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Mechanical and Durability Performance of Nano Metakaolin Blended Cement Mortars

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ABSTRACT

Although works have been carried out to explore the influence of adding Kaolin (K), silica fume (SF) or fly ash (FA) in micro size and nano metakaolin (NMK) mixture on the main characteristics of blended cement mortar as partial replacement of cement by weight separately or combination of nano-micro mixture. The synergistic role of nano-micro mixture was rarely studied on the elevated heat temperatures and sulphate resistance performance of blended cement mortars specially for an economic nano material as NMK. This research is to investigate the efficiency of adding NMK, K, SF or FA mixture, as cement partial replacement added separately with different percentages, on durability properties of blended cement mortar. Moreover, studding the combination of NMK with other SCMs as SF and FA with different percentage of cement replacement by weight was studied on some durability characteristics related to elevated heat and sulphate protection. In addition, the influence of adding kaolin in micro size without dispersion and NMK with dispersion to mixture (size effect) was also studied on some durability characteristics. Mortar specimens were tested at normal temperature and tested after 2-hour exposure at higher elevated temperatures of (200, 400, 600 and 800^{o}C) at 28 days age. Based on the maximum mortar compressive strength for (K, NMK, SF, FA) added separately %5 NMK was the optimum replacement ratio and with combination of micro and nano size 10%NMK+5% SF were the optimum cement replacement ratios, while for elevated heat resistance of blended cement mortars were remarkably enhanced by using 10% NMK+5%FA and 10%NMK+10%FA mixtures for the reduction in compressive strength values at 800^{o}C, and for sulphate resistance using 10%NMK+15%FA mixture instead of using optimum K and NMK cement replacement ratio. Summing up, Adding the optimum dose of nano-particles helped to produce a denser microstructure and more durable matrix. Finally, the results showed that the compressive strength of the cement mortars with NMK at normal or elevated heat were higher than plain cement mortar with the same w/b ratio. At 5% NMK, the enhancement in compressive strength was 66.66% at 60 days age, while the enhancement in compressive was 22.74% at 200^{o}C.

Keywords: Kaolin, Nano Metakaolin, Pozzolanic materials, Elevated heat temperature, Sulphate resistance, Microstructure.

INTRODUCTION

The research in nanomaterials has revealed a lot of possibilities in varied industries and scientific endeavors [1]. As Concrete is probably the most extensively used construction material in the world [2], it's a challenge for engineers to improve its performance. The mechanical performance of cementitious structures depends on phenomena that occur at the micro and the nano-scale.

The potential benefits of using Nanomaterials over other SCMs are their high reactivity, the need for smaller amounts, resulting in cement replacement; and cost effectiveness [3]. Nanomaterials have been widely used in the development of cement paste and mortar with improved mechanical, physical, structural and durability characteristics. Nano materials with various morphologies have been widely investigated for enhancing cement and concrete composites including spherical materials (e.g., nano-SiO_2, nano-TiO_2, nano-Al_2O_3, nano-$CaCO_3$, nano-Fe_2O_3, nano-Fe_3O_4, etc.) or as nanotubes or fibers (e.g., carbon nanotubes and carbon nanofibers, respec-tively) or as nano sheets (e.g., nano-clay) or as nano platelets (e.g., nano graphene oxide) [4].

Supplementary cementing materials (SCMs) in micro and nano sizes have become an integral part of high strength and high performance concrete mix design. The most common cementitious materials that are used as concrete constituents, in addition to Portland cement, are fly ash (FA), ground granulated blast furnace slag, silica fume (SF), rice husk ash as well as metakaolin (MK) [5].

Pozzolans in micro or nano size chemically react with calcium hydroxide liberated during hydration to form cementitious compounds. The large surface area of nanoparticles and their abundance because of their small size can facilitate the chemical reactions necessary to produce a dense cement matrix with more C-S-H (calcium-silicatehydrate) in concrete and less calcium hydroxide as well as block water penetration and therefore lead to improvements in durability including the resistance to chloride penetration, freezing and thawing, and deicing salting scaling [6]. This, in turn, will enhance the overall concrete performance while also reducing cement consumption [6], [7] & [8].

Summing up, Incorporation of nanomaterials into the matrix to improve concrete mechanical properties has emerged as a promising research field [9]. The huge specific surface area of nano-size silica particles enhances their chemical activity, as pozzolanic material [10]. Nanoparticles can also strengthen the interfacial transition zone (ITZ) between the cement paste and the aggregate, which would lead to improved strength and permeability [7]. Recent studies reported that nano-scale materials con-taining an amorphous silica (SiO_2) such as colloidal nano-silica (CS), nano metakaolin (NMK) and nanostructured slag which char-acterized with high surface areas, are unstable and tends to react faster when used as an additive in the cementitious matrix [11-13].

Kaolin is type of clay having micro size in its nature; it means that there is a locally natural too cheap source for nano metakaolin [5]. Nano metakaolin (NMK) which is a valuable pozzolanic material, is a thermally activated alumino-silicate material obtained by calcining kaolin at 800ºC. NMK contains typically SiO_2 and Al_2O_3 and is highly reactive. Kaolin from natural sources may be notably impure, even after beneficiation [14].

The proposed nano material (NMK) is characterized by various advantages: (i) economic – this material is very cheap (cost effective), (ii) availability – this material is locally available, and (iii) unique physical properties (e.g., large surface area and platelet-like morphology which makes it favorable to use in cementitious matrix reinforcement [15].

El-Gamal et al. 2015 [16] used kaolin was supplied from Middle East Mineralogical (MEMCO), Egypt. The NK was fired at 750ºC for 3 h to obtain NMK with a Blaine surface area of $1.8*10^4$ cm^2 g^{-1}. Morsy et al. 2014 [17] used kaolin with average dimensions 200 nm *100 nm * 10 nm and Blaine surface area of ≅48 m^2 g^{-1}. The raw kaolin consists of kaolinite, illite, and quartz as major mineral phases, whereas NMK contains only illite and quartz.

Using high cement replacement ratio of the ultra high surface area of nano particles may lead to particles agglomeration. Accordingly, the recommended nano replacement ratio is not more than 4%, otherwise either reduction in the cementitious material overall performance is expected or special dispersion processes need to be used. Another drawback, of using high ratio of nanoparticles in concrete, is that distributing huge surface area can lead to plastic shrinkage cracks [18,19]. In order to provide efficient use of the nano and micro silica advantages and to avoid some drawbacks, Sakshi [20] suggested that using optimum ratio of combined micro and nano particles may create more strong and durable cementitious materials, and this experimental work studied deeply.

Efficiency of mixing kaolin was less explored, in literature, compared to NMK separately or NMK combined with SF or FA for the direct durability performance of concrete (e.g. elevated heat resistance).

Morsy, M. S. et al 2018 [15] concluded that enhancements for NMK were about 24% compared with the unexfoliated MK blended mortar and 54% compared with the plain ordinary mortar. The

BET analysis confirmed that; NMK provides significant refinement in pore structure of blended mortar. The phase composition analysis by TGA and SEM indicate that NMK acts not only as a filler to improve the packing inside the cementitious matrix, but also as an activator to promote hydration and pozzolanic reactions. When MK reacts with calcium hydroxide released during cement hydration, the main phases produced are CSH, C_2ASH_8 and C_4AH_{13} which contribute to strength [21]. The inclusion of nano metakaolin (NMK) into cement paste and mortar significantly enhances the compressive and flexural strength and resulted in quite dense, compact and uniform microstructure [22,23].
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 [7] 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 [24-27]. Partial replacement of MK by the weight of cement (5–20%) affects pore size causing variation in micro-structural properties, mechanical properties and corrosion behavior [23]. Justice and Kurtis 2007 [28] reported that increased compressive strength by 15-50% (depending on MK type, w/c and age) as compared to control mixture was measured for concretes produced with MK. Also, maximum increase in compressive strength was at 15% replacement level.
Zaki and Khalil 2012 [29] concluded that the application of nanometakaolin particles with newly developed super plasticizer improves the workability and strength of high performance concrete since NMK interpenetrates polymer network, and causes increase in compressive strength of 36,39 and 20 % at 3, 7 and 28 days respectively.
In order to provide efficient use of NMK particles advantages and to avoid some drawbacks, [17] suggested that using optimum ratio of combined micro SF or FA with NMK particles may create more strong and durable blended cement mortars.
Sensitivity study was initially implemented to evaluate the efficiency of the available micro and nanometakolin particles mixing techniques. Two different techniques were used for mixing, first method using Kaolin as an additives without dispersion as easy economic solution using it in field directly in mixture, and the second method by dispersion of NMK in ultra sonic cleaner then added to mixture after dispersion immediately to avoid the reduction in blended cement mortar strength. Initial study was performed to obtain the optimum cement replacement ratio, of either K, NMK, SF, FA, NMK+SF and NMK+FA particles based on the mortar maximum compressive strength up to 120 days. To get the optimum mixing ratio for blended cement mortars, suggesting replacement ratios for separate replacement ratios as (2.5,5,7.5,10,12.5,15) for each K and NMK. While to get the optimum ratios of incorporating nano- micro particles, suggesting replacement ratios of NMK, SF and FA are (5% or 10%) for each.
These replacement ratios were commonly suggested in literature to enhance the cementitious material's strength and durability performances[24,30]. To assure no conflict occurred due to changing total replacement ratios for mixtures, the total replacement ratio of using NMK was kept equal to the optimum measured SF and FA replacement ratios. Durability influence of the proposed for all mixtures combined mixtures of NMK+SF and NMK+FA were compared with the cases of using either the optimum separate cement replacement ratios of K, NMK, SF and FA at same percentages of replacement (15% and 10%). Elevated heat temperatures resistance and sulphate resistance were investigated, as both representing main durability performances of blended cementitious mortars.
The aim of study has been extended also to investigate the influence of the prepared NMK on the mechanical, durability and microstructural characteristics of hardened blended cement mortars. In this research work, durability influence of using NMK mixture in both micro and nano size separately, as cement partial replacement, and also combination of micro and nano size as NMK +SF or NMK+FA mixtures were investigated. Mortar sulphate resistance and elevated heat temperature; were the targeted durability performances.

