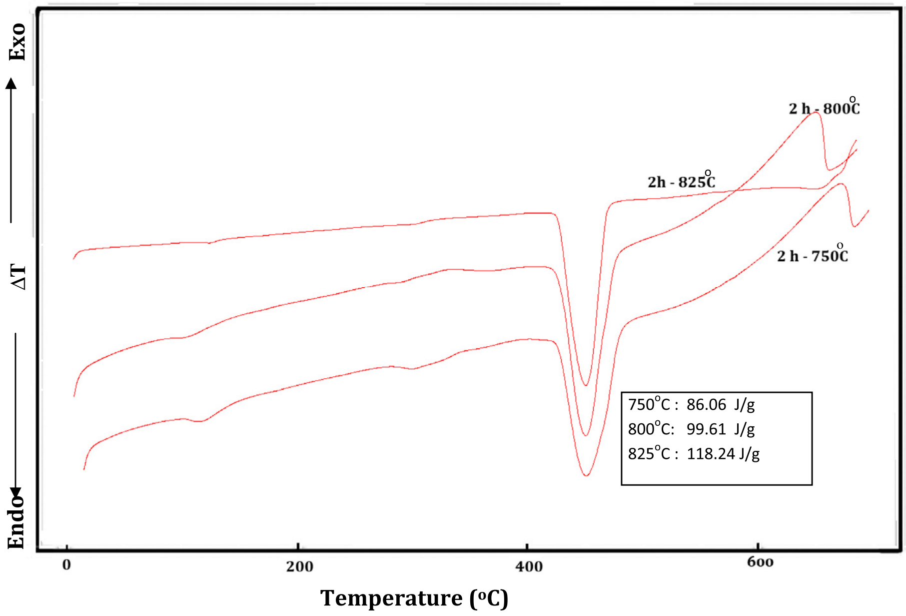

Fig. 10 Hydraulic (pozzolanic) activity of NMK, prepared by firing of alumina – rich nano-kaolin NK at 750, 800 and 825 °C, for NMK (80%)–CH (20%) pastes (water/solid = 1).

intensity of the endothermic peak characterizing the C–S–H phases increases with age of hydration as shown from the DSC thermograms. In addition, the amounts of heat required for the decomposition of CH decreases with the time of hydration as a result of its consumption by NMK hydration; there appeared relatively low heat values for NMK(750)-CH samples as compared to those obtained for NMK(800)–CH and NMK(825)–CH samples. Moreover, the amounts of heat required for the decomposition of C–S–H phases are relatively high for NMK(750)–CH samples as compared to those obtained for NMK(800)–CH and NMK(825)–CH samples. Furthermore, the DSC thermograms of hydrated NMK–CH pastes, prepared from NMK prepared by firing of NK at different temperatures 750, 800 and 825 °C, after 2 h of hydration indicate the relatively high pozzolanic reactivity of NMK(750) sample from early ages of hydration as compared to NMK(800) and NMK(825) samples (Fig. 10).

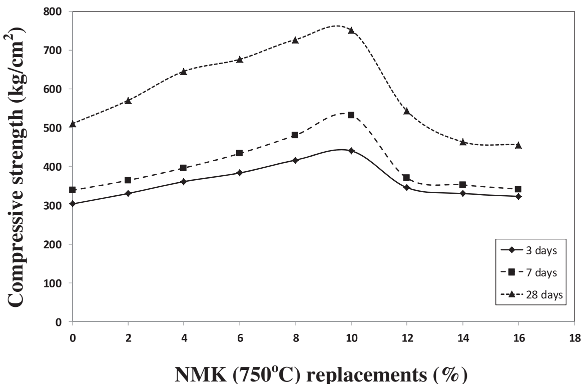

Fig. 11 Compressive strength versus NMK(750) replacements of OPC for the hardened OPC–NMK pastes at different curing ages (water/solid = 0.30).

