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Hydration and Physico-Mechanical Characteristics of OPC Pastes Admixed with Nano-ferric Oxide

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Abstract: ***The present work aims to study the effect of ferric oxide nanoparticles (NF) on the hydration as well as physico-mechanical characteristics of cement pastes admixed with 1.0, 2.0 and 3.0 mass% NF of cement. In a previous work, the NF was prepared by thermal decomposition of $Fe(CH_3COO)_2(OH)$ at 275, 600 or 800°C. It was found that the crystal size of NF as well as the water of consistency of admixed pastes increase and the setting times elongate with firing temperature. It was also found that 1.0 mass % NF prepared at any temperature shows the optimum amount to give a reasonable results up to 90 days. On the other hand 1.0 % NF prepared at 275°C gives better results than those fired at 600 and 800°C. As the amount of NF increased, the properties are negatively affected. The results of combined water, DTA, DSC and FT-IR are in a good agreement***.

Keywords: Nano-ferric oxide (NF), Water of consistency, Setting time, Physico-mechanical characteristics

1. Introduction

Nanotechnology is widely regarded as one of the twenty-first century's key technologies, and its economic importance is sharply on the rise. In the construction industry, nano-materials has potentials that are already usable today, especially the functional characteristics such as increased strength, self-cleaning capacity, fire resistance, and additives based on nano-materials make common materials lighter and more resistant to wear. It has been demonstrated that nanotechnology has invented products with many unique characteristics which could significantly provide solutions current construction issues and many change the requirement and organization of construction process [1].

Nano engineering or nano modification to the cement based materials is an active area of research at present [2]. But, comparing with the other fields, concrete has been slow to catch the emerging enhancements of nanotechnology. Nanotechnology and nanostructures materials represent an evolving technology that has an impact on a wide number of industry and markets. It deals with the synthesis of materials, structures and/or devices having dimensions up to ≈ 100 nm with new properties. This is mainly due to the lack of basic understanding of concrete at nano level and the lack of broad understanding of what nano modification means to concrete [3]. Concrete is a nano-structured multi phased composite material consisting of an amorphous phase, nano- to micro meter sized crystals and bound water. Therefore, addition of suitable nano-particles can alter many properties of concrete. Nanomaterials have different properties as the increased relative surface area and new quantum effects. They have much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength [4].

The effect of the addition of some metal oxide nanoparticles to concrete which can both reduce the permeability of concrete to ions and increase the strength, thereby improving durability was carried out. In civil engineering field, most of the research works till date are conducted with nano silica (nano SiO_2) [5-13]. Nano silica increased the strength, flexibility, workability and durability of concrete as well as the viscosity of the fluid phase of concrete and fill the voids between cement grains. It reacts with calcium hydroxide (CH) forming more calcium silicate hydrate (CSH). The mechanical properties of concrete are controlled by CSH which is a nano porous, nano-structured material [3]. Nano silica acts as a nucleation site for formation of CSH giving high strength than conventional concrete [3,14-16]. Incorporating nano silica improved the hydration of cement due to the large reactive surface area of nano particles [2,17].

There has been few research carried out to study the effect of nano TiO_2 in concrete mixes [18-23]. TiO_2 is an inert material, it will not participate in the reaction within the cement paste, but the rate as well as the peak of hydration of concrete increased due to the heterogeneous nucleation. Nano TiO_2 improves compressive and flexural strengths as well as enhanced the abrasion resistance of concrete [24].

Partial replacement of cement with nano Fe_2O_3 (NF) increased the flexural and compressive strengths as well as fire resisting of cement paste and concrete [25-31]. Another nano-material which has been incorporated with concrete is nano Al_2O_3 [32-36]. Partial replacement of cement with nano Al_2O_3 (NA) particles improves the compressive, flexural and split tensile strengths of mortar, but decreases its workability and setting time.

Some researchers have employed nanoparticles into cementitious materials-based on Portland cement (PC) to modify some properties of this system. A paper presents an overview of works carried out on the effect of using nano-Al_2O_3, nano-Fe_2O_3, nano-Fe_3O_4 and nano-clay into the cementitious materials. Some properties of the modified composites as heat of hydration, workability, setting time, mechanical strength, water absorption and durability were reviewed [37].

Yazdi et al, [29] studied the mechanical properties, at 7 days, of mortars modified with NF. Cement was partially replaced with 1, 3 and 5 mass% NF. The results showed an increase in both compressive and tensile strengths with the addition of 1 and 3 mass% NF, whilst 5 mass% NF decreased the strengths. Nazari et al, [26,27] 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 that the workability reduced with NF content and both the initial as well as final setting times shortened with NF. 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 mass% NF, respectively. Therefore, 1.0 mass% NF is the optimal amount.