Experimental

Materials

Cement (CEM I 42.5 N) - obtained by the SWEDY company and complies with Egyptian standard specification (ESS 4756-1) [31] -was used for all blended cement mortar specimens and K, NMK, SF and FA particles were used as pozzolanic materials. The fine aggregate was natural siliceous with a maximum grain size of 1.4 mm, specific gravity of 2.5. and SiO_2 content of the sand was 98% at minimum. Natural kaolin clay was used in this investigation. The NMK (nano-clay) used is kaolinite clay with Blaine surface area ≅48 m^2/g the average dimension 100 ×50 × 10 nm brought from (Sinai desert-Egypt) supplied by Middle East Mining Investments Company (MEMCO), Cairo, Egypt. The chemical structure input in the manufacture of NMK is ($Al_2Si_2O_7$). The oxide composition of ordinary Portland cement, kaolin and nanometakaolin (NMK) are summarized in Table 1.
For all mixes constant HAWRA dosage was used to achieve fairly comparison. The limits of HAWRA dosage mentioned in the material data sheet (0.6–2.5%) by weight of cement), were respected during the workability study. Sikament-163 M, complying with ASTM C494 type (F) [32], was used as Superplasticizer (i.e. high water reducer) to control workability of cementious material specimens with constant ratio1.25% of water/binder weight.
Tap water was used for both mixing and curing the test specimens according to the requirement of the (ECP 203-2007) [33]. Hydrated lime, which meets the specifications of ASTM C207 [34] type N was used as a saturated soluble solution for curing the specimens (saturated lime water (LW). The soluble was left for enough time to deposit, and then the clear water of LW was used. The prepared mixtures had pH value as 12.77 and the corresponding measured total dissolved salts TDS value was 2200 ppm.

Table 1: Chemical Composition of Starting Raw Materials (Mass %).

Component	Weight Percentage		
	CEM I	Kaolin (before calcination)	NMK (after calcination) [16]
Silicon (SiO_2)	20.7	49.86	57.53
Aluminum (Al_2O_3)	4.69	34.10	38.63
Iron (Fe_2O_3)	3.63	0.30	0.35
Manganese (Mn_2O_3)	0	0.01	0.01
Calcium (CaO)	63.3	0.09	0.11
Magnesium (MgO)	1.63	0.26	0.30
Phosphorus (P_2O_3)	0	0.35	0.41
Potassium (K_2O)	0.87	0.02	0.03
Sodium (Na_2O)	0.21	0.03	0.01
Titanium (TiO_2)	0	0.88	1.02
Sulphur (SO_3)	3.25	0.59	0.56
Loss on Ignition (LOI)	1.72	13.44	0.93

Kaolin Activation and Dispersion

In order to get active amorphous metakaolin, The kaolin has to be thermally treated at high temperatures. The kaolin was thermally treated at 800°C for 2hrs to attain complete dehydroxylation and to get active nanometakaolin (NMK). As reported in previous studies, the clay minerals have strong tendency to form stacks owing to vander walls' forces. furthermore, the enhanced performance of nano modified composites could only be obtained if good dispersion is attained. To achieve nanoscale dispersion, delamination and, thereby exfoliation of these mineral platelets is prerequisite.

Dispersant solution was prepared by dissolving metakaolin powder (differs for each mix) in half water mixing for all mixes was added to the dispersant solution and stirred to insure homogenity of NMK in ultrasonic sonicator for 15 mins. (Sonics VCX500 with 500 Watt ultrasonic processor) -as shown in Fig.1 just before adding the suspension to mortar mixer directly before mixing.

Fig.1 The used Ultra sonic Cleaner for dispersing nano particles in mixing water

Mortar preparation and identification

The mortar was prepared using cement-sand weight ratio of 1:2.75 and water/binder ratio of 0.4. and HAWRA with ratio1.25%. Constant ratios were used for all mixtures to achieve fair comparison. A rotary mixer was used for mixing.The ingredients were homogenized on an electric mixer to assure complete homogeneity.The blended cement mortar was prepared using ordinary Portland cement that was partially substituted pozzolanic materials in nano or micro size (separately or combined of two pozzolanic material) as illustrated in Table .2. Due to the great surface area of the used kaolin clay, the authors decided to incorporate it with small amounts to avoid the inter-particles fusion or agglomeration during casting the blended mortars. On the other hand, the flow test was performed according to ASTM C1437 [35].
Cubes with dimensions of 50x50x50 mm were produced for compressive strength test. The compressive strength test was performed according to ASTM C 109/C109M-13 [36]. Prisms with dimensions 40×40×160 mm were produced for flexural strength test according to ASTM C348-14 [37] and cylinders with dimensions 150×70 mm were produced for splitting tensile strength test according to ASTM C496M-11 [38].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 lime water for 28 days. All specimens were cured in limewater except one control mix was cured in tap water.

Table 2: Mix design of blended cement mortars used in the preparation of studied mortars (on weight basis)

Mix no.	Code of mix	Mix proportion of mortar, gm								Flow* %
		Cem.	Sand	Water	HRWRA	NMK	K	SF	FA	
1	C	450	1237.5	180	5.625	-		-	-	136.2
2	CL	450	1237.5	180	5.625	-	-	-	-	136.2
3	NMK2.5	438.75	1237.5	180	5.625	11.25	-	-	-	160.8
4	NMK5	427.5	1237.5	180	5.625	22.5	-	-	-	180.5
5	NMK7.5	416.25	1237.5	180	5.625	33.75	-	-	-	195.3
6	NMK10	405	1237.5	180	5.625	45	-	-	-	214.96
7	NMK12.5	393.75	1237.5	180	5.625	56.25	-	-	-	195.3
8	NMK15	382.5	1237.5	180	5.625	67.5	-	-	-	170.7
9	K2.5	438.75	1237.5	180	5.625	-	11.25	-	-	170.7
10	K5	427.5	1237.5	180	5.625	-	22.5	-	-	190.4
11	K7.5	416.25	1237.5	180	5.625	-	33.75	-	-	205.1
12	K10	405	1237.5	180	5.625	-	45	-	-	219.9
13	NMK5SF5	405	1237.5	180	5.625	22.5	-	22.5	-	87.01
14	NMK5SF10	382.5	1237.5	180	5.625	22.5	-	45	-	77.2
15	NMK10SF5	382.5	1237.5	180	5.625	45	-	22.5	-	121.5
16	NMK10SF10	360	1237.5	180	5.625	45	-	45	-	106.7
17	NMK5FA5	405	1237.5	180	5.625	22.5	-	-	22.5	185.43
18	NMK5FA10	382.5	1237.5	180	5.625	22.5	-	-	45	190.4
19	NMK10FA5	382.5	1237.5	180	5.625	45	-	-	22.5	219.9
20	NMK10FA10	360	1237.5	180	5.625	45	-	-	45	224.8
21	NMK10FA15	337.5	1237.5	180	5.625	45	-	-	67.5	234.65
22	SF5	427.5	1237.5	180	5.625	-	-	22.5	-	72.24
23	S10	405	1237.5	180	5.625	-	-	45	-	57.5
24	FA5	427.5	1237.5	180	5.625	-	-	-	22.5	150.98
25	FA10	405	1237.5	180	5.625	-	-	-	45	180.5

*Flow% = [(final flow recorded -lower diameter of the used cone) / lower diameter of the used cone]*100

Mixing Techniques

Mixing Technique for Kaolin (K)

- Add water and HAWRA to rotary mixer.
- Stirred for 1 min.
- Add K for mixture.
- Then stirred for about 1 min at a high speed in a mortar mixer to ensure a homogeneous dispersion of K.
- As mixer is stirring, add SF or FA (if applicable) to the rotary mixer.
- Mixing at medium speed for another 30 sec.
- As mixer is stirring add cement to the rotary mixer.
- Mixing at medium speed for another 1;5 min.
- As mixer is stirring, sand is gradually added while mixer is running at medium speed.
- Mixing for 2 min.
- Rest for 30sec the walls were scraped and then mixed continuously for 1 anther min at high speed.
- Perform flow test

Mixing Technique for Nano metakaolin

- Add sonicated NMK mixture.
- Stirred for 1 min.
- Add HRWRA to rotary mixer.
- As mixer is stirring, add rest of the mixing water.
- Then stirred for about 1 min at a high speed in a mortar mixer to ensure a homogeneous dispersion of NMK.
- As mixer is stirring, add SF or FA (if applicable) to the rotary mixer.
- Mixing at medium speed for another 30 sec.
- As mixer is stirring add cement to the rotary mixer.
- Mixing at medium speed for another 1; 5 min.
- As mixer is stirring, sand is gradually added while mixer is running at medium speed.
- Mixing for 2 min.
- Rest for 30 sec. the walls were scraped and then mixed continuously for another 1 min anther at high speed.
- Perform flow test.

