Effect of Nano-clay on Mechanical Properties and Microstructure of Ordinary Portland Cement Mortar

M. S. Morsy, S. H. Alsayed and M. Aqel

Abstract— **The effect of nano-clay on the mechanical properties and microstructure of Portland cement mortar was investigated. The main objective of this research is to constitute a blended cement mortar with high mechanical properties. The nano-clay used in this investigation was nano-kaolin. The nano-metakaolin (NMK) was prepared by thermal activation of kaolin clay for 2 hours at 750 ^{o}C. The blended cement used in this investigation consists of ordinary Portland cement (OPC) and nano-metakaolin. The OPC was partially substituted by NMK of 0, 2, 4, 6 and 8% by weight of cement. The blended cement mortar was prepared using cement-sand ratio of 1:2 by weight with water-binder ratio (w/b ratio) as 0.5. The fresh mortar pastes were first cured at 100% relative humidity for 24 hours and then cured in water for 28 days. The compressive strength, tensile strength, phase composition and microstructure of mortar were investigated. The results showed that the compressive strength and the tensile strength of the cement mortars with NMK were higher than plain cement mortar with the same w/b ratio. The enhancement in tensile strength was 49%, whereas the enhancement in compressive was 7% at 8% NMK**

Index Terms— Mortar; Nano-Metakaolin; Strength; Phase composition; Microstructure

I. INTRODUCTION

Nano-SiO_2 has been used to increase strength, flexibility and aging resistance of polymers [1]. The effect of nano-SiO_2 on the mechanical properties of high-volume fly ash high-strength concrete (HFAC) has been studied [2-7]. The heat of hydration, strength and pore size distribution was also investigated. A comparison was made between fly ash incorporating nano-SiO_2, fly ash, and nano-SiO_2 alone in terms of weight change after immersion in saturated lime solution. The addition of nano-SiO_2 to high-volume high-strength concrete leads to an increase in strength. The pozzolanic activity of nano-SiO_2 can activate fly ash, causing weight increment. The addition of fly ash causes higher porosity at short curing time, whereas nano-SiO2, which acts as an accelerating additive, produces better compacted structures, even at short curing times [2].

The latest development in concrete technology shows that the use of mineral admixtures such as silica fume (SF) and fly ash (FA) is essential for producing high-performance concrete. In recent years, there has been a growing interest in the use of metakaolin (MK) for this purpose [7–11]. MK which is a valuable pozzolanic material, is a thermally activated alumino-silicate material obtained by calcining kaolin clay within the temperature range of 700–850 oC [7,9,12]. Kaolin from natural sources may be notably impure, even after beneficiation. During heating, it is essential to convert unreactive kaolin to reactive MK. The impurities present in the precursor kaolin may become activated with respect to dissolution in alkaline cement pore fluid. The most important impurities in this context are muscovite and potassium-rich feldspar. Heated and unheated potassium feldspar and muscovite is mixed with Ca(OH)2 and water at ≈22 oC for up to 28 days. Significant alkali release is obtained even from unheated minerals.

MK contains typically SiO2 and Al2O3 and is highly reactive. It has been reported that the replacement of cement by 5–20% MK results in significant increase in compressive strength for high-performance concretes and mortars at 28 days, and particularly at early ages [8–11]. The replacement also resulted in improvement in concrete durability, including the resistance to chloride penetration, freezing and thawing, and deicing salting scaling [8, 10]. The corrosion behavior of steel reinforcement in cement has been studied with partial replacement of cement by MK (5% to 20%). In most cases, mortars and concrete containing material with pozzolanic characteristics have (in normal condition), porosity values equal or superior to that of OPC concrete [13]. This evolution of the porosity depends on the characteristics of pozzolanic materials, such as fineness, mineralogy, loss on ignition, chemical composition and water/binder ratio used [14]. It is well known that the critical factor affecting the performance and durability of concrete structure is the pore size distribution, rather than the total porosity. MK has been studied extensively because of its high pozzolanic properties [15–18]. Owing to its fineness and chemical composition, MK shows a closer resemblance to silica fume porosity but differ than fly ash porosity [19]. Partial replacement of MK by the weight of cement (5–20%) affects pore size causing variation

M. S.. Morsy is a member of Specialty Units for Safety & Preservation of Structures, College of Engineering, King Saud University, SA (corresponding author to provide phone: +966 548198926; fax: +966 1 4673600; e-mail: msmorsy@ yahoo.com).