Nazari and Riahi [30] investigated the optimal NF content that gave the highest tensile strength, of concretes at 7, 28 and 90 days. Cement was partially replaced with 0.5, 1.0, 1.5 and 2.0 mass% NF. Two different curing conditions were employed, either water curing or saturated limewater curing. The NF specimens cured in saturated limewater had higher strength than that cured in water. The same article studied also the percentage of water absorption, velocity and coefficient of water absorption of binary blended concrete with replacement NF. The results showed that using NF up to maximum replacement of 2.0 mass% NF produces concrete with improved resistant to water permeability. NF can improve the filler effect as well as its pozzolanic action and thereby increases the quantity of CFH gel which responsible for the reduction of water permeability.

Khoshakhlagh et al. [25] studied the heat of hydration of pastes admixed with NF up to 70 h. Cement was partially replaced with 0, 1, 2, 3, 4 and 5 mass% NF. It was found that the replacement of NF accelerated peak times and dropped heat rate values due to the acceleration of cement hydration. Cement was partially replaced with the same NF levels and 1 mass%, of superplasticizer was employed. The strengths increased with the addition of NF, at all ages. The addition of 4 mass% 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 addition of 1, 2, 3, 4 and 5%, respectively. It was reported that NF acted as a foreign nucleation site that accelerated CSH gel formation as a result crystalline $Ca(OH)_2$ amount especially at early age of hydration as well as the strength increased.

The effect of magnetite nanoparticles on the hydration characteristics of ordinary Portland cement (OPC) paste admixed with 0.05, 0.1, and 0.3 mass% of magnetic fluid Fe_3O_4 nanoparticles by mass of cement was studied [38]. An aqueous stable magnetite fluid containing Fe_3O_4 nanoparticles, with mean diameter in the range of super-paramagntism, was prepared via co-precipitation method from ferrous and ferric solutions. The compressive strength of hardened admixed OPC pastes shows higher values than those of neat OPC pastes at all curing times. The chemically-combined water contents have almost the same general trend and nearly comparable values as those of neat cement pastes. XRD patterns of neat OPC pastes show the main hydration products such as CSH, Portlandite and calcium sulphoaluminate hydrates. The addition of Fe_3O_4 fluid nanoparticles illustrates the formation of calcium ferrite silicate hydrate (ivalite) as a new hydration product with a reasonable hydration character [38].

The aim of the present investigation is to study the hydration characteristics of OPC pastes admixed with nano-ferric oxide (NF) prepared at different temperatures up to 800°C.

2. Materials and Methods

2.1. Materials

The materials used in this investigation are Ordinary Portland cement (OPC) provided from Suez company, Suez, Egypt, and basic Ferric acetate $[Fe(CH_3COO)_2OH]$ was used as chemical grade. The chemical analysis of OPC is SiO_2 = 19.58, Al_2O_3 = 4.76, Fe_2O_3 = 3.39, CaO = 62.88, MgO = 1.67, SO_3 = 2.99, K_2O = 0.14, Na_2O = 0.22, Cl^- = 0.03 and Loss on ignition = 4.07 , mass%. The phase composition of OPC is C_3S = 59.72, C_2S = 10.53, C_3A = 6.88 and C_4AF = 10.30 mass%, whereas its surface area is 3025±50 cm^2/g.

The nano-ferric oxide (NF) was prepared after firing of basic ferric acetate at 275, 600 and 800°C for one hour soaking time and characterized [31]. The phase composition of the sample fired at 275°C shows the appearance of magnetite Fe_3O_4 with some hematite Fe_2O_3. As firing temperature increases the hematite appears on the expense of magnetite as shown in Fig. (1). The crystal size of the sample fired at 275, 600, 800°C is examined by the aid of TEM about 14.6, 16.98 and 18.6nm, respectively [31].

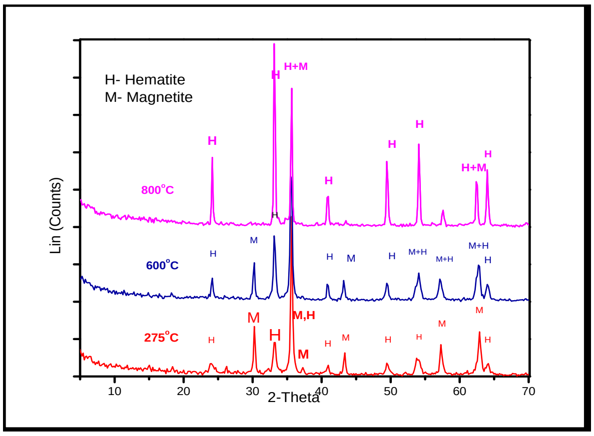

Figure 1: XRD of NF prepared by thermal decomposition at different temperatures [31]

2.2. Methods of Investigation

The dry constituents of each mix of OPC as well as well as admixed with 1, 2 & 3 wt % NF prepared at 275, 600 and 800°C were mechanically blended for one hour in a porcelain ball mill using four balls to attain complete homogeneity, then kept in air tight containers till the time of paste preparation.