Microstructure Properties, Mechanical and, Durability Tests

Microstructure Properties of K, NMK and Cement Mortars specimens Scanning Electronic Microscope SEM

The crystalline phases present in the raw materials were identified using the X-ray diffraction technique. Nicklefiltered Cu K∝ radiations at 40 kV and 20 mA were used throughout in a Philips PW 1390 diffractometer at Faculty of Science, Tanta University, Egypt.
SEM examinations were performed to verify the mechanism predicted by the compressive strength tests. The addition of pozzolanic materials in micro and nano size was found to influence the hydration behavior and influence the microstructure of hardened cement mortar. A scanning electron microscope is essentially an electron beam based microscope used to examine the surface structure of prepared specimens using a JSM-6510 L.V SEM, it was operated at 30KV at faculty of Agriculture, Mansoura University, Egypt.
Structures of specimen can be viewed at very high magnifications by Transmission Electron Microscope (TEM) using a JEOL 2100 TEM at 200 KV at faculty of Agriculture, Mansoura University, Egypt. This test was used to indicate nano-powder size and shape.

Mechanical properties tests

Testing of cement mortar compressive strength cubes were tested according to ASTM C 109/C109M-13 [36], testing of cement mortar flexural prisms were tested according to ASTM C348-14 [37], and splitting tensile strength test was carried out using cylindrical cement specimens were tested according to ASTM C496M-11 [38],as shown the testing machine in Fig. 2. All mortar specimens were tested at different ages in room temperature within two minutes after being removed from the water curing tank at 3, 7, 28, 60, 90 and 120 days age, three mortar specimens were tested and the average values were reported for all mixes at different ages.

Fig.2 The Compressive strength test

Durability performance of mortar specimens

A) Elevated heat temperature resistance test

Different cement replacement ratios with NMK, K, NMK+SF, NMK+FA, FA and SF were investigated under elevated temperatures. 19 blended cement mortars mixtures were exposed to elevated heat temperatures after 28 days at (200, 400, 600 and 800^0C) for 2hrs, the investigated mixes were tested to measure the compressive strength, flexural strength and splitting tensile strength.

B) Standard sulphate resistance test

Different cement replacement ratios with NMK, K, NMK+SF, NMK+FA, FA and SF were investigated under sulphate attack. Compressive strength test was conducted for 6 blended cement mortars mixtures (immerged in sodium sulphate) after being exposed to sulphate attack at (1, 4, 6, 12, 16 and 18) months and length change test was carried out for 2 blended cement mortars mixtures recording expansion in bars.

Sulphate resistance of mortars prisms was performed according to standard EN 196-1:2005 [34] as Courard et al. 2003 [39]. The method involves the determination of changes in length specimens when stored in a standard sulphate solution. The specimens were placed in sulphate solution having a concentration of 16.0 ± 0.5 g/l and prepared by adding reagent-grade sodium sulphate (Na_2SO_4) to water for shrinkage prisms as shown in Fig. 3a. Length change for mortar prisms were measured up to one year as shown in Fig.3b.

Sulphate resistance test was implemented on mortar control sample (C) and (10%NMK+15%FA) mix. These samples were chosen in order to evaluate the sulphate resistance impact due to using different pozzolanic material in nano-micro particles sizes as partial cement replacement with partial replacement 25% of cement weight . According to the test specifications, the average length change, for each standard mortar bar, was measured every two weeks up to 1 year.

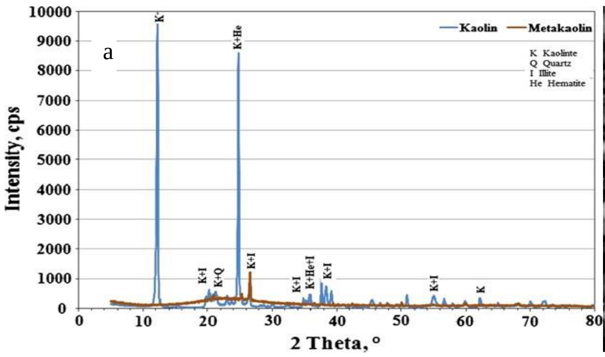
Fig. 3a Comparator used to measure the length of mortar bars Fig. 2b Specimen bars in sulphate solution for length change test

Test Results and Discussion

Mineralogical and morphological analyses for K and NMK

Fig. 4a. shows the XRD patterns for the as received kaolin and the thermally activated nanometakaolin (i.e. after K calcinations at 800 ^{0}C for 2 hrs in automatic electrical furnace to assure complete decomposition); in addition, quartz has been detected and the kaolin (K) mineral composition shown in Table2. As clear, the pattern interpretation led to identification of the following mineral phases; kaolinite, illite and quartz. The sharp intense peaks indicate its crystalline nature. The calcination led to remarkable peak broadening at (2θ = 15^o–35^o) which indicates the formation of non-crystalline (amorphous) material (i.e. the conversion of kaolinite, $2SiO_2.Al_2O_3.2H_2O$, into metakaoinite (in nano size). In addition, the kaolinite peak at (2θ = 12.41^o) completely disappeared, that suggests a breaking of the bonds between kaolinite layers [40] while quartz is preserved.

Fig. 4b shows the SEM micrographs of the thermally activated (calcined) kaolinite known as (NMK). The MK possessed plate like structure; however, the platelets are stacked in layers owing to interlayers wander walls' forces. therefore calcination of these platelets is a must to obtain high surface area and to increase its efficiency as a filler. As it is also clear from the figure, the calcined MK is characterized by large length to thickness aspect ratio (i.e. it is highly recommended in cementitious matrix reinforcement), and the mineral platelet thickness is very thin less than 100 nm, although its dimensions in length and width can be measured in hundreds of nanometers.



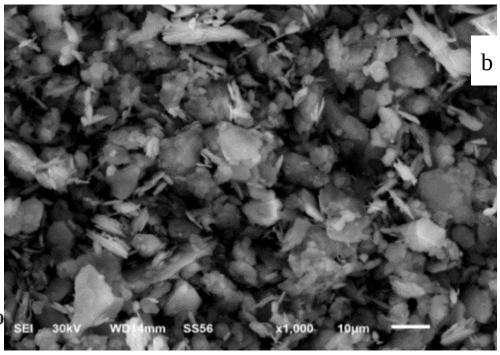


Fig.4a XRD patterns as received kaolinite (K) and thermally activated NMK
Fig.4b SEM micrograph of NMK

Table2 Kaolin (K) mineral composition

Compound Name	Chemical Formula	Mineral Composition
Quartz	$Si O_2$	96
Kaolinite	$Al_2 (Si_2 O_5) (OH)_4$	3.5

Transmission Electron Microscope (TEM) of K crystalline structure and also the amorphous nature of K particles. TEM images of the received kaolinite (K) affirm the presence of microstructures, thin platelets have been identified. The The kaolinite before heat treatment is characterized by large length to thickness aspect ratio, it is especially favorable in matrix reinforcement, and the mineral platelet thickness is only 1-10nm, although its dimensions in length and width can be measured in hundreds of nanometers, with a majority of platelets in 100-200 nm range before purification and calcination as shown in Fig. 5a. While TEM images of the activated NMK affirm the presence of nanostructures, very thin platelets have been identified and nano plates in 9.5–67 nm range were after calcination as shown in Fig. 5b.

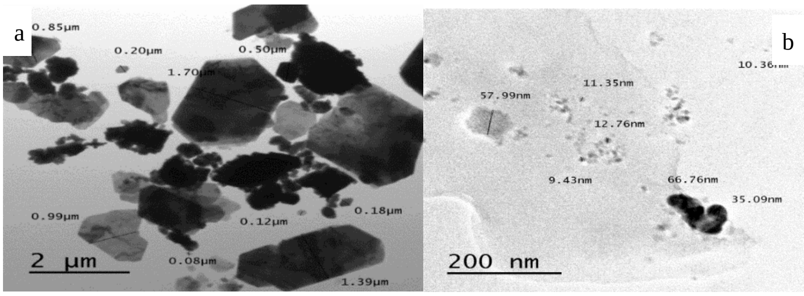


Fig. 5a TEM micrograph of K   Fig. 5b TEM micrograph of NMK

Mechanical properties

Generally, Replacement of cement by ultrafine NMK particles was found to alter the hydration behavior and posses differences in the microstructure of the hardened mortars. The hardened cement mortar containing NMK exhibited denser and more compact microstructure with relatively less void content. The strengthening effect of NMK particles would be further achieved in mortar because the ultrafine particles improve not only the cement paste but also the interfacial transition zone between cement paste and aggregate, which exhibit a good bonding and this will enhance the mechanical performance of NMK- blended cement mortar. The NMK caused remarkable modification in the interfacial transition zone structure and increased the bond between the cement paste and aggregate due to the physical packing effect. Also, the pozzolanic activity of the K and NMK resulted in the creation of additional calcium silicate hydrate which deposit in the interfacial transition zone.
Further increasing the NMK content over 5% resulted in poor hydration products as well as there are unhydrated cement grains appeared due to the agglomeration of MK and NMK around cement grains. Although the cement paste pattern of this mixture showed some difference, their microstructures were containing patchy and porous structure. Moreover, at 5% replacement of cement by weight NMK recorded more significant efficiency than FA or SF.

Maximum Compressive strength for mixes

A) NMK mixes with different percentages up to 120 days age

The compressive strength test results for NMK mortar mixes used separately with different percentages of NMK up to 120 days age are shown in Fig.6. Regardless the cement replacement ratio, all the mortar specimens show strength increment (i.e. due pozzolanic activity) with using NMK in nano size in matrix. Inclusion of NMK in cement mortars mixes enhanced the compressive strength at both early and later ages compared to the control mix.
The results showed that 5% replacement ratio of cement (5%NMK) recorded the best enhancement. With 66.66% increase in compressive strength above the control mix at 60 days age.