S. H. Alsayed, is the head of Specialty Units for Safety & Preservation of Structures, College of Engineering, King Saud University, SA (e-mail: shalsayed@ksu.edu.sa).

M. Agel is with the Specialty Units for Safety & Preservation of Structures, College of Engineering, King Saud University, SA (e-mail: maagel@ksu.edu.sa

in micro-structural properties, mechanical properties and corrosion behavior [20].

The presesnt research is thus aimed at investigating the effect of nano-metakaolin (NMK) on mechanical properties and microstructure of Portland cement mortar.

II. EXPERIMENTAL WORK

A. *materials*

The materials used in this study were nano-clay of Blaine surface area ≈ 48 m2/g and average dimension 200*100*20 nm. The ordinary ordinary Portland cement (OPC) supplied by Yamama Cement Company, Saudi Arabia and complies with Saudi Arabian standard (SAS 143/1979).

The oxide composition of kaolin and ordinary Portland cement is shown in Table 1. The morphology of kaolin is presented in Fig. 1. The nano clay used in this investigation is kaolin clay supplied by Middle East Mining Investments Company (MEMCO), Cairo, Egypt. The nano-kaolin was heated for 2 hours at 750°C to give active amorphous NMK.

TABLE 1
CHEMICAL COMPOSITION OF MATERIAL (MASS %)

Oxide Composition	Ordinary Portland Cement	Kaolin
CaO	63.85	0.16
SiO_2	19.83	61.24
Al_2O_3	5.29	20.89
Fe_2O_3	3.53	6.38
MgO	0.52	0.38
SO_3	2.43	0.17
Na_2O	0.21	1.61
K_2O	0.07	0.71
TiO_2	---	0.70
p_2O_5	-----	0.12
Total	95.73	92.36
Ignition loss	2.82	13.62

B. *Mortar Preparation*

The mortar was prepared using cement-sand ratio of 1:2 and water/binder ratio of 0.5%. The blended cement mortar was prepared using ordinary Portland cement that was partially substituted by NMK as illustrated in Table 2. The ingredients were homogenized on an electric mixer to assure complete homogeneity. The mortar pastes were molded into 5 cm cubes for compressive strength and briquette for tensile strength. The molds filled with mortar were vibrated for one minute to remove any air bubbles. The samples were kept in molds at 100% relative humidity for 24 hours, and then cured in water for 28 days.

TABLE 2:
DRY MIX COMPOSITION OF BLENDED CEMENT, (MASS, %)

Mix Designation	OPC	NMK
M0	100	0
M1	98	2
M2	96	4
M3	94	6
M4	92	8

The compressive strength and tensile strength tests were performed on wet specimens. The crushed samples of compressive strength tests were grounded for thermal analyses.