The water of consistency and the initial as well as final setting times were determined using Vicat Apparatus according to ASTM methods [39]. The mixing of cement powder for further investigation was carried out with the required water of consistency. The required amount of water was poured into the crater by the aid of a trowel. The mixing operation was then completed by continuous vigorous mixing for three minutes with gauging trowel. At the end of mixing, the pastes were directly poured in 2cm cubic stainless steel moulds into two approximately equal layers. Each layer was compacted and pressed until homogenous specimen was obtained then manually vibrated for a few minutes to remove any air bubbles to give a better compaction of the paste. Immediately after molding, the specimens were cured in 100% R.H. at room temperature 23±2 °C for 24 h., then demoulded and cured under water up to 90 days. Hydration behavior of each mix was followed by the determination of combined water contents from the ignition loss of dried pastes, bulk density, total porosity [40]. The compressive strength of cement pastes was determined according to ASTM C191[39] Some selected hydrated cement pastes were also investigated using DTA, DTG, DSC, FTIR and SEM techniques to show the formed hydration products.

3. Results and Discussion

3.1. Hydration of cement pastes admixed with NF nanoparticles

3.1.1. Water of consistency and setting time

The water of consistency as well as initial and final setting times of the cement pastes admixed with 1, 2 and 3 mass% of NF prepared at 275, 600 and 800°C are tabulated in Table 1. The water of consistency of various cement pastes admixed with NF is generally slightly higher than that of neat Portland cement pastes. This may be due to the higher surface area of (NF) nanoparticles in comparison with (OPC). The initial setting time of admixed cement pastes is shortened at 2.0 and 3.0 mass% NF prepared at 275 °C. On the other hand, NF fired at 600 and 800 °C shows only elongation at 1.0 % and still constant up to 3.0 % which may be attributed to the increase of water of consistency as well the increase of crystal size of NF.

3.1.2. Chemically combined water contents

The combined water contents of the hydrated admixed cement pastes with 1, 2 and 3 mass% NF prepared at 275, 600 and 800°C up to 90 days are tabulated in Table 2. The data shows a continuous increase of the combined water contents with curing time for all cement pastes. Cement pastes admixed with 1, 2 and 3 mass% NF show higher values of combined water than those of neat OPC pastes at the later ages of hydration, since the iron oxide nanoparticles act as filler or nucleating agent which accelerates the rate of hydration.

The increase of combined water contents of cement pastes admixed with 2 and 3 mass% NF are mainly due to the increase of the mixing water. As the amount of NF increases up to 3 mass% the combined water contents increase due to that the quantity of NF is higher than that required for combination with the portlandite during hydration, consequently leads to excess silica leaching out [27]. The increase of leached silica may be due to the alkali-silica reaction with high water content.

Table 1: Water of consistency and setting times of cement pastes admixed with1, 2 & 3 % NF prepared at different temperatures

Mix Comp.	Water of consistency	Setting time, min	
		initial	Final
(a) NF prepared at 275°C			
1% NF	28.3	88	179
2% NF	28.7	80	188
3% NF	29.2	77	190
(b) NF prepared at 600°C			
1% NF	28.4	94	187
2% NF	29.6	95	195
3% NF	30.01	97	199
(c) NF prepared at 800°C			
1% NF	28.3	88	189
2% NF	28.7	80	190
3% NF	29.2	77	193

Table 2: Combined water contents of cement pastes admixed with 1, 2 & 3% NF prepared at different temperatures

Time, days	**Combined water contents, %**			
Mix	3	7	28	90
OPC	15.15	15.57	17.10	17.81
(a) NF prepared at 275°C				
1% NF	15.62	16.38	18.38	18.92
2% NF	15.58	16.76	18.53	19.10
3% NF	16.46	17.46	18.53	19.33
(b) NF prepared at 600°C				
1% NF	14.91	16.64	17.85	18.97
2% NF	14.87	16.87	18.29	19.52
3% NF	14.81	17.04	18.30	19.25
(c) NF prepared at 800°C				
1% NF	15.3	15.81	17.64	18.10
2% NF	15.91	16.25	17.99	18.38
3% NF	16.13	16.54	18.14	18.58

On prolong hydration (90 day) the admixed cement pastes give higher combined water contents than those of neat OPC paste. Generally, the combined water contents of all cement pastes increase with curing time due to the continuous hydration and formation of hydration products. Also, as the firing temperature of NF increases the combined water contents diminish due to the increase of the crystal size with firing temperature.