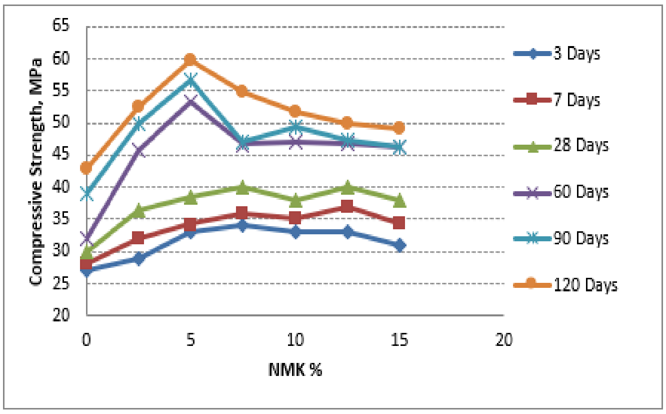


Fig. 6. Compressive strength results for mixtures containing NMK at different ages up to 120 days

Among the conducted pozzolanic materials (NMK, K, SF and FA), it can be concluded that 5%NMK showed the best enhancement in compressive strength at both early and later ages as shown in Fig.6

B) Optimum percentage of mixing with different materials at early ages and up to 120 days

Replacing 10 and 15% of the cement weight for mixes 5%NMK+10%SF and 5%NMK+5%FA mix significantly increased the mortar compressive strength recording 44 and 43.4 MPa respectively, at 28 days age as shown in Fig. 7.

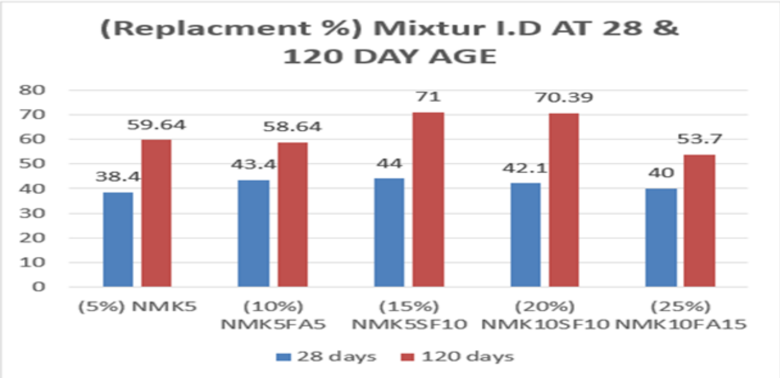


Fig.7. Max. Compressive strength results with different % replacement of cement at 28 and 120 days age

Replacing 15% and 20% of the cement weight for mixes 5%NMK+10%SF and 10%NMK +10% SF significantly increased the mortar compressive strength recording 71 and 70.39 MPa, respectively at 120 days as shown in Fig. 7.

Parametric study, based on the compressive strength of mortar specimens, is useful approach to determine the optimum nano-micro mixture ratio. NMK particles has a superior effect in gaining early strength by using NMK by 5% (optimum %) having nano particle size and increasing SF% up to 10% having micro particle size gave better enhancement for compressive strength at early ages than other mixtures percentages and control cement mixture. This early strength effect of NMK is due to its influence in accelerating the pozzolanic transformation of C_3S, C_2S and CH into the C-S-H gel which is responsible for giving the mortar mixture its strength. Gaining NMK enormous early strength is also attributed to the high packing efficiency of nano-particles in the presence of SF particles [41]. Therefore, nano metkaolin has currently limited application in construction industry in Egypt order to assure good quality control and hence microstructural homogeneity.

NMK particles combined with SF particles have a superior effect in gaining later strength by increasing NMK% up to 10% (more than optimum %) in nano size corporatizing with SF by 5% or 10% in micro size gives better enhancement for compressive strength at later ages than other mixtures percentages and control cement mixture. This means that NMK is effective in gaining early strength and this reason explained before. Conversely, SF existence in mixture clarify that SF has a problem of not gaining high early strength due to a delay in the pozzolanic reaction [41].

Maximum flexural strength for mixes

Results of flexural strengths of cement mortar samples containing different proportions of NMK, K, NMK+SF, NMK+FA, SF and FA were conducted. It can be concluded from Fig.8 that using NMK only as partial replacement with 7.5% of cement have a significant effect on high early flexural strength obtained at 28 days by improvement of 65.38% compared to mix CL (control mixture), while using mixtures containing both NMK in nano size incorpating to SF in micro size increased flexural strength significantly. While mixture 10%NMK+5%SF recorded the highest strength at all ages which increased flexural strength by 68.27%, 89.31% and 93.31 %, respectively compared to mix CL obtained at 28, 90 and 120 days, respectively. Finally, this gradation gives superior in filling pores having more dense micro structure than control mixture or NMK particles only.

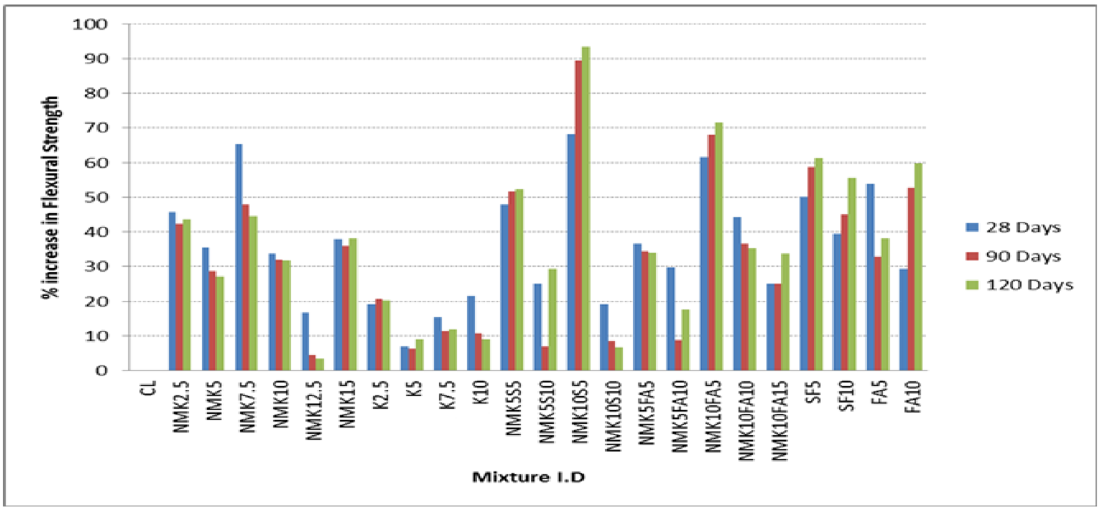


Fig. 8. Percent increase in flexural strength over control mixture in lime water

Maximum splitting tensile strength for mixes

It can be concluded from Fig.9 that for 28 days age using 10%NMK+5%SF increased splitting tensile strength by 51 % compared to mix CL obtained at 28 days, while using 10%NMK+10%FA in increased splitting tensile strength by 56.5 % compared to mix CL obtained at 28 days. Finally, this gradation gives superior in filling pores having more dense micro structure than control mixture.

The results indicate that the splitting tensile strength of specimens are improved by adding NMK particles only in the cement mortar up to 7.5 wt. % NMK .In addition, NMK particles are able to act as a nano fillers and recover the pore structure of the specimens by decreasing harmful pores[42]. This could lead to improve the mechanical properties.

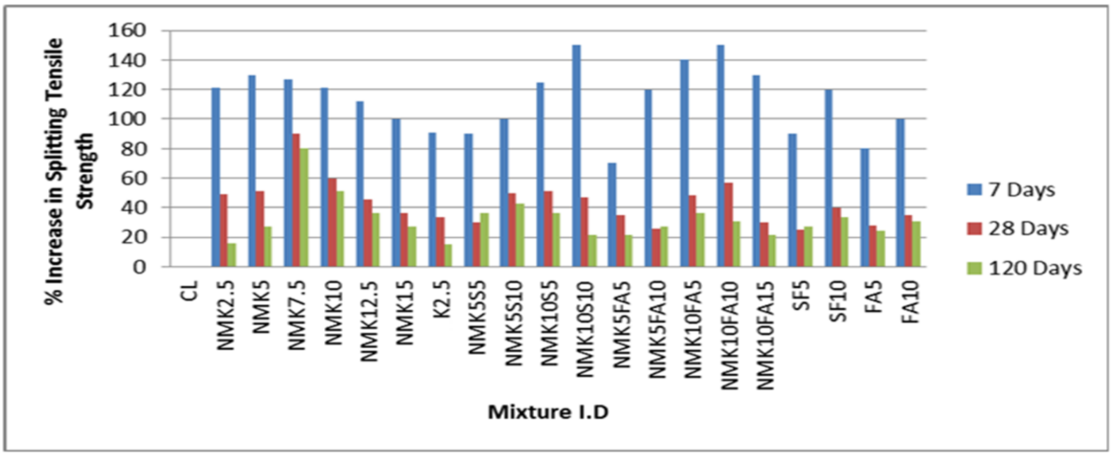


Fig. 9. Percent increase in splitting tensile strength for the investigated mixtures at 7, 28 & 120 days.