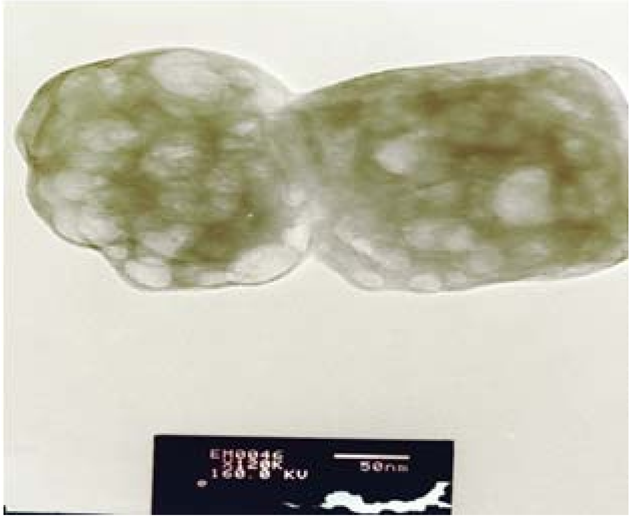


Fig. 1. TEM micrograph of NMK

C. *Testing*

Compressive Strength

The compressive strength tests were performed on 50 mm cube samples using 3000KN compressive machine (Test Plant Toni PACT II) on according to ASTM C-109 [21]. Three samples per batch were tested, and the average strength was reported. The loading rate on the cubes was 0.72 mm/min.

Tensile Strength

The tensile strength tests were performed on mortar briquettes using Zero-Mor model Z2 tensile testing machine according to ASTM C-307 [22]. Three samples per batch were tested and the average strength was reported.

Differential Scanning Calorimeter

Differential thermal analysis was conducted using Shimadzu DSC-50 thermal analyzer at a heating rate of 20oC/min. The samples chamber was purged with nitrogen at a flow rate of 30 cc/min.

Microstructure

The scanning electron microscope (FEL-Spectra) was used for identification of the changes occurred in the microstructure of the formed and/or decomposed phases. The resolution of SEM (FEL-Spectra) was 4 nm.

III. RESULTS AND DISCUSSION

Figure 2 shows the variation of 28 days compressive strength of blended mortar for different NMK ratios. The compressive strength of NMK mortar is found to increase with the increase in NMK ratio from 2 to 8%. The compressive strength of mortar with 8% ratio of NMK was 7% higher than control mortar.

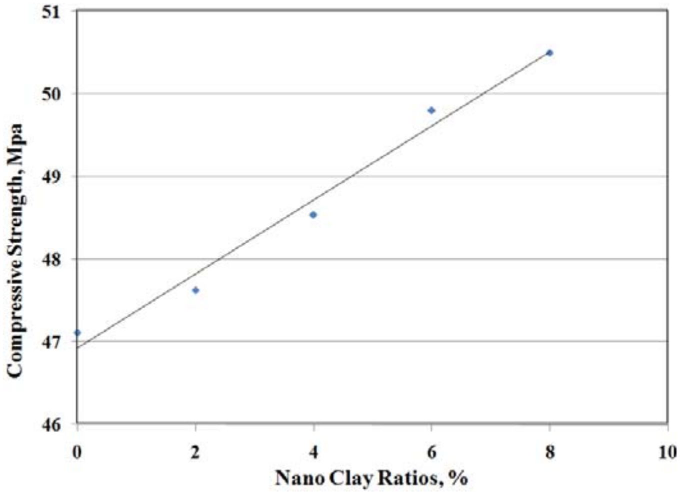


Fig 2. Compressive strength of NMK mortar hydrated for 28 days

The following mathematical model between compressive strength and NMK ratios was found as:

$$y = 0.447 \cdot x + 46.92$$

Where y : is compressive strength of mortar
x : is percentage replacement of NMK

The above equation showed a correlation coefficient R2= 0.983 as shown in Fig. 2. As NMK belongs to mineral admixture, it can improve the macro-structural and mechanical properties of blended cement. The improvement in physical and chemical properties by the addition of NMK explained as follows: ultra-fine particles of NMK filled the voids in cement thus making the microstructure of cement paste denser. The pozzolanic reaction of NMK with free lime released during hydration process produces excess calcium silicate hydrate that gets deposited in pore system thus resulting in the improvement of mechanical properties. The slow increase of compressive strength with increasing NMK loading; may be due to agglomeration of NMK particles around cement grains which lead to retard cement hydration