3.1.3. Differential thermal analysis

Figure (2) shows the DTA/DTG curves of OPC and OPC admixed with 3mass% NF fired at 275°C and cured for 90 days. The curves show four endothermic peaks located at 60-275°C, 350-400°C, 420-500°C and 680-740°C. The endothermic peaks at (60-275°C) and (350-400°C) are mainly attributed to the decomposition of CSH tobermorite-like gel as well as calcium sulphoaluminate hydrates AFt or AFm and calcium ferrite silicate hydrate or CFH [30,38]. The endothermic peak located at (420-500°C) is due to the hydroxylation of portlandite. The last endothermic peak at (680-740°C) is due to the decomposition of $CaCO_3$. [41].

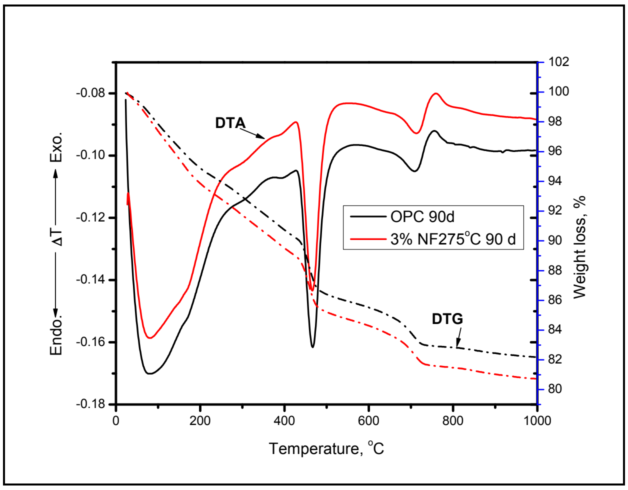

Figure 2: DTA/DTG thermograms of OPC and admixed with 3% NF prepared at 275°C cured for 90 days

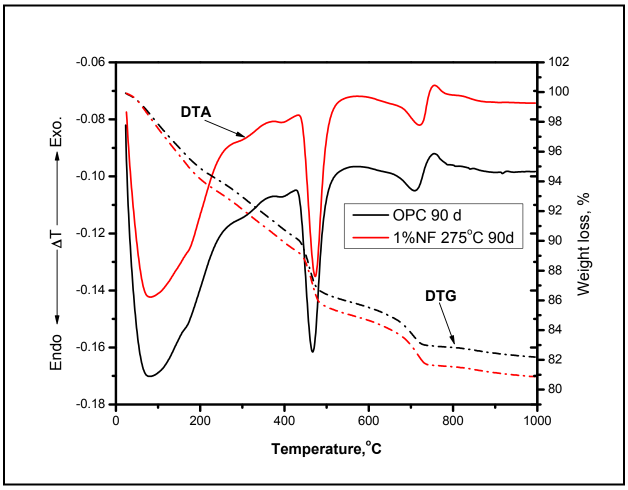

Figure 3: DTA/DTG thermograms of OPC and admixed with 1% NF prepared at 275°C cured for 90 days

DTG curves of OPC and OPC admixed with 3 mass% NF are graphically plotted in Fig. 2. It is clear that the NF accelerates the rate of hydration as shown from the weight loss up to nearly 420 °C due to the decomposition of CSH tobermonite-like gel as well as sulphoaluminate hydrates and calcium ferrite silicate hydrate (CFSH) [30,38]. The admixed cement paste with 3mass% NF gives TG loss of 8.32 mass% in comparison with 7.20 mass% of OPC paste. This is due the nucleating effect of NF. On the other hand, the weight loss of the dehyroxylation of portlandite up to 600°C is 7.32 and 7.15 mass% of admixed Portland cement with NF and neat OPC paste, respectively.

The DTG loss of the decomposition of $CaCO_3$ at 680 to 725°C is 3.63 and 3.44 mass% for OPC admixed with 3% NF and neat OPC paste. The DTG losses of OPC as well as admixed cement pastes are a result of change in the carbonation of the cement paste [38]. It can be said that the nano-ferric oxide accelerates the rate of hydration as seen from the DTG of decomposition of CSH tobermorite-like phase, sulpho-aluminate hydrates AFt & AFm, CFSH as well as portlandite and $CaCO_3$.

Figure (3) illustrates the DTA/DTG curves of hydrated OPC as well as admixed pastes with 1% NF prepared at 275°C and hydrated for 90 days. The curves show the same endothermic peaks located at nearly 60-275°C, 350-420°C, 420-500°C and 680-720°C. The low temperature endothermic peak is attributed to the decomposition of CSH at nearly 100°C and the other broad endotherm located at 180 is due to the decomposition of ettringite AFt as well as monosulphate hydrate AFm. The endotherm at 350-420°C is related to the decomposition of CFSH or the gel phases. The endotherm at nearly 470°C represents the dehydroxylation of portlandite. The last endothermic peak at 709-718°C corresponds to the decomposition of $CaCO_3$.