Considering that constant cement-sand ratio, w/c ratio and HAWAR % in all mixes to avoid the conflict due to changing supplementary cementitious materials as a replacement of cement by weight. In addition, the optimum ratio of mixing 10%NMK+5%SF based on the maximum compressive strength of mortar samples at later ages up to 120 days age.

According to Hosseini et al. 2010 [42] there are four main reasons behind the strength improvement resulting from adding nano-silica fond in NMK to the cement mortar which matches our results in this study. First of all, the nucleus-like action which means that the well dispersed nano-silica in the cement mortar mixture acts as a nucleus that bond strongly with cement hydrate to form conglomeration with nano-particles inside it as a nucleus and also promote the hydration process due to the large surface area and high activity of the nano-particles. Secondly, the enhancement in quick producing of calcium silicate hydrate due to the great surface area of nano particles and in turn this C-S-H gel fill the voids to give the cement mortar denser structure and improve the binding of the matrix. Thirdly, the ability of suitable quantity of nano-particles with uniform spacing among these particles to control and restrict the formation of calcium hydroxide crystals and as a result produce more compact and uniform cement mortar matrix. Fourthly, the micro-filling effect of nano particles that facilitates filling the voids and pores of cement mortar with the small size nano particles thus enhances the strength and minimize porosity. Those four reasons are supported by the results obtained in this study.

Finally, partial replacement of cement with optimum ratios of supplementary cementitious materials incorporating nano and micro particle size enhanced the strength, elevated heat resistance and sulphate resistance of cementious materials. On Contrary to the using nano material or micro size separately.

Durability characteristics

Elevated heat temperatures

A) Effect of elevated heat temperatures on mechanical properties

It can be generally noticed that for control samples, exposure to elevated high temperatures should a dramatically loss in the compressive strength. These losses in compressive strengths increased with increase of heat temperature level. On the other hand, the influence of high rise temperature on the blended mixes showed a variety range of change in the compressive strength. As exposure to 200^{0}C resulted in an increase in compressive strength for all investigated blended mixtures. Whereas, at higher temperature levels, the change ranged between enhancements and reductions as shown in Figs. (10-14). Moreover, at relatively higher temperatures, blended cement mortar mixes showed a reduction in flexural strength of magnitude relatively lower compared to the control mix, as for mixture 10%NMK+10%SF exploded at 800^{0}C (the same trend in compressive, flexural and splitting tensile strength).

For compressive strength results, Fig.10 shows the variation of compressive strengths for the investigated mixes as result of exposure to elevated temperatures. On the other hand, the percentage changes in the measured compressive strengths for the conducted mixes are plotted in Fig.11. Moreover, despite 5%SF mix which recorded highest compressive strength, it had high reduction in strength at 800^{0}C, conversely 10%NMK+10%FA mix recorded lowest reduction in compressive strength up to 800^{0}C, thus incorporating both NMK and FA to cement mortar mixtures generally enhance their mechanical properties, more dense micro structure and more durable blended cement mortar exposed to elevated heat temperatures and mix NMK10FA10 can be considered as fire resistance.

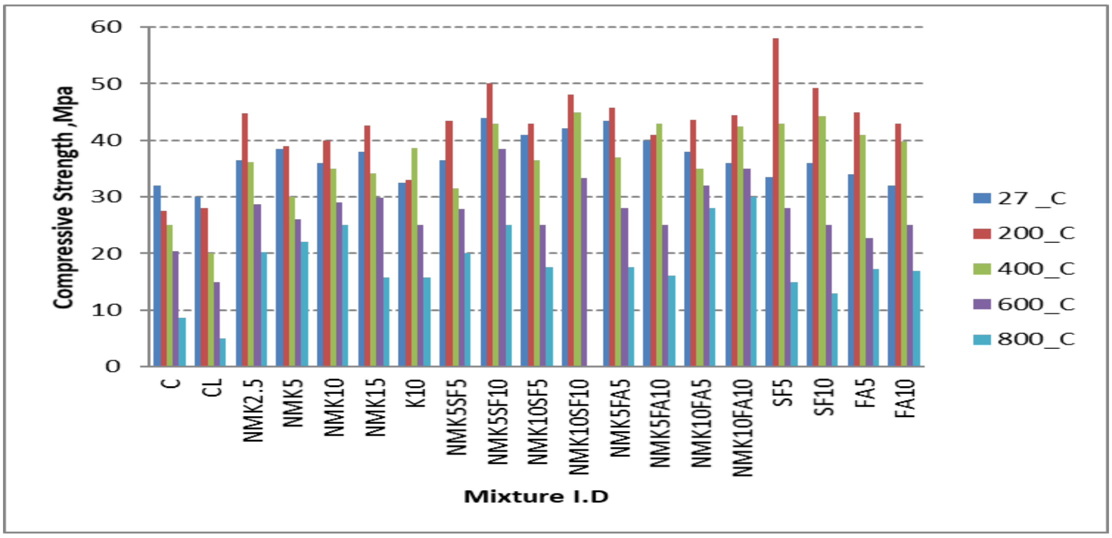


Fig. 10 Compressive strength for all investigated mixtures exposed to elevated temperatures

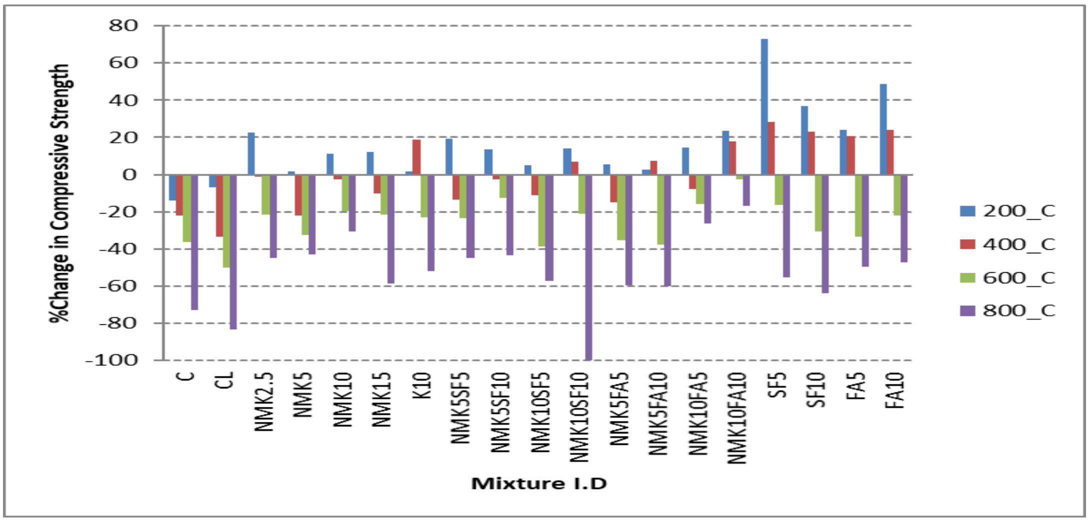


Fig. 11 Compressive strength change% for all investigated mixtures exposed to elevated temperatures

For Flexural strength tests, Fig. 12 shows the influence of the elevated temperatures on the flexural strengths for the investigated mixes. It can be noticed that, for all blended cement mortars the max. gaining in strength was by mix 2.5%NMK at 400^{0}C with improvement 66.05%, as well as mix NMK5SF10 was the lowest reduction in strength at 800^{0}C with 89.7% comparing both of mixes with its same mixes at 27 ^{0}C.

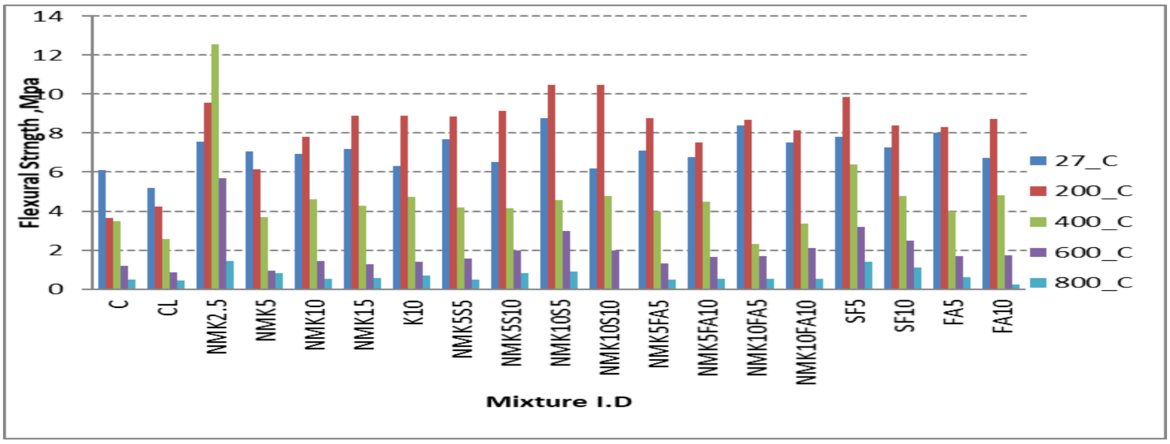


Fig. 12 Flexural strength for the investigated mixtures exposed to elevated temperatures

For splitting tensile strength tests, Fig.13 shows the variation of splitting tensile strengths for the investigated mixes as result of exposure to elevated temperatures. On the other hand, the percentage changes in the measured splitting tensile strengths for the conducted mixes are plotted in Fig.14. Generally, blended cement mortar mixtures showed an increase in splitting tensile strength at relatively lower temperatures, blended cement (200-400^{0}C), as by using 5% SF or 10% FA -as partial replacement by cement weight- mix FA10 recorded high splitting tensile strength up to 200^{0}C with 4.34 MPa by improvement 60.54% compared with the same mix at 27^{0}C, while mix NMK10SF10 recorded high splitting tensile strength up to 400 ^{0}C.

