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Thermal durability of OPC pastes admixed with nano iron oxide

Ahmed A. Amer [a,*], **Tarek M. El-Sokkary** [b], **Nagwa I. Abdullah** [a]

[a] *Faculty of Science, Chemistry Department, Zagazig University, Zagazig, Egypt*
[b] *Housing and Building National Research Center, Cairo, Egypt*

Abstract Nanotechnology helps in producing materials with prospective properties, for each field of science (physics, chemistry, bio-science as well as construction materials). Nanoparticles belong to the materials in the field of civil engineering which have a high surface area to provide high chemical reactivity. Some researchers have employed nanoparticles into cementitious materials based on ordinary Portland cement to modify the properties of this system. They have important advantages for the hydration and microstructure of cement paste to increase the rate of hydration and the amount of formed CSH gel. The aim of this work is to investigate the influence of NF on the fire resistance of OPC pastes. The NF was synthesized by thermal decomposition of basic ferric acetate fired at 275, 600 and 800 °C. The crystal size of the prepared NF as previously determined was 14.6, 16.98 and 18.68 nm, respectively. OPC admixed with 1 wt% NF prepared at 275 °C gives the higher fire resistance than those admixed with 2 or 3 wt%. It shows the higher bulk density, compressive strength and lower porosity up to 450 °C than the blank OPC. As the firing temperature of NF increases the fire resistance diminishes.

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Introduction

Nanotechnology has changed our vision, expectations and abilities to control the material world. The developments in nano-science can also have a great impact on the field of construction materials and other fields in science (physics, chemistry, bioscience, etc.) [1]. Also, Nano-technology is one of the most active research areas with both novel science and useful applications that has gradually established in the last two decades. It is the creation of materials and devices by controlling of matter at the level of atoms, molecules and super molecular (nano-scale) structure. Better understanding and engineering of cement based materials at the nano-level will definitely result in a new generation of concrete, stronger, more durable and possibly, with the whole range of newly introduced "smart" properties [2]. Nanoparticles are among prospective materials in the field of civil engineering which have a

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high-surface area for providing high chemical reactivity [3]. They act as nucleation centers, contributing to the development of the hydration of OPC paste. However, due to the high surface area very strong attractive properties can be obtained. Some researchers have employed nanoparticles into cementitious materials based on Portland cement (PC) to modify some properties of this system. Regarding the addition of nanoparticles to PC paste, they have important implications for the hydration and the microstructure of the paste such as an increase in the initial hydration rate, as in the amount of CSH gel of the paste through pozzolanic reaction, porosity reduction, and improvement of mechanical properties of the CSH gel itself (greater alumina-content, longer silicate chains) [4]. Therefore, the formation of nanoparticles of the hydration products (C–S–H, calcium hydroxide, ettringite, monosulfate, unhydrated particles and air voids), to overcome durability issues, is a crucial step in the concrete eco-efficiency [5]. To date, nanotechnology applications and advances in the construction as well as building materials fields have been uneven [6].

Many studies have focused on the effect of addition of some metal oxide nanoparticles to concrete which can both reduce the permeability of concrete to ions and increase the compressive strength, thereby improving durability. In civil engineering field, most of the research works till date are conducted with nano-silica (nano-SiO_2) (NS) [7–15] and nano-titanium oxide (nano-TiO_2) (NT) [16–21]. On the other hand, a few studies were conducted with nano-Al_2O_3 (NA) [7,22–26], nano-Fe_2O_3 (NF) [27–32], nano-Fe_3O_4 and nano-clay (NC) in comparison with those regarding NS or NT [33]. Metal oxide nano particle addition accelerates chemical reactions during the initial hydration thus strengthening cement compositions, thereby not only decreasing permeability but also improving the mechanical properties [34].

Li et al. [30] studied the mechanical properties of NF mortars. The compressive and flexural strengths at the 7th and 28th days of the cement mortars mixed with nanoparticles were higher than those of a plain cement mortar. Yazdi et al. [31] studied the mechanical properties, at 7 days, of mortars modified with NF. Cement was partially replaced with 1, 3 and 5 wt% NF. The results showed an increase in both compressive and tensile strengths with the addition of 1 and 3 wt% NF, while 5% NF decreased the strengths.