Figure 3 shows 28 days tensile strength results of blended mortar for different NMK ratios. It is observed that the tensile strength of NMK mortar increases as the NMK ratio increases. Basically, the NMK enhances the tensile 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 mortar 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_2SiO_5) which is mainly amorphous material and behaves as a highly reactive artificial pozzolan. The reaction of alumino-silicate elements in NMK with the lime elements of calcium oxide and hydroxide in cement leads to the addition in bond strength and solid volume; resulting in higher tensile strength of hardened cement paste. The pozzolanic reaction between the calcium hydroxide and amorphous silica is usually slow during a prolonged period of moist curing but it reacts rapidly in alkaline environment such as pore solution of fresh Portland cement mortar. Evidently, the reaction of NMK with portlandite or calcium-hydroxide (CH) is capable to form supplementary calcium-silicate-hydrate similar in composition and structure to those obtained from Portland cement hydration. The addition of NMK can enhance the nucleation of CH. Consequently, NMK can raise the hydrate reaction of cement and produce more hydration crystals, which can be observed from the SEM pictures. Furthermore, the platelet of NMK particles acts as a fiber between hydration products leading to bridging the micro cracks in the matrix and providing resistance to crack propagation and crack opening before being pulled out or stressed to rupture. The following mathematical model between tensile strength and NMK ratios was found as:

$$y = 0.219 \cdot x + 3.606$$

Where y : is indirect tensile strength of mortar
x : is percentage replacement of NMK

The above equation showed a correlation coefficient R2= 0.992.

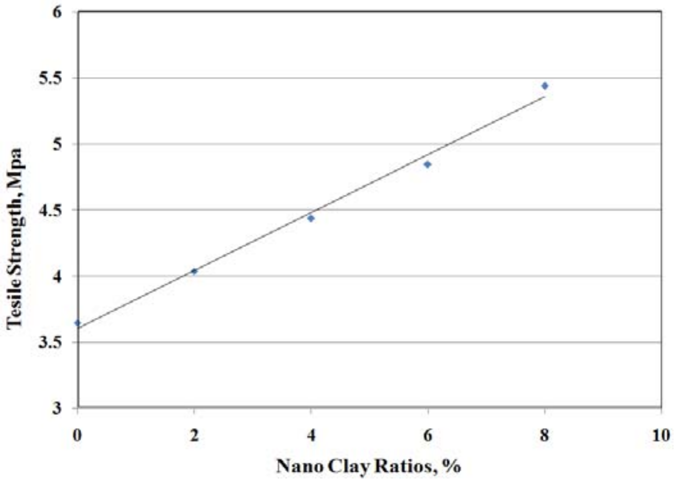


Fig. 3. Tensile strength of NMK mortar hydrated for 28 days

Figure 4 shows the variations of the Differential Scanning Calorimetry (DSC) thermograms of hydrated NMK mortar hydrated for 28 days. Evidently, there were almost five endothermic peaks. The first endothermic peak located at 105-110oC, which is mainly due to the decomposition of calcium silicate hydrates (CSH). The second endothermic peak observed at 160oC represents the decomposition of the gehlenite hydrate (C_2ASH_8). The third endothermic peak located at 350oC, represents the decomposition of hydrogarnet (C_3ASH_6). The fourth endothermic peak appearing at 470oC represents the decomposition of CH. The fifth endothermic peak appeared at 580oC represents the decomposition of quartz. The mean features of the thermograms were characterized by a consumption of the peak area of CH and an increase of the peak area of CSH, C_2ASH_8 and C_3ASH_6 phases as the NMK increases up to 8%. The enthalpy of formed CH during hydration decreases from 30.23 J/g to 14.17 J/g for control and 8% NMK respectively. Moreover, the addition of NMK led to the transformation of CH phases from well crystalline to ill-crystalline. Also the presence of NMK in mortar pastes led to an increment in the enthalpy of CSH from 45.81 J/g to 46.91 J/g, whereas the enthalpy of C2ASH8 increased from 0.289 J/g to 1.68J/g and the enthalpy of C3ASH6 increases from 0.85 J/g to 0.881 J/g. Therefore, the increase of phase's enthalpy indicates the formation of well crystalline phases. Further, crystallizations produced by NMK and CH can fill up the pores and enhance microstructure and mechanical properties of cementitious materials.