The DTG curves of the hydrated OPC as well as admixed with 1mass% NF prepared at 275°C cured for 90 days are shown in Fig. 3. The curve of OPC admixed with 1 mass% NF shows DTG of 8.63% due to the decomposition of hydrated phases up to 420°C in comparison with 7.10 mass% of OPC paste. This means that the substitution of OPC with 1.0 mass% NF improves the rate of hydration. On the other hand, the OPC and OPC admixed with 1.0 mass% NF give 7.15 and 6.63 mass% of portlandite, respectively. The decrease of DTG of portlandite in OPC admixed with 1.0 mass% NF may be due to the low crystallinity of this phase as seen from the DSC results. It can be said that 1.0 mass% NF accelerates the hydration of OPC due to its nucleating effect in addition to its high surface area. Finally, the weight loss of OPC and OPC admixed with 1.0 mass% NF is 3.44 and 3.87%, respectively. The increase of the weight loss of OPC admixed with 1.0 mass% NF of the decomposition of $CaCO_3$ may be due to the carbonation of some of portlandite to give $CaCO_3$.

The DTA/DTG curves of the OPC admixed with 3 mass% NF prepared at 275 and 600°C cured for 90 days are seen in Fig. 4. The curves show the same hydration products such as CSH tobermorite-like phase, AFt, AFm, CFSH, portlandite and $CaCO_3$ [38].

Figure 4 shows the DTG of the hydrated OPC admixed with 3 mass% NF prepared at 275 and 600°C cured for 90 days. The TG losses of OPC + 3 mass% NF fired 275°C are 8.322, 7.322 and 3.629% in comparison with those admixed with 3% NF fired at 600°C which are 8.506, 7.015 and 3.464%, respectively. It is clear that the increase of firing temperature increases the amount and/or the crystallinity of portlandite as well as the $CaCO_3$. This is in a great agreement with the results of the DSC.

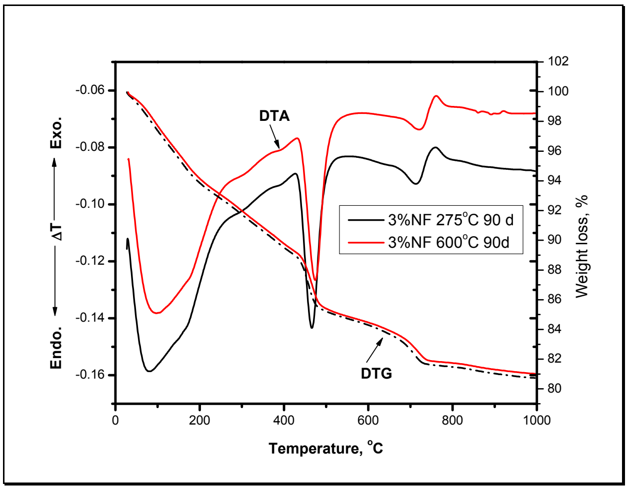

Figure 4: DTA/DTG thermograms of OPC and admixed with 3% NF prepared at 275 as well as 600^{o}C cured for 90 days

3.1.4. Differential scanning calorimetry DSC

The DSC curves of hardened OPC and admixed pastes with 1 mass% NF prepared at 275, 600 and 800^{o}C hydrated for 3 days are shown in Fig. 5. The first endothermic peaks located up to 420^{o}C are mainly due to the decomposition of CSH toberomorite-like phase as well as ettringite ferrite AFt, monosulphate ferrite AFm in addition to CFSH (ilavite) [38]. The second peaks present at nearly 460^{o}C are due to the dehydroxylation of portlandite of all hardened cement pastes. The enthalpy of OPC as well as OPC+1.0 mass% NF prepared at 275, 600 and 800^{o}C is -5.258, -3.827, -5.279 and -6.230 J/g, respectively. It is clear that the substitution of 1.0 mass% NF prepared at 275^{o}C decreases the crystallinity of the portlandite. On the other hand, NF prepared at 600 and 800^{o}C enhances the crystallinity of portlandite at early ages of hydration (3 days).