Nazari et al. [28,29] studied the workability and the setting times of concretes modified with NF. Cement was partially replaced with 0.5, 1.0, 1.5 and 2.0 wt% NF. The results showed a reduction in the workability with NF content. Also, both the initial and final setting times shortened with the addition of NF. The authors studied also, the flexural strength of concrete at the same levels of NF content, at 7, 28 and 90 days. The flexural strength increased with the addition of NF. The enhancement in the 28 days flexural strength was 13.64%, 18.18%, 13.64% and 9.1% with the addition of 0.5%, 1.0%, 1.5%, and 2.0% NF, respectively.

Khoshakhlagh et al. [27] studied the heat of hydration of pastes modified with NF up to 70 h. Cement was partially replaced with 0, 1, 2, 3, 4 and 5 wt% NF. It was found that the substitution of NF accelerated peak times and dropped heat rate values. Cement was partially replaced with the same NF levels and 1 wt% superplasticizer was employed. The strengths showed an increase with the addition of NF, at all ages. The addition of 4% NF gave the highest strengths. The enhancement in the 28 days compressive strength was 20.57%, 31.33%, 52.53%, 71.83% and 67.1% with the replacement of 1%, 2%, 3%, 4% and 5%, respectively. It was reported that NF acted as a foreign nucleation site that accelerated CSH gel formation and as a result crystalline $Ca(OH)_2$ amount especially at the early age of hydration increased and hence the strength increased.

Upon exposure to high temperatures, concrete undergoes changes in chemical composition and physical structure [35]. The release of free water and the expulsion of bound water occurred at 300 °C. At temperature exceeding 500 °C, $Ca(OH)_2$ and C–S–H in the cement paste start decomposing until C–S–H collapses at higher temperatures. The free water and water of hydration evaporate at 110–220 °C, water of C–S–H gel at 220–400 °C, water of portlandite at 400–500 °C [36–38].

The present work aims to prepare nano-iron oxide (NF) which is synthesized by thermal decomposition of basic ferric acetate as a precursor at different temperatures such as 275, 600 and 800 °C. The effect of incorporation of NF to ordinary Portland cement paste on the fire resistance up to 800 °C was studied.

Materials and methods

Materials

The material used in this investigation is Ordinary Portland cement (OPC) provided from Suez cement Company, Suez. Basic ferric acetate [$Fe(CH_3COO)_2OH$] was of chemical grade. The chemical composition of the used OPC was: $SiO_2 = 21.51$, $Al_2O_3 = 5.07$, $Fe_2O_3 = 4.39$, $CaO = 64.21$, $Na_2O = 0.23$, $K_2O = 0.29$, $SO_3 = 3.25$ and I.L. 2.40%.

Methods of investigation

The dry constituents of each mix were mechanically mixed for one hour in a porcelain ball mill using two balls to attain complete homogeneity and then kept in air tight containers until the time of paste preparation. The NF was prepared by thermal decomposition of basic ferric acetate calcined at 275, 600 and 800 °C [39].

Mixes were prepared by substitution of OPC with 1, 2 and 3 wt% NF synthesized at 275 °C.

Preparation of cement pastes

The water of consistency and the initial as well as final setting times were determined according to ASTM methods using a Vicat apparatus (**ASTM: C191**) [40].

The mixing of cement powder was carried out with the required water of consistency (ASTM: C191) [40]. Immediately after molding, the specimens were cured in 100% R.H. at room temperature 23 ± 2 °C for the first 24 h, then demolded and cured under water up to 28 days.

To show the effect of fire on the cement pastes, the cubes were cured for 28 days under water then heat treated at different temperatures. The rate of heating was 3 °C/min up to the desired temperature as 105, 250, 450, 600 and 800 °C with a soaking time of one hour, then left in the furnace overnight and kept in desecrator for further investigations.