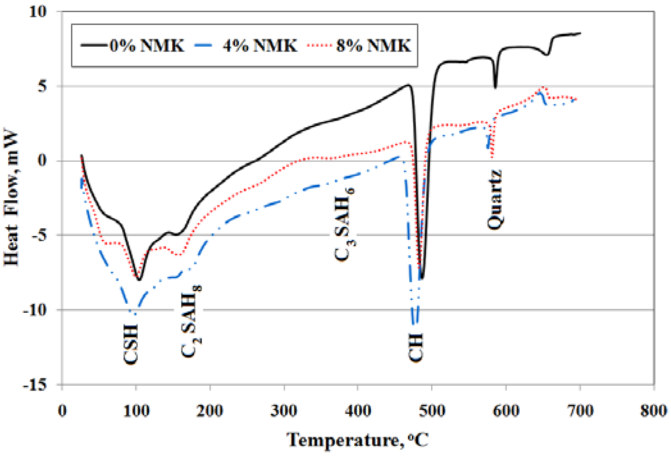
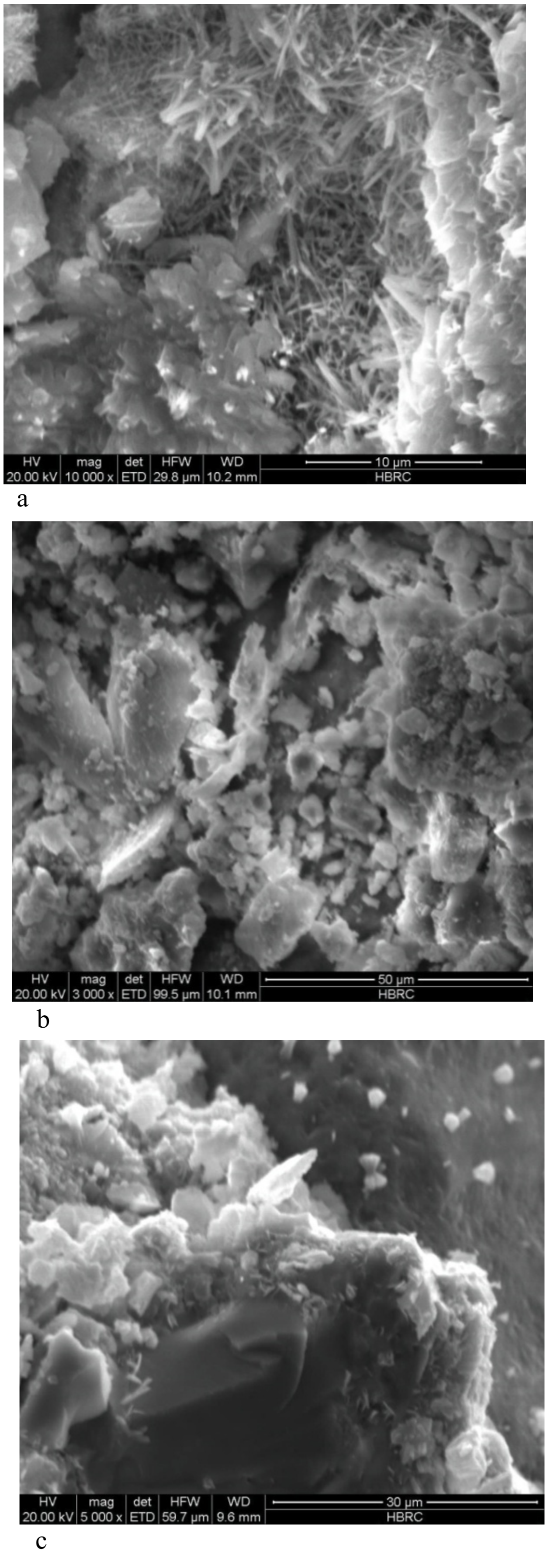