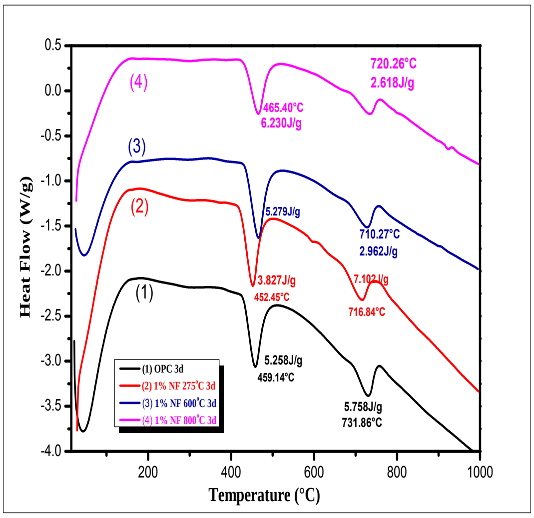

Figure 5: DSC thermogram of OPC and hydrated cement pastes admixed with 1%NF at different temperature cured for 3 days

It was found that as the firing temperature of NF increases or the hematite content increases as shown from the XRD patterns the crystallinity of portlandite enhances or the hematite accelerates the hydration of OPC. The figure shows also that the enthalpy of $CaCO_3$ of the OPC and admixed with 1.0 mass % prepared at 275, 600 and 800^{o}C is -5.758, -7.102, -2.962 and -2.618 j/g, respectively. From these values it was found that the amorphous portlandite can be carbonated faster than the crystalline phase, i.e., the enthalpy of $CaCO_3$ goes in the opposite direction of portlandite.

Figure 6 presents the DSC curves of hydrated OPC and admixed with 1 mass% NF prepared at 275, 600 as well as 800^{o}C hydrated for 90 days. The curves show the same hydration products up to 420^{o}C. The DSC curves located at nearly 470^{o}C due to the dehydroxylation of portlandite. The enthalpies of OPC as well as admixed with 1 mass% NF prepared at 275, 600 and 800^{o}C are -6.921, -4.095, -6.381 and -11.16 J/g, respectively. These enthalpies of the decomposition of portlandite are higher than those hydrated for 3 days. This is may be due to the continuous hydration of Portland cement liberating portlandite. It is explained in terms of the increase of the amount and/or the degree of crystallinity of portlandite. On the other hand, the less crystalline portlandite liberated from OPC admixed with NF prepared at 275^{o}C increases the crystallinity of portlandite at later ages (90 days). This means that 1.0 mass% NF prepared at 275^{o}C is sufficient to accelerate the hydration of portlandite cement up to 90 days. The DSC curves located at 712-728^{o}C are due to the decomposition of $CaCO_3$ of admixed OPC.

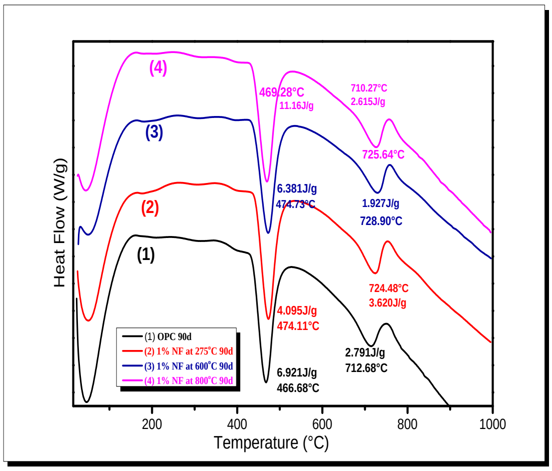

Figure 6: DSC thermogram of OPC paste and admixed with 1mass% NF fired at 275, 600 & 800^{o}C cured for 90 days

The DSC curves of neat OPC and admixed pastes with 3 mass% NF prepared at 275, 600 and 800^{o}C hydrated for 3 days are seen in Fig. 7. The peak located at ≈ 470^{o}C related to the dehydroxylation of portlandite of admixed OPC with 3 mass% NF that decomposes at higher temperatures than those containing only 1 mass% NF. The increase of NF accelerates the hydration of Portland cement at early ages of hydration. The enthalpies of OPC as well as admixed cement pastes are -5.258, -11.59, -8.916 and -5.211 for OPC and admixed with 3 mass% NF prepared at 275, 600 and 800^{o}C, respectively. It is clear that the enthalpy of admixed OPC with 3 mass% NF behaves in opposite direction to that containing only 1 mass%. It means that as the amount of NF increases up to 3 mass% the NF prepared at 275°C is more accelerator than that fired at 600 and 800°C. The endothermic peaks present at nearly 730°C are due to the decomposition of $CaCO_3$. The enthalpies of OPC as well as admixed pastes with 3 mass% NF prepared at 275, 600 and 800°C are -5.285, -2.369, -3.391 and -3.547 J/g, respectively. It was found that the more crystalline portlandite retards its carbonation, i.e., NF prepared at 275°C accelerates the carbonation than those prepared at 600 and 800°C.