The weight loss of the heat treated samples can be determined in relation to the original weight of cement pastes cured for 28 days. The bulk density and total porosity of thermally treated cement pastes were determined after immersing the pastes overnight under kerosene [41,42]. The compressive strength of cement pastes was determined according to ASTM Designation: (C150-2007) [43].

Results and discussion

Thermal decomposition of basic ferric acetate

Mineralogical composition of NF

Nano-sized iron oxides were prepared by thermal decomposition of basic ferric acetate in a muffle furnace at a heating rate of 5 °C/min and one hour soaking time at 275, 600 and 800 °C to identify the phases formed and then the crystal size. The products of basic ferric acetate fired at different temperatures were examined by XRD analyzer as shown in Fig. 1. Sample fired at 275 °C shows the formation of magnetite as the main phase in addition to some of hematite. The presence of magnetite in the fired product at 275 °C is mainly due to the insufficient atmospheric air which can oxidize magnetite Fe_3O_4 to hematite Fe_2O_3. It is clear that as the firing temperature increases the hematite increases at 600 °C at the expense of Fe_3O_4. Magnetite is nearly converted to hematite with a small amount of magnetite (Fe_3O_4) at 800 °C. When ferric acetate is fired in open atmosphere (tubular furnace), hematite Fe_2O_3 can be completely formed at 275 °C [44].

The thermal behavior of basic ferric acetate during heating in nitrogen atmosphere at a rate of 20 °C/min was determined by using the thermal analyzer technique. Figs. 2 and 3 show the DTA and TG curves of ferric acetate heated up to 800 °C. Fig. 2 illustrates the presence of four endothermic peaks at 75–125, 125–150, 150–300 °C and 700–800 °C. The first endothermic peak is due to the removal of moisture whereas the second and third endothermic peaks are attributed to the desorption of acetone and carbon dioxide, respectively as shown in the following equation [45]:

$$2Fe(CH_3COO)_2OH \rightarrow Fe_2O_3 + 2CH_3COCH_3 + 3CO_2$$
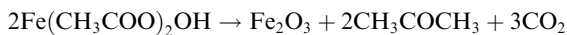
The fourth endothermic peak may be due to the transformation of γ-Fe_2O_3 to α-Fe_2O_3 [46].
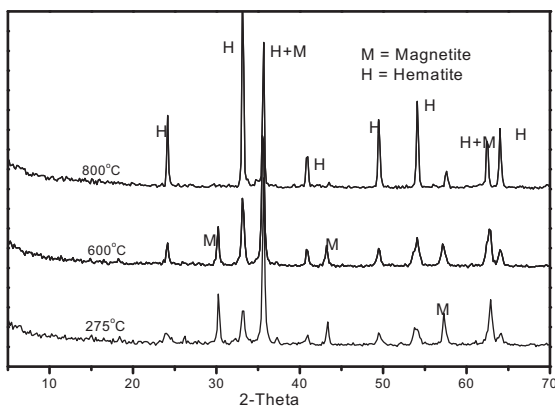

Fig. 1 X-ray diffraction (XRD) of NF samples prepared from basic ferric acetate by thermal decomposition at different temperatures.
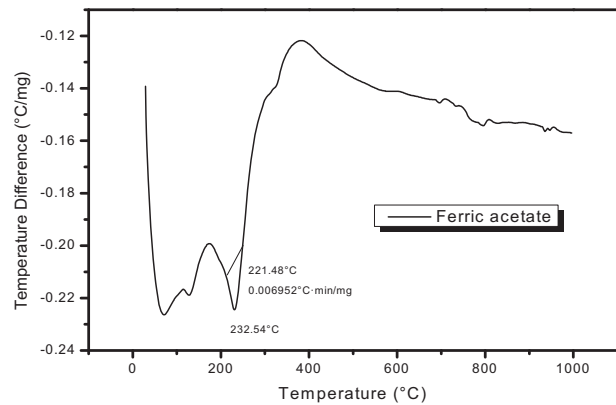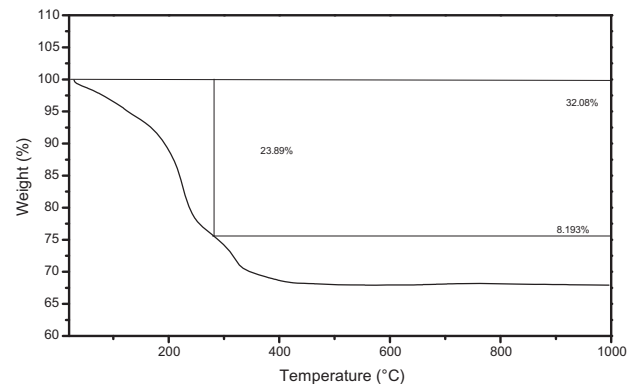