As mentioned previously, the maximum losses in strength at 800^{0}C indicated that this mixture was not fire resistance, while for minimum losses in strength at 800^{0}C indicated that this mixture was fire resistance cement blended mortar, and as shown in mix NK10 with 10% K -replacement of cement by weight- recorded min losses in splitting tensile strength, for K10 with 10% K -replacement of cement by weight- recorded improvement in splitting tensile strength at 2000C by 11.74% and at 800^{0}C losses in strength was 69.57 compared to the same mix at 27^{0}C (minimum loss = fire resistance), while for NMK5FA5 mix recorded improvement in splitting tensile strength at 800^{0}C losses in strength was -72.74% compared to the same mix at 27^{0}C. Finally, Fig.13 shows that mix containing SF or FA showed the best performance, while mixNK10 was the best in fire resistance for splitting tensile strength.

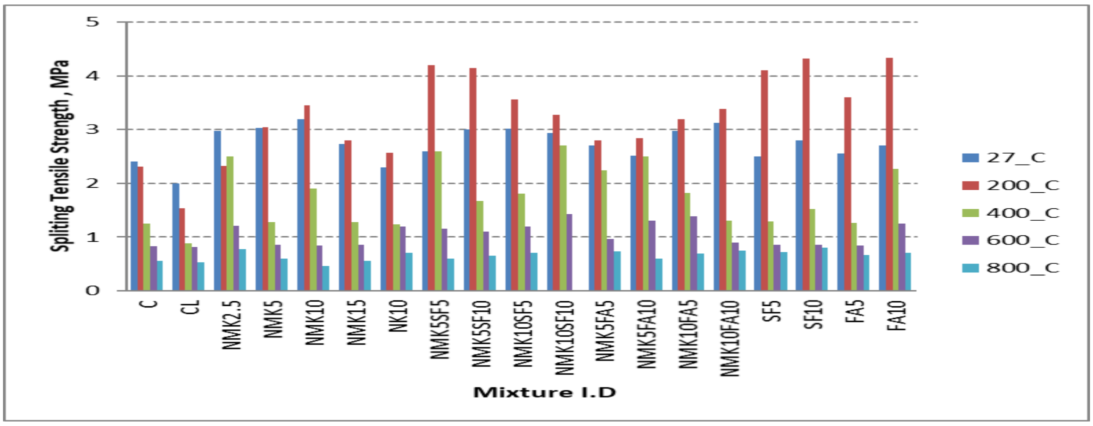


Fig. 13 Splitting tensile strength for the investigated mixtures exposed to elevated temperatures

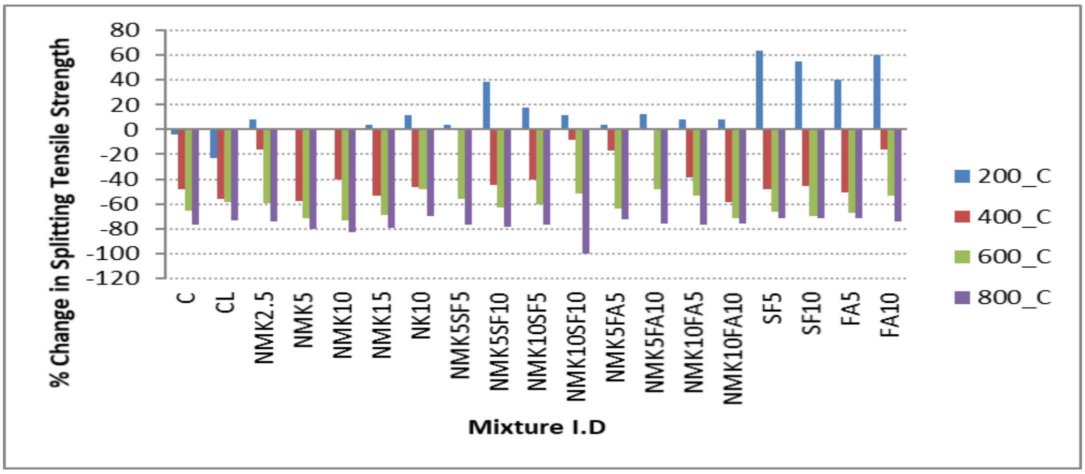


Fig.14 Splitting tensile strength change% for the investigated mixtures exposed to elevated temperatures

B) Effect of elevated heat temperatures on mass loss

For all investigated mortar specimens, the mass loss% increased with the increase of elevated temperature may be due to evaporation of water particles in cement mortars as shown in Fig.15. Mixes NMK15 and NMK10FA10 recorded the highest mass loss %, while mix NMK10SF5 showed the lowest mass loss %, in compared to control mix CL at 800^{0}C. The adsorbed and interlayer water begin to escape at temperatures above 650–800^{o}C. The mass loss further increased from 600 to 800^{o}C but at a slightly lesser rate. This moisture loss may due to the release of chemically combined water which is a part of cement hydrate products and is most difficult to evaporate.

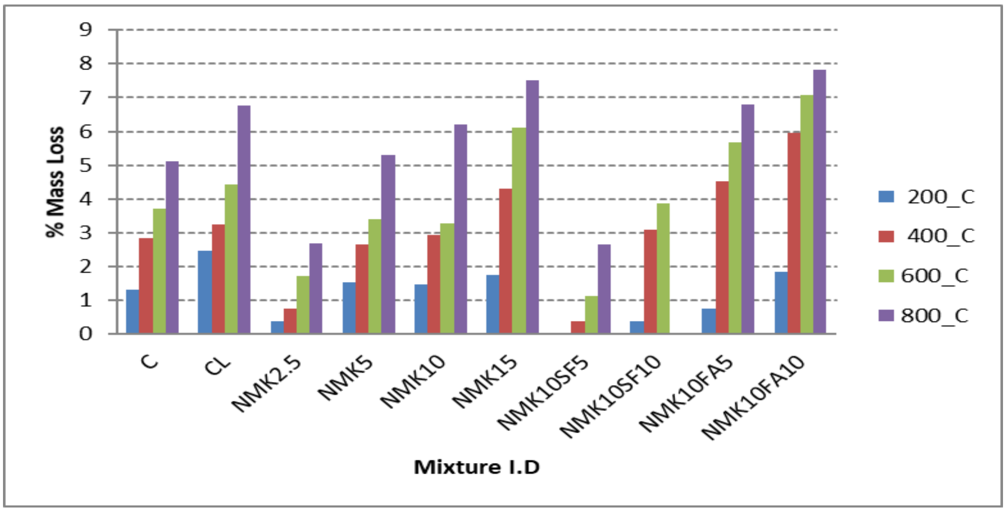


Fig. 15 Test results of mass loss% in blended cement mortars

Sulphate test results

A) Effect sulphate attack on compressive strength

The results of compressive strength for mixes exposed to Na_2SO_4 up to 18 months was recorded and Fig.16 shows mortar cubes after exposed to sulphate solution before testing. For mix K10 after prolonged periods of exposure to Na_2SO_4 solution there was a significant strength gain after 4 months then strength reduction up to 18 months, while for multi blended cement mortars mix NMK5SF5 and mix NMK10FA15 (with high levels of NMK and FA) there was little strength gain up to 4 months then strength reduction after exposure to Na_2SO_4 solution up to 1 year compared with the same mixes at 27 ^{0}C these results agree with Khatib et. al. [43].

Table. 3 and Fig. 17 present the results of change percentage compressive strength for mixes exposed to Na_2SO_4 up to18 months. Although K10 mix gained strength after 1 month by 0.1%, K10 mix had strength reduction after prolonged periods of exposure to Na_2SO_4 solution up to18 months, NMK10FA15 mix recorded less reduction in strength gain having high sulphate resistance up to 18 months as well as control mix C recorded highest reduction in strength.

Fig.16 Mortar cubes after exposed to sulphate solution

Table. 3 Change % in compressive strength for mixes exposed to Na_2SO_4

Period in months	Change in compressive strength for mixes exposed to Na_2SO_4%					
	C	K10	NMK5SF5	NMK10SF5	NMK10SF10	NMK10FA15
1	0	0	0	0	0	0
4	-0.03	0.10	0.02	-0.15	-0.18	0.01
6	-0.14	-0.06	-0.02	-0.26	-0.24	-0.02
12	-0.35	-0.19	-0.12	-0.37	-0.29	-0.07
16	-0.54	-0.38	-0.21	-0.42	-0.33	-0.15
18	-0.58	-0.48	-0.24	-0.43	-0.35	-0.17

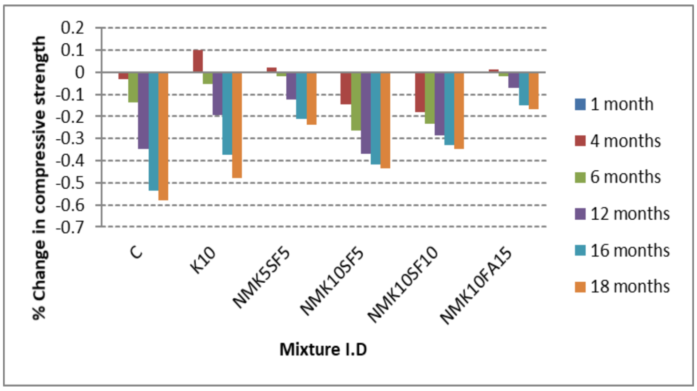


Fig.17 Change % in compressive strength for mixes exposed to Na_2SO_4

Finally, NMK increase resistance to sulphate attack which agree with Khatib and Wild 1998 [43]. Additionally, as CH is one of the reactants in sulphate attack and NMK has been shown to reduce CH content, and then sulphate resistance improved. The damage and strength loss % has been attributed to the replacement of Ca in C–S–H by Na lead to a reduction in the mixture cementing properties [44].