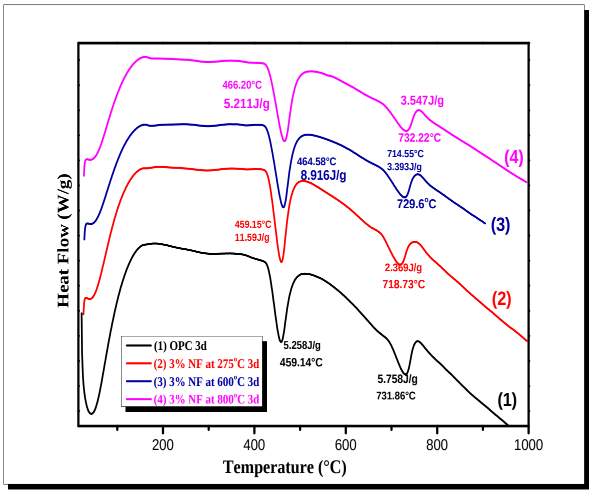

Figure 7: DSC curves of OPC paste and admixed with 3mass% NF fired at 275,600 & 800°C cured for 3days

3.1.5. FTIR spectra of hydrated cement pastes

Figure 8 illustrates the FTIR spectra of hydrated OPC pastes admixed with 1, 2 and 3 mass% NF prepared at 800°C and cured up to 28 days. The OH band from $Ca(OH)_2$ appears at 3640 cm^{-1} while the water bands appear at approximately 3440 stretching and 1660 bending cm^{-1}, respectively [42,43]. A broad band at 3448 cm^{-1} attributed to a stretching vibration of water bond in the hydration products [44]. ν3 and ν2 stretching bands generated by the C–O groups in the calcite appeared at around 1434 and 875 cm^{-1} [45]. Characteristic sulphate absorption bands are generally found in the range 1200–1100 cm^{-1} due to the υ3 vibration of the SO_4^{2-} group in sulphates [46]. Bands in the region 1100-900 cm^{-1} are due to silicate group [43,46]. The band for CSH appears at 975 cm^{-1} (Si–O stretching vibrations) [44,47]. The out-of-plane Si-O bending ν4 appear at 525 cm^{-1} while in-plane Si-O bending ν2 at 460 cm^{-1}. The broad bands located at 3400 and 1650-1640 cm^{-1} are assigned to the stretching and bending vibrations of water lattice in CSH, CSAH and CFSH hydrates. The band that appeared around 950 cm^{-1} is attributed to CSH which increases with time. The observed bands at about 1080 and 485 cm^{-1} may be due to SO_4^{-2} associating with ettringite formation or ettringite-ferrite phase [48,49]. It is also clear that 1.0 mass% NF shows the lower ν3 and ν2 stretching bands generated by the C-O group in the calcite at 1434 and 871 cm^{-1}. The carbonation extent increases with the amount of NF such as 2 and 3 mass%. On the other hand, OPC paste shows the higher rate of carbonation than all admixed cement pastes. The small OH bands from $Ca(OH)_2$ of the admixed cement paste may be due to its reaction with Fe_2O_3 and leached SiO_2 formed CFSH. This means that NF enhances crystallinity of portlandite and then retards the carbonation of cement paste.

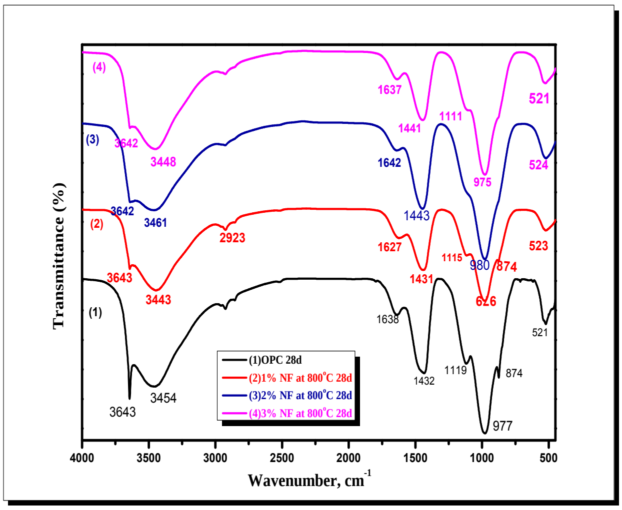

Figure 8: FTIR of OPC and admixed with 1, 2 & 3mass% NF fired at 800°C hydrated for 28 days

Figure 9 shows the FTIR spectra of OPC pastes hydrated for 3 and 28 days. The OH band from $Ca(OH)_2$ appears at 3643 cm^{-1} while the water band appears at nearly 3440 cm^{-1} stretching and 1600 cm^{-1} bending, respectively [42,43]. broad band at 3448 cm^{-1} attributed to stretching vibration of water bound in the hydration products. From the spectra it is clear that the band of $Ca(OH)_2$ increases from 3 to 28 days due to the continuous hydration of silicate phases liberating free lime with time.