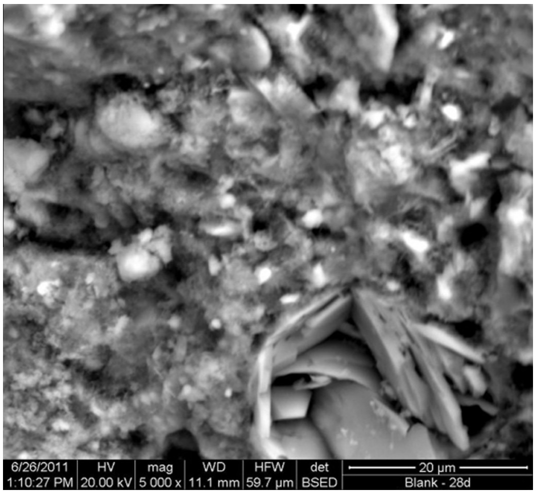

Fig. 12 SEM micrograph of the hardened OPC (Blank) cement paste after 28 days of hydration.

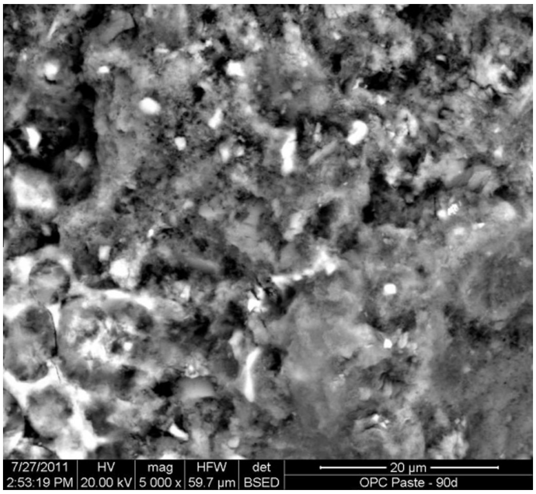

Fig. 13 SEM micrograph of the hardened OPC (Blank) cement paste after 90 days of hydration.

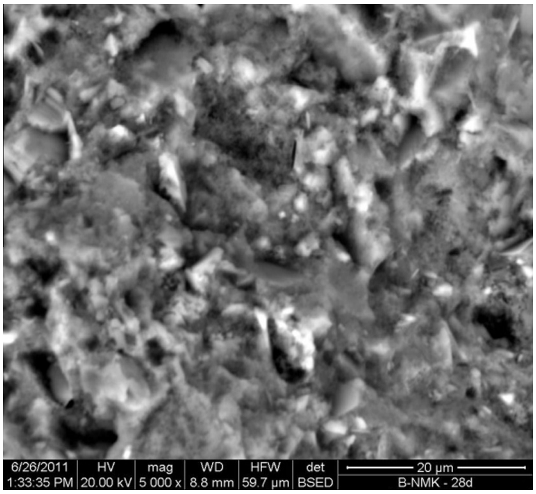

Fig. 14 SEM micrograph of the hardened OPC (B) – NMK paste after 28 days of hydration.

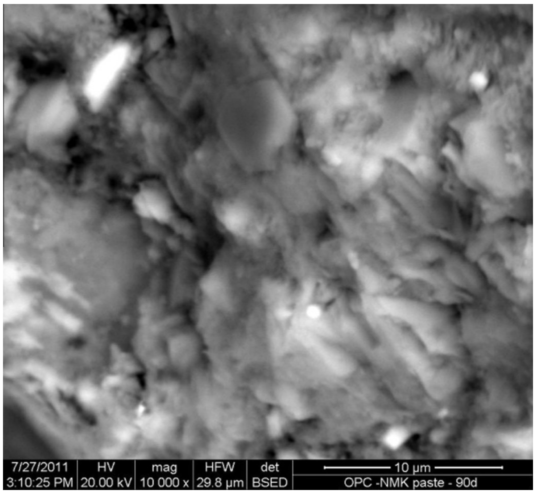

Fig. 15 SEM micrograph of the hardened OPC (B) – NMK paste after 90 days of hydration.