Fig. 2 DTA-thermogram of ferric acetate.

Fig. 3 TG thermogram of ferric acetate.

Hematite (α-Fe_2O_3) is the only thermally stable polymorph prepared by oxidative thermal treatment of iron salts [47]. Magnetite is one of the most thermally unstable iron oxides. It turns first into maghemite (γ-Fe_2O_3, brown) around 200 °C, and then to hematite around 400 °C. Therefore, hematite is a common contamination of any iron oxide polymorph prepared under heat [48].

Fig. 3 illustrates the thermal gravimetric analysis (TG) of the basic ferric acetate. It gives TG loss of 23.89%, up to 240 °C. This is mainly due to the loss associated with the desorption of acetone and carbon dioxide from ferric acetate with the formation of hematite [44]. As the firing temperature increases up to 400 °C the total loss is 32.09%. The difference between the loss at 275 and 400 °C is due to the formation of magnetite Fe_3O_4 which is accompanied by the release of oxygen.

Microstructure and morphology of NF

The SEM observation of the basic ferric acetate [Fe(CH$_3$COO)$_2$OH] fired at 275 and 800 °C are shown in Figs. 4 and 5. It is clear that the sample fired at 275 °C illustrates the dark aggregate of magnetite with some white crystals of hematite. On the other side, the sample fired at 800 °C shows the appearance of hematite as white clusters [47,48]. Also, it can be observed that the Fe_2O_3 grains have a spherical disturbed shape. The dark aggregate of sample fired at 800 °C may be due to some cleavage or pores or some magnetite in the sample.
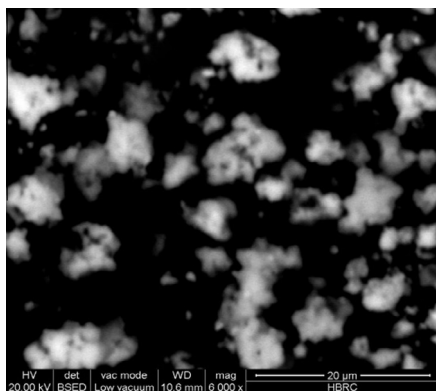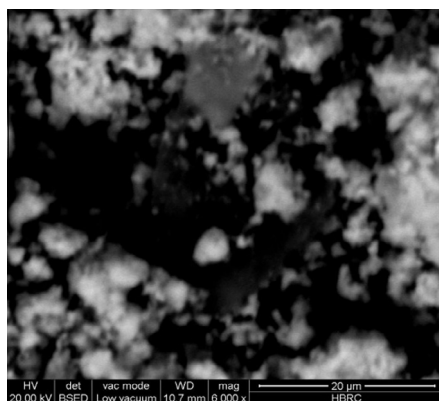
Fig. 4 SEM of nano iron oxide prepared at 275 °C.

Fig. 5 SEM of nano iron oxide prepared at 800 °C.

Crystal size of NF

The crystal size of nano iron oxide prepared at 275, 600 and 800 °C is examined by the aid of TEM. It was found that the crystal size of the samples fired at 275, 600 and 800 °C is 14.6, 16.98 and 18.6 nm, respectively [39].