The basic requirements for high sulphate resistance are achieved by the partial replacement of cement with NMK+SF or NMK+FA cause of fine pore structure. They are also achieved after relatively short periods, the percentage pore volume occupied by fine pores decreases, although the total pore volume also decreases slightly. These data suggest that the sulphate-resisting properties of the NMK mortar are developed at early stage.

While Al-Akhras 2006 [45] explained the increase in sulphate resistance of the NMK matrix to the following mechanisms: reduction in the total amount of tricalcium aluminate hydrate in the blended cement mortar matrix. Formation of secondary CSH by pozzolanic reaction that is effective in filling and segmenting large capillary pores into small, discontinuous capillary pores through pore size refinement; thus, the total permeability of the cement matrix decreased. The filler action of multi blended cement in micro and nano size, due to its fine particle size, compared to the particle size of cement, further densified the pore structure of the blended cement matrix with (NMK+SF) or (NMK+FA). However, the inclusion of 25% cement replacement (10%NMK+15%FA) in the cement matrix showed the high resistance of sodium sulphate attack.

The results show an increase in the chemical resistance in blended cement mortars containing NMK incorporating with FA in comparison with mortars containing K only or NMK incorporating with SF (as partial replacement by cement weight).

B) Effect of sulphate attack on length change (Standard sulphate resistance test)

Fig. 18 presented the resistance of multi blended cement mortar NMK10FA15 mix and control mix to sodium sulphate solution and recording result up to 1 year. Cement was partially replaced by 10 %NMK and 15 % FA by weight. The sulphate expansion % results demonstrate that the sulphate resistance is increased as the replacement level of cement with (NMK+FA) increases, up to at least 25% replacement. The results showed that plain cement mortar prisms experienced expansion after only a few days of exposure to sodium sulphate. After 30 days, the variation in length was 27.7% expansion. On the contrary, NMK prisms incorporated with FA mix NMK10FA15 had initially expansion and then did not change length signicantly in either direction for the duration of the test (1 year).

It can be concluded that multi blended cement mortar have high resistance to sodium sulphate solution compared with control mix. Cement was partially replaced with (NMK+FA) up to 25% with 10%NMK+15%FA.

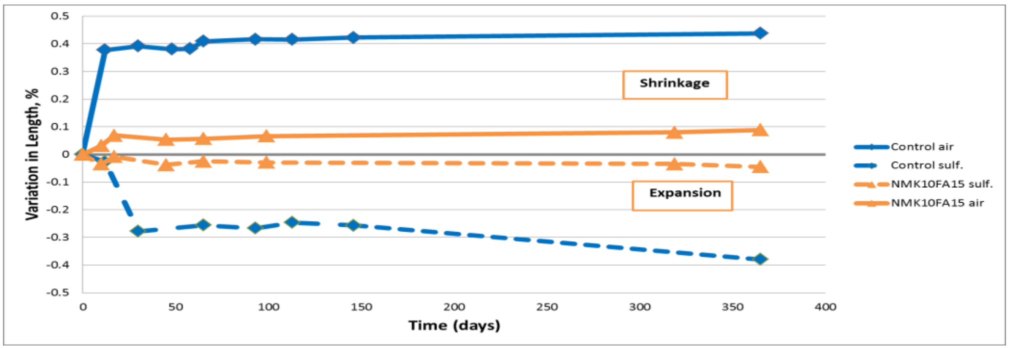


Fig.18 Shrinkage and expansion percentage of control and NMK10FA15 mortar bars immerged in sodium sulphate solution

Replacing cement with 10%NMK+15%FA mixture outperformed the separate replacement with NMK, FA or SF on mortar sulphate resistance reached moderate level than control specimen which is less effected by shrinkage.

The drying shrinkage decreases in the uncured conditions with adding nano clay in the mortar compared to the control ones. this can be attributed to the effect of nano clay which behaves not only as a filler to improve microstructure, but also in self curing action when it is mixed into cement, and after it is hardened, nano clay will slowly release this water to an unhydrated cement during the critical early phases of curing which assist in more complete hydration of cement which contributes to increase com pressive strength and decrease drying shrinkage and this result agree with Sonosi 2015 [46].

Sulphate attack is controlled by the concentration of SO_4, alkali (in solution outside the mortar or pore solution inside the mortar), and the mount of C_3A and C_3S in cement. In the aggressive chemical environment of a Na_2SO_4 solution at high metakaolin content by 10 %, CH availability becomes restricted, and the expansion is very much smaller and this result agree with Khatib and Wild 1998 [43].

Based on the SEM images, replacing 15% of cement by 5% NMK+ 10%FA mixture provided more dense micro structure, with decrease of calcium hydroxide CH ratio and increase in C-S-H which is complied with Li et al. 2004 [47] and Zaki et al. 2010 [29]. Moreover, 5% NMK replacement of cement specimens is more dense and durable cement mortar than control specimens after thermally treated at 27, 200 and 600 ^{0}C.

Microstructure analysis of cement mortars specimens SEM

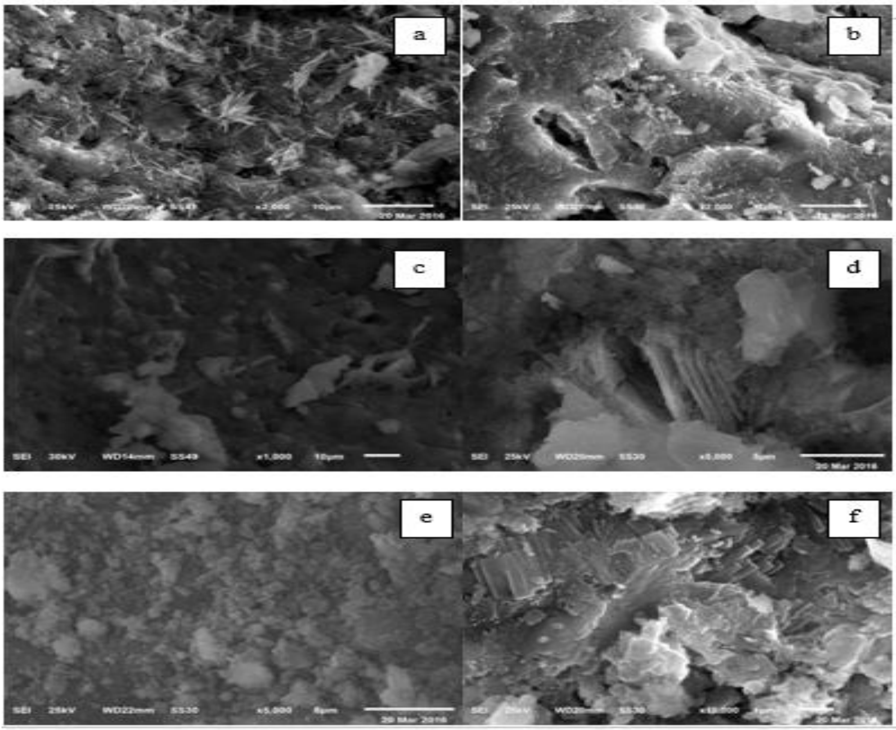


Fig .19 SEM micrographs of all mortars cured in lime water at 27^{0}C a) control mortar (CL) and; b) 10%SF; c) 5%NMK+5%SF, d) 10%FA; e) 5%NMK+10%FA; and f) 10%NMK+15%FA

Fig.19 shows SEM of selected cement mortar specimens which made of different materials with different percentages of cement replacement by weight at more than 1 year cured in lime water. Fig. 19a for control mix CL, Fig. 19 b, c for mixes containing 10% SF only and 5%NMK+5%SF, while Fig. 19 d,e,f for mixes containing 10%FA, 5%NMK+10%FA and 10%NMK+15%FA. The micro structure of mixes 10% SF and 10%FA are denser than the micro structure of control mixture mix C as shown in Fig.19 a, b and d. Moreover the micro structure of mixes cement mortar containing NMK in corporation with SF or FA mixes are more denser than the micro structure of control mix CL. In addition, all mixtures show less calcium hydroxide (CH) crystals than the control mixture mix CL.