Physico–mechanical properties of the hardened OPC–NMK cement pastes

Compressive strength

Compressive strength tests were carried out on the hardened OPC–NMK blended cement pastes using an initial water/solid ratio of 0.30; made by the partial substitution of OPC by different percentages of NMK(750) of 0%, 2%, 4%, 6%, 8%, 12%, 14% and 16%, after 3, 7 and 28 days of hydration.

The strength results are graphically represented in Fig. 11 as a function of NMK content (%).

Evidently, the compressive strength of the different OPC–NMK pastes increases with the age of hydration up to 28 days; this is due to the progressive hydration which leads to an increase in the amount of hydration products acting as binding centres between the unhydrated parts of cement grains. It was found that, at each hydration age the strength increases with the NMK content of OPC–NMK blended cement pastes up to 10%; this was followed by a reduction of strength values at 12%, 14% and 16% NMK substitutions. The decrease of the compressive strength after 10% is mainly due to the dilution of OPC content which has more hydraulic properties than NMK.

Therefore, the maximum improvement in the compressive strength of the hardened OPC–NMK cement pastes was found at 8–10% NMK as a partial substituent of OPC.

Morphology and microstructure

Morphology and microstructure of the neat OPC paste (designated as blank). The morphology and microstructure of the hardened neat ordinary Portland cement (OPC) paste, as obtained from SEM examination, are shown in Figs. 12 and 13 after 28 and 90 days of hydration, respectively.

Evidently, the SEM micrograph of OPC paste (Blank), prepared using an initial W/C ratio 0.30, after 28 days of hydration displayed the formation of nearly amorphous and micro-crystalline hydration products around the remaining unhydrated parts of cement grains; these hydrates are mainly as calcium silicate hydrates (CSH) as well as calcium hydroxide (Fig. 12). There appeared larger crystalline hydrates, composed of rod – like crystals and large plates, with the presence of some pores in the microstructure.

After 90 days of hydration of OPC paste (Blank), the SEM micrographs showed the presence of fibrous particles and amorphous hydrates of calcium silicate hydrates (CSH) as well as small hexagonal crystals of calcium hydroxide (CH); the presence of some residual pores could also be distinguished in the structure (Fig. 13).

Morphology and microstructure of OPC–NMK blended cement paste (designated as B–NMK or OPC–NMK). The results of SEM examination of OPC–NMK paste; made by substitution of OPC by 7% of NMK by using an initial water/solid ratio 0.30, are shown in Figs. 14 and 15 after 28 and 90 days of hydration, respectively.

After 28 days of hydration, the SEM–micrographs are shown in Fig. 14. Obviously, a more dense structure was observed for the hardened OPC–NMK (designated as B–NMK) paste after 28 days of hydration; almost all hydration products are mainly composed of amorphous and gel – like CSH with lower degrees of crystallinity.

The SEM–micrographs obtained after 90 days of hydration for the hardened OPC–NMK (B–NMK) paste displayed a more dense structure composed mainly of amorphous hydration products which fill a major part of the total pore system of the hardened paste (Fig. 15). Such a structure provides a paste with a stronger hydraulic character and higher strength characteristics.

Conclusion

From the previous results it can be concluded that:

(1) The SEM and TEM of NMK displayed the predominance of NMK particles having sizes of 50–200 nm.
(2) Firing of NK at 750 °C leads to the production of NMK with the highest pozzolanic activity.
(3) The compressive strength values obtained for OPC–NMK blended cement pastes, having different NMK contents (2–16%) indicated that the optimum content of NMK in OPC–NMK blends is 8–10%.
(4) The partial substitution of OPC by 7% NMK leads to the formation of highly amorphous hydration products which fill a major fraction of the entire pore system of the hardened OPC–NMK (designated as B–NMK) paste.
(5) For the neat hardened OPC paste, however, the hydration products are composed of amorphous and micro-crystalline hydrates with the appearance of some residual pores in the structure.
(6) The hardened OPC–NMK paste has a denser structure as compared to the neat OPC paste at the different ages of hydration since the amorphous hydration products possess higher strength characteristics as compared to crystalline hydrates.

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