Fire resistance of cement pastes

Fire is one of the hazards that attack building constructions. The damage of buildings is due to their continuous exposure to fire caused by high temperatures. The chemical processes stimulated by temperature in the particular phases of cement paste have a significant influence on the thermal deformation, cracking, spalling and compressive strength losses.

Many authors provide evidence that the loss of water, either free, adsorbed or chemically combined water, induced by high temperatures, affect the microstructure of cement paste, capillary and total porosity increase as well as the nanoporosity associated with CSH gel collapses [49]. In the temperature range 100–300 °C, these evolutions are mainly attributed to the loss of free and bound water from the CSH gel. The loss at 550 °C is mainly due to the dehydroxylation of portlandite.

The effect of fire on the mechanical properties of cement pastes admixed with nano iron oxide (NF) can be studied by the determination of the weight loss, apparent porosity, bulk density, and compressive strength of hardened cement pastes treated up to 800 °C.

Effect of NF content on fire resistance

Weight loss. The effect of fire on the cement pastes containing 0, 1, 2 and 3 wt% NF cured in tap water for 28 days then heat treated up to 800 °C was studied. The values are graphically plotted as a function of heat treatment temperature and NF content in Fig. 6. It is clear that the weight loss increases with temperature due to the evaporation of free water and the decomposition of hydration products.

As the temperature increases, the weight loss of all cement pastes increases. Portland cement pastes give lower values than those containing 2 and 3 wt% NF up to 450 °C. This may be due to the low mixing water which tends to decrease the weight loss. At 600 °C the weight loss of OstePC pa is higher than all cement pastes containing 1, 2 and 3 wt% NF. Generally, cement pastes incorporated with 1 wt% NF show the lowest weight losses up to 800 °C due to their lower mixing water in relation to 2 and 3 wt%. The weight loss of cement pastes increases with the NF content up to 800 °C. The decrease of the weight loss of admixed cement pastes at higher temperatures may be attributed to the effect of NF to enhance the formation of hydration products which precipitated in the open pores with low free water. Therefore, the neat OPC pastes give higher weight losses.

Bulk density. The bulk density of thermally treated OPC pastes admixed with nano iron oxide is graphically represented up to 800 °C in Fig. 7. The bulk density of all cement pastes decreases from 105 up to 250 °C, due to the removal of free and/or adsorbed water as well as combined water from CSH and CASH. This leads to the formation of micro-cracks from the decomposition of hydration products forming a sort of opening of the pore system of cement pastes then the bulk density decreases. From 250 °C up to 800 °C the bulk density is accompanied by an increase for all cement pastes. This is attributed to the volume shrinkage leading to a dense structure, as well as the reaction of aluminosilicate material with the decomposed CaO from $Ca(OH)_2$ forming ceramic and hard products.

Bulk density of cement pastes with NF is higher than ordinary Portland cement pastes at all firing temperatures. This is due to that NF particles act as a foreign nucleation site which could accelerate C–S–H gel formation as a result of increased crystalline $Ca(OH)_2$ amount that leads to a more compact and dense structure [34]. It is clear that the bulk density of OPC
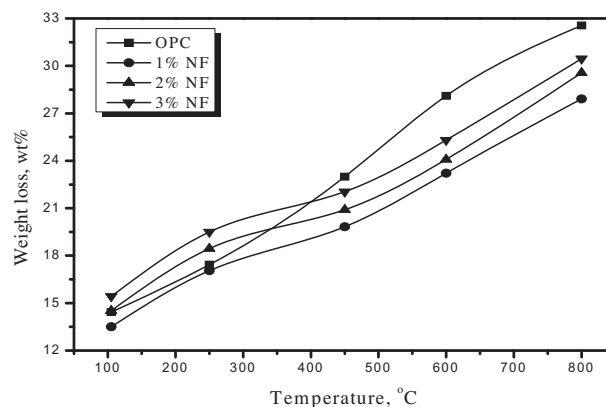