The microstructures of cement mortar specimens containing NMK in corporation with SF or FA as shown in Fig. 19 are more dense than the microstructure of the control sample. In addition, all mixtures show less calcium hydroxide (CH) crystals than the control mixture mix CL. Which CH appears as large thin elongated crystals due to the expected pozzolanic activity of different added pozzolanic materials (nano or micro size) particles

The microstructures of blended cement mortar mix 10%FA is porous with the presence of many voids Fig.19d some of the surfaces of FA particles were found to be coated with layers of small amounts of hydration products. Some of the hexagonal CH and ettringite needles, which grow in vacant areas in paste, were also observed. FA particles were observed in two forms: particles with a smooth surface and particles covered by layers made of hydration products and pozzolanic reaction. In the first form, it appeared that some FA particles were still smooth, suggesting that they were unreacted or acted as an inert material with the ability to increase the packing effect and served as a precipitation nucleus for hydration compounds. The second form showed hydration and pozzolanic products around the FA particles. By presence of NMK with replacement up to 5 % and FA with 10 % replacement by mix 5%NMK+10%FA Fig.19 e, a lot of FA particles covered by hydrates appeared in the structure as the FA and NMK were activated by $Ca(OH)_2$. The pozzolanic reaction of FA and NMK was enhanced at the later ages with a marked consumption of the free $Ca(OH)_2$. The surfaces of FA particles covered by CSH were caused by the reaction of FA and NMK with $Ca(OH)_2$ and other hydration products. As the hydration process continued, thicker layers of hydration products on the FA and cement grains could be

distinguished, although some particles still remain unreacted and acted as filling materials. Moreover, the increase of NMK replacement up to 10 % mix 10%NMK+10%FA, leads to an increase of unreacted NMK particles which acted as a filler material, serving as a precipitation nucleus for $Ca(OH)_2$ and CSH gel and filling the voids between cement grains Fig. 19 e, the formation of micro cracks was also observed. It is evident that the hydration products still underwent through both pozzolanic and hydration reactions.
Comprehensive study may be required, based on more SEM images; to approve that using 5%NMK +10%FA mixture can provide the densest microstructure than that of the mortar containing FA alone and this result agree with Morsy et al. 2010 [37].

Based on the SEM images, replacing 15% of cement by 5%NMK+10%FA mixture provided more dense micro structure, with decrease of calcium hydroxide CH ratio and increase in C-S-H which is complied with Li et al. 2004 [47] and Zaki et al. 2010 [29].

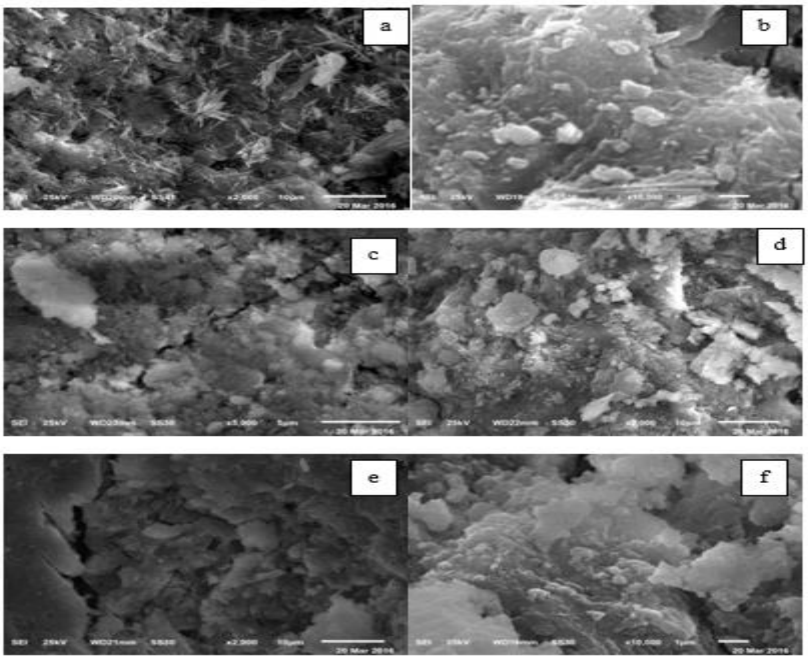


Fig. 20 SEM micrographs of control & blended cement mortars at 28 days of curing: a) control mortar (CL) at 27 ^{0}C; b) 5 %NMK at 27 ^{0}C; c) CL at 200 ^{0}C, d) 5 %NMK at 200 ^{0}C; e) CL at 600^{0}C; and f) 5%NMK at 600 ^{0}C

Fig. 20 Shows the SEM of control mortar (CL) and blended cement mortar containing 5% NMK mix NMK5 and thermally treated at 27, 200 and 600 ^{0}C.
Evidently, the microstructure of the control mortar at 27 ^{0}C displays the existence of microcrystalline and nearly amorphous, CSH; in addition to large crystals of CH and revealed non uniform arrangement of hydration products as shown in Fig.20 a. Furthermore, the micrograph of blended cement mortar containing 5% NMK displayed the presence of a nearly amorphous CSH and dense microstructures shown in Fig.20 b. It was clear that, the microstructure of NMK mortar, thermally treated at 200 ^{0}C, was perfectly stable for thermal treatment and illustrates a dense structure of hydrated products as shown in Fig.20 d. This can be clearly understood from the microstructure of the hardened blended cement mortar 5% of NMK after thermal treatment at 200 ^{0}C which displayed the existence of CSH and CH. Therefore, the replacement of OPC by 5% of NMK resulted in an improvement of the thermal stability of the hardened blended cement mortar made of mixture NMK5 as indicated from the SEM micrograph shown in Fig.20d.

Based on the SEM images, 5% NMK replacement of cement specimens is more dense and durable cement mortar than control specimens after thermally treated at 27, 200 and 600 ^{0}C.

Therefore, the current SEM observations can be applied to illustrate the durability enhancement achieved on cementious materials made of the proposed NMK mixture with 5% NMK replacement of cement at 27^0, 200^0,600 ^{0} C better than control mix (CL).

Conclusions

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

- Among the conducted pozzolanic materials (NMK,K,SF and FA) with 5% partial replacement ratio, NMK showed the best enhancement in compressive strength at both early and later ages.
- Inclusion of NMK in cement mortars mixes enhanced the compressive strength at both early and later ages compared to the control mix. The results showed that 5% replacement ratio of cement recorded the best enhancement. 66.66% increase in compressive strength was recorded at 60 days for mix containing 5% NMK above the control mix.
- Combination use of NMK and SF showed the best enhancement in both compressive and flexural strengths. Mix containing 10% NMK as well as 5 % SF gave the best enhancement in compressive strength as well as flexural strength. At 120 days age, the enhancements were 65.12% and 93.31% for compressive and flexural strengths, respectively.
- For splitting tensile strength, mortar mix containing 7.5% NMK showed the best enhancement among the conducted mixes at all age. 127%, 90% and 80.3% enhancement ratios over the control mix were recorded at 7, 28 and 120 days age, respectively.
- Implementation of NMK as nano material in cement mortars mixes opens a new Chanel towards using of low cost nano materials in cement based composites. The cost for achieving a unit improvement in both hardened as well as durability properties is comparable to the cost of the property unit for the control mix. This enables overcoming the drawback of using other nano materials of high cost.
- Portland cement mortars exposed to elevated temperatures showed enhancements in compressive strength values at 200 °C except for the control one that showed a noticeable reduction in the compressive strength. This increase may be due to the acceleration of hydration process due to higher temperature effect.
- Cement mortars replaced partially by both of NMK and FA showed the best performance when exposed to elevated temperatures. This could be noticed for mixes NMK10FA5 and NMK10FA10 for which the reduction in compressive strength values at 800°C were 26.32% and 16.67%, respectively compared to the same mixes at ambient temperature 27°C.
- Multi blended cement mortar mixes containing both of NMK as well as SF showed better performance at elevated temperature at relatively low levels (200°C). Whereas, at the highest levels, they lost all of their strengths as noticed for mix NMK10SF10 that was destroyed completely at 800 °C.
- For different replacement ratios 0, 5, 10, 15, 20% by cement weight, the higher compressive strengths recorded at 200°C were 28, 58, 49.2, 50, 48 MPa for mixes CL, SF5, SF10, NMK5SF10, NMK10SF10, respectively. The change in the compressive strength for these mixes was -6.67, 73.13, 36.67, 13.64, 14.01% respectively, compared with the same mixes at 27°C.
- At 800°C, the higher compressive strength recorded for different replacement ratios 0, 5, 10, 15, 20% by cement weight were 5, 22, 25, 28, 30 MPa recorded for mixes CL, NMK5, NMK10, NMK10FA5, NMK10FA10, respectively. The change in the compressive strength for theses mixes was -83.33, -42.71, -30.56, -26.32, -16.67%, respectively, compared with the same mixes at 27°C.
- Mixture NMK10SF10 showed the higher elevated temperature resistance up to 200^0C with gaining in flexural strength by 68.98% compared with the same mixes at 27^0C.
- Multi blended cement mortar mixes incorporating both of NMK and FA (mix NMK10FA10) showed higher splitting strength (0.75 MPa) at 800°C.
- The mass loss test results with elevated temperature showed that, the mass loss increased almost constantly up to 400°C and thereafter the loss started to increase at a slightly lesser rate. The mass loss further increased from 600 to 800°C but at a slightly higher rate. This loss

is due to release of chemically combined water which is a part of cement hydrate products and is most difficult to evaporate.

- Exposure to 50% Na_2SO_4 solution showed significant increase in compressive strength up to 4 months age for multi blended cement mortars with high levels of replacement with both NMK and FA (mix 10%NMK+15%FA) and a slight decrease in strength up to 18 months age in compared with the same mix without exposure.
- The sulphate expansion results demonstrate that the sulphate resistance is increased as the replacement level of cement with NMK increases, up to 25% replacement (mix NMK10FA15). Refinement in pore structure and reduction in CH content increase with increase in NMK content (for moist-cured mortar), and these two factors are considered to be the principal factors affecting improvement in sulphate resistance.
- The microstructure analysis conducted on cement mortar mixtures demonstrated that the enhancing in mechanical properties with NMK addition is primarily due to its high packing efficiency in filling voids. This is likely the main reason for the low permeability and due to its effect in promoting pozzolanic reaction because of its high surface area especially for blended cement mortars.
- At high temperature poor microstructure is associated with generation of undesirable configuration of CSH crystals, and increased cracking, which means that NMK had a superior positive effect on producing cement mortar mixtures with novel properties

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