Fig.4. DSC thermograms of NMK mortar hydrated for 28 days

Figure 5 shows the SEM micrographs of NMK cement mortar hydrated for 28 days. The test samples for microstructures were obtained from the central part of mortar specimens. It is clear that, the micrograph displays all hydrated products like CSH, CH and calcium silicate aluminates hydrate. Figure (5-a) shows the microstructure of cement mortar without NMK. It was found that CSH gel existed in the form of 'stand-alone' clusters, lapped and jointed together by many needle hydrates. At the same time, deposit CH crystals were distributed in the cement paste. Figure (5-b and c) shows the microstructures of mixtures M2 and M4, which are of higher strength. They were different compared to plain cement mortar, i.e., the texture of hydrate products was denser and compact. Although the cement mortar pattern of these two mixtures showed some differences, their microstructures were uniform and compact. The microstructure was consistent with increments of 7% and 49% in compressive and tensile strength respectively at 8% NMK replacement. The NMK could improve the microstructure and strength of cement mortar by a mechanism as follows; when a small quantity of the nano-particles were uniformly dispersed in the cement mortar, the hydrate products of cement will deposit on the nano-particles due to their great surface energy during hydration and grow to form conglomeration containing the nano-particles as nucleus. The nano-particles located in the cement mortar as nucleus will further promote and accelerate cement hydration due to their high activity. In the consideration of the nano-particles uniformly disperse situation, a good microstructure could be formed with the uniformly distributed conglomeration. At the same time the aggregates, sands and other particles are considered as centroplasm that acts as skeleton, and gel as transmitter substance.



a

b

c

Fig. 5. SEM micrographs of hydrated NMK mortar hydrated for 28 days, a) Cement mortar containing 0% NMK, b) Cement mortar containing 4% NMK, c) Cement mortar containing 8 % NMK

The binding force between centroplasm and transmitter substance has an important effect on the strength of concrete. Innumerable nano-particles distributed in cement paste as 'sub-centroplasm' can tightly bond with the hydrated products around the transition zone between the nanoparticle and hydrate products. On the other hand, the nano-particles among the hydrate products prevent the crystal from growing, such as CH and AFm, and such fine crystals are favorable for the strength of cement paste. Also, the nano-particles fill pores to increase the strength as silica fume does. However, when the nano-particles cannot be well dispersed, as the case of extensive nano-particles content, the aggregating nano-particles create weak zone in the form of voids, consequently, the homogeneous hydrate microstructure could not be formed, and low strength will be expected. On the other hand, as the NMK can participate in the hydration process to generate CSH through reacting with CH, so the strength increases with the content of NMK increases even when small quantity of NMK is not very well dispersed. The strength of the cement mortars with nano-particles has an improvement, as demonstrated in this study. Furthermore, it can be predicted that the strengthening effect of nano-particles would be further enhanced in concrete because the nano-particles improve not only the cement paste, but also the interface between paste and aggregates [23].

IV. CONCLUSIONS

Based on the experimental studies presented in this paper, the following conclusions can be drawn:

- Compressive and tensile strength of the cement mortars with NMK is higher than that of the plain cement mortar with the same w/b ratio.
- The enhancement of tensile strength was 49% above control mortar; whereas the enhancement of compressive strength was 7% at 8% NMK replacement.
- The NMK in cement mortar acts as a nano-fiber due to its morphology.
- The SEM observations confirmed that the NMK was not only acting as filler, but also as an activator to promote hydration process.

REFERENCES

[1] Q. Zhang, J. Wang and S. Cheng, Study on the CPE/Nano SiO2 blends, J. Funct. Polym. 15 (3), 2002, pp. 271–275.

[2] G. Li, Properties of high-volume fly ash concrete incorporating nano-SiO2, Cem. Concr. Res. 34, 2004, pp. 1043–1049.

[3] JA. Kostuch, V. Walters, TR. Jones, High performance concretes incorporating metakaolin: a review. In: Dhir RK, Jones MR, editors. Concrete 2000. London, UK: E&FN Spon; 1993. pp. 1799–1811.