Fig. 6 Weight loss of OPC pastes admixed with 1, 2 and 3 wt% NF prepared at 275 °C with heat treatment temperature.
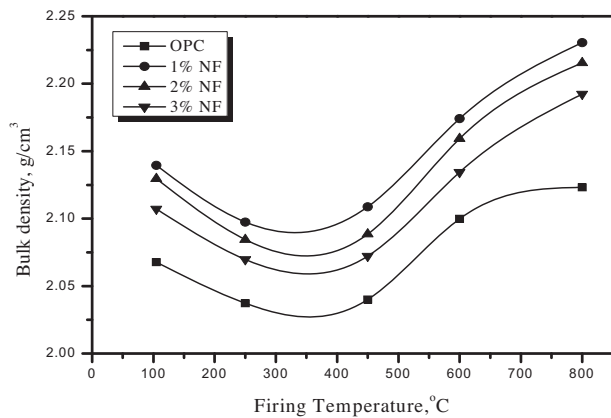
Fig. 7 Bulk density of OPC admixed with 1, 2, and 3 wt% NF prepared at 275 °C as a function of heat treatment temperature.

paste is lower than that incorporating with NF. 1 wt% NF gives higher bulk density than that containing 2 and 3 wt% NF.

Total porosity. The values of total porosity of cement pastes admixed with 0, 1, 2 and 3 wt% NF are graphically plotted as a function of heat treatment temperature and NF content in Fig. 8. It is clear that the total porosity decreases for all cement pastes up to 250 °C. This is mainly due to the self auto-claving of cement pastes which leads to an increase in the rate of hydration and formation of hydration products that precipitated in the open pores. Therefore, total porosity of the cement pastes decreases. On the other side, the increase of NF content in the cement pastes gives higher values of total porosity due to the increase of water of consistency. As the temperature increases up to 600 °C, some amount of water from CSH and CASH in addition to water from the dehydr-oxylation of $Ca(OH)_2$ evaporates. This leads to an increase in the total porosity of cement pastes.

Generally the total porosity of cement pastes incorporated with NF is lower than that of the plain OPC paste free from NF. This is mainly due to the filler effect of the nano-particles
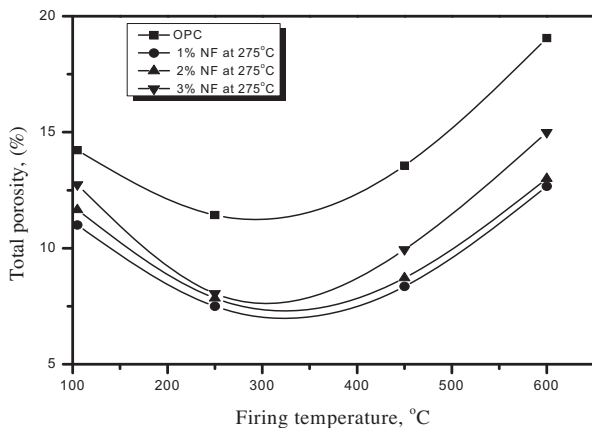
(NF). It is also clear that 1 wt% gives lower porosity than that containing 2 and 3 wt% NF.

Nazari and Riahi [32] studied the effect of nano-Fe_2O_3 on the water absorption of admixed cement pastes. It was found that Fe_2O_3 nanoparticles up to 2 wt% produce concrete with improved resistance to water permeability or the porosity decreases.