[4] M. S. Morsy and H. Aglan, Development and Characterization of Nanostructured-Perlite-Cementitious Surface Compounds, Journal of Materials Science, 42(24), 2007, pp. 10196-10202.

[5] M. S. Morsy., H. Aglan and M. M. Abd El Razek, Nanostructured Zonolite-Cementitious Surface Compounds for Thermal Insulation, Construction and Building Material Journal, 23, 2009, pp. 515-521.

[6] H. Aglan,. M. S. Morsy, A. Allie and F. Fouad, Evaluation of fiber reinforced nanostructured perlite-cementitious surface compounds for building skin applications, Construction and Building Material Journal, 23, 2009, pp. 138-145.

[7] S. S. Shebl, L. Allie, M. S. Morsy, H. A. Aglan, Mechanical behavior of activated nano silicate filled cement binders, J Mater Sci, 2009, 44, pp.1600–1606

[8] MA Caldarone, KA Gruber, RG Burg. High-reactivity metakaolin: a new generation mineral admixture. Concr Int 1994;16(November), pp. 37–40.

[9] BB Sabir, S Wild, JM Khatib. on the workability and strength development of metakaolin concrete. In: Dhir RK, Dyer TD, editors. Concrete for Environmental Enhancement and Protection. London, UK: E&FN Spon; 1996, pp. 651–6.

[10] MH. Zhang, VM. Malhotra Characteristics of a thermally activated alumino-silicate pozzolanic material and its use in concrete. Cem Concr Res 1995;25(8), pp. 1713-25.

[11] F. Curcio, BA Deangelis, S. Pagliolico, Metakaolin as a pozzolanic microfiller for high-performance mortars. Cem Concr Res 1998;28(6), pp. 803–9.

[12] J. Ambroise, S. Maximillen, J. Pera, Properties of metakaolin blended cements. Adv Cem Mater 1994;1(4), pp. 161-8.

[13] F. Massazza, G. Oberti, Durability of pozzolanic cements and Italian experience in mass concrete. In: Malhotra VM, editor. Second inter conference on durability and concrete, Montreal, Canada, vol. II. Montreal, Canada: American Concrete Institute; 1991. pp. 1259-83.

[14] O. Gjorv. High strength concrete. In: Malhotra VM, editor. Advances in concrete technology. Montreal, Canada: American Concrete Institute; 1992. pp. 21–77.

[15] PS Silva, FP Glasser, Phase relation in the system CaO–Al2O3–SiO2–H2O relevant to MK–lime hydration. Cem Concr Res 1993;23, pp. 627-39.

[16] NJ. Coleman, CL. Page. Aspects of the pore solution chemistry of hydrated cement pastes containing MK. Cem Concr Res 1997;27(1), pp. 147-54.

[17] S. Wild, JM Khabit, A Jones, Relative strength pozzolanic activity and cement hydration in superplasticised MK concrete. Cem Concr Res 1996;26(10), pp. 1537-44

[18] J. Bai, S. Wild, BB Sabir, JM Kinuthin, Workability of concrete in incorporating PFA and MK. Mag Concr Res 1999;51(3), pp. 207-26.

[19] M Frı´as, MI Sa´nchez de Rojas, JG Cabrera, The effect that the pozzolanic reaction of MK has on the heat evolution in MK–cement mortar. Cem Concr Res 2000;30(2), pp. 209-16.

[20] R. Siddique and J. Klaus, " Influence of metakaolin on properties of mortar and concrete:A review", Applied Clay Science, 2009, 43(3-4), pp. 392-400.

[21] ASTM C 109/ C 109M-02, Standard Test Method for Compressive Strength of Hydraulic Cement mortars (Using 2-in. or [50-mm] Cube Specimens)

[22] ASTM C 107-03, Standard Test Method for Tensile Strength of Chemical-Resistant Mortar, Grouts, and Monolithic Surfacings

[23] K. Liao, P. Chang Y. Peng, and C. Yang, "A study on Characteristics of Interfacial Transition Zone in Concrete" Cem. Concr. Res. 34, 977 (2004).