Compressive strength. The compressive strength of cement pastes admixed with NF and heat treated up to 600 °C is plotted in Fig. 9. It is clear that the compressive strength of cement pastes increases up to 350 °C as a result of enhancing the hydration of cement pastes [50] as well as increasing the rate of hydration due to self autoclaving which increases the hydra-tion products especially CSH that precipitated in the open pores. Therefore, the compressive strength of cement pastes increases for all cement pastes. At 450 °C the compressive strength of cement pastes is higher than that of the control at 105 °C and nearly the same values at 250 °C. As the temper-ature increases up to 600 °C, the compressive strength of cement pastes decreases due to the decomposition of the cementitious materials CSH, as well as $Ca(OH)_2$ forming micro-cracks. All cement pastes containing NF give higher strength values at all heating temperatures than those of OPC pastes. Also, 1 wt% NF shows higher values than those incorporating with 2 and 3 wt% NF due to the decrease of water of consistency. The addition of NF as a foreign nucle-ation site could accelerate CSH gel formation, as a result of increased crystalline $Ca(OH)_2$ content and hence increased the strength. The sharp drop of compressive strength of all cement pastes is mainly attributed to the decomposition of $Ca(OH)_2$ leading to the formation of CaO with microcracks which has no binding properties and fast hydration. The mech-anism to refine the pore structure by nano-particles is explained as follows. Assuming that the nano-particles are uni-formly dispersed in the cement and each particle is contained in a cubic model, the distance between the nano-particles can be determined. After the hydration starts, hydrates spread and envelop the nano-particles. If the content of nano-particle sand and the distance between them are appropriate, the crys-tallization will be controlled under a suitable condition limiting

Fig. 8 Total porosity of OPC pastes admixed with NF prepared at 275 °C as a function of heat treatment temperature.
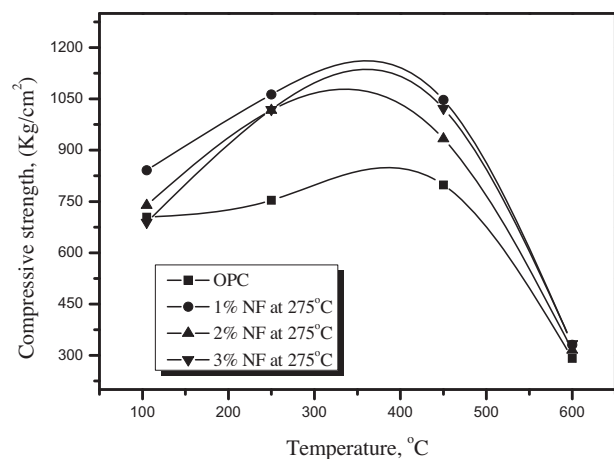

Fig. 9 Compressive strength of OPC admixed with NF (prepared at 275 °C) as a function of NF content and heat treatment temperature.

the growth of $Ca(OH)_2$ crystal by nano-particles. In addition, nano-particles in the cement paste can also promote hydration of cement due to their high activity. This makes the cement matrix more homogeneous and compact [51].

An earlier study was concerned with the preparation of Cu–Zn nano ferrite particles admixed with cement to show the effect of heat treatment at 200 and 400 °C. Cement pastes were tested at normal temperature, and others were tested after 2 h of exposure at elevated temperatures of 200 and 400 °C. The results showed that the optimum content of nano-ferrite was 1 wt% to produce the maximum increase in the compressive strength [52].

Ginebara et al. [53] reported that particle size can greatly affect the rate of cement hydration. Their findings indicate that a reduction in particle size can lead to a more rapid setting and hardening of cement paste due to stronger electrostatic attractive forces and a greater specific surface area.

Scanning electron microscopy studies on the microstructure of cement mortar admixed with NF showed that the nanoparticles fill the pores and reduce the large crystals of $Ca(OH)_2$ and the hydration products are denser and compact. The increase of Fe_2O_3 nanoparticles up to 5 wt% reduces the mechanical properties [53].

Conclusion

The following conclusions can be derived from the above findings:

1. Thermal heat treatment of basic ferric acetate fired at 275, 600 and 800 °C gives magnetite as the main phase with hematite at 275 °C. At 600 °C, hematite increases at the expense of magnetite whereas that fired at 800 °C shows nearly hematite with little magnetite.
2. OPC admixed with 1 wt% NF prepared at 275 °C gives the optimum amount to achieve fire resistance when compared to 2 and 3 wt% NF. It shows higher compressive strength as well as bulk density and lower total porosity as a function of heat treatment temperature.
3. Bulk density and total porosity of cement pastes decrease with heat treatment up to nearly 350 °C and then increase, whereas the compressive strength increases up to 450 °C then decreases with heat treatment up to 600 °C.

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