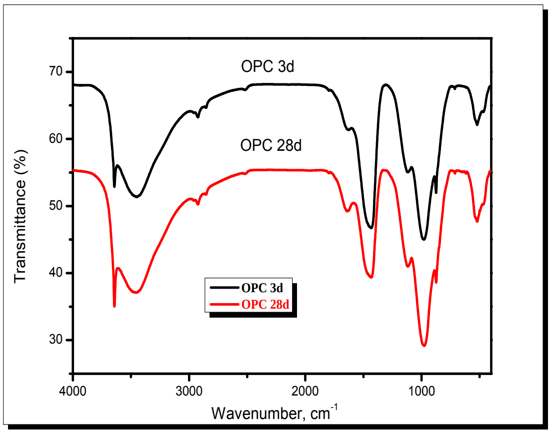

Figure 9: FTIR of OPC pastes hydrated for 3 and 28 days

3.1.6. Total porosity

The total porosity of hardened OPC pastes and admixed with 1, 2 and 3 mass% NF fired at 275, 600 and 800°C cured up to 90 days are tabulated in Table 3. Obviously, the total porosity decreases with curing time for all cement pastes due to the filling up of a part of the available pore volume with some of hydration products. Hardened NF admixed cement pastes give lower values of total porosity than those of the neat Portland cement pastes. This is due to the higher rate of hydration of admixed cement pastes in comparison to OPC especially at later ages. Regarding to the addition of nanoparticles to PC pastes, they have important implication 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 [50].

Table 3: Total porosity of OPC and OPC admixed with 1,2,and 3% NF prepared at different temperatures cured up to 90 days

Time, days Mix	Total porosity, %			
	3	7	28	90
OPC	35.45	34.23	33.05	31.81
(a) NF prepared at 275^{o}C				
1% NF	34.77	34.18	30.61	29.30
2% NF	35.61	34.23	32.69	30.14
3% NF	35.97	34.28	32.80	31.60
(b) NF prepared at 600^{o}C				
1% NF	34.00	33.31	30.93	29.76
2% NF	34.47	34.48	32. 13	30.05
3% NF	34.53	34.20	33.00	31.30
(c) NF prepared at 800^{o}C				
1% NF	32.58	32.16	31.52	30.30
2% NF	32.67	32.73	32.67	30.80
3% NF	34.69	34.36	34.20	33.10

As the hydration proceeds, there is a noticeable difference between the values of porosity of all cement pastes. The high total porosity of OPC admixed with 3% NF fired at 800^{o}C is mainly due to the decrease of surface area of NF nanoparticles which has low pozzolanic reaction. Cement pastes admixed with 3 mass% NF fired at 275^{o}C gives higher values than those containing 2 and 1 mass%. The lower porosity of OPC paste at 3 days is due to the lower water of consistency. The porosity of OPC paste is higher than that of NF admixed cement pastes. Also, 1.0 mass% NF gives the lower values of porosity after 7days up to 90 days. It was found that the total porosity decreases in the direction 3 > 2 > 1 mass% NF. These results are in good agreement with those of combined water contents. 3 mass% NF fired at 800^{o}C admixed cement pastes give higher porosity than those of OPC pastes at all ages of hydration. This may be due to the increase of crystal size and low surface area of NF particles which retard the hydration then increase the porosity. NF nanoparticles can improve the filler effect and also the high pozzolanic action of fine particles, which increase substantially the quantity of CSH gel. If this phenomenon joints with the low w/c ratio, it can improve the microstructure in the interfacial transition zones and thus CFSH cement gel decreases the water permeability which increases the density and compressive strength [30].

The water permeability of the specimens improved up to 3 mass% of nano iron oxide. NF particles as a foreign nucleation site could accelerate $Ca(OH)_2$ content especially at early ages and hence increase the strength. In addition, NF nano-particles are able to act as nano-filler and recover the pore structure of the pastes by decreasing harmful pores to improve the water permeability**.** 3 mass% NF fired at 800^{o}C admixed with OPC gives higher values of total porosity than those of OPC pastes. The increase of NF up to 3 mass% increases its quantity than the required for combination with liberated portlandite during the hydration, thus leads to excess silica leaching out forming CFSH with high water content which increases the porosity [27].

3.1.7. Bulk density

The bulk density of the hardened neat OPC pastes and admixed with 1, 2 and 3 mass% NF fired at 275, 600 and 800^{o}C cured up to 90 days is tabulated in table 4. The results indicate that the bulk density for all cement pastes increases up to 90 days. As the hydration reaction proceeds, more hydration products are formed and then precipitated in the pores originally filled with water leading to increase the bulk density. The hardened OPC pastes admixed with NF have relatively higher values of bulk density than those of neat OPC at later ages of hydration. The substitution of NF nanoparticles with the cement up to 3 mass% acts as a foreign nucleation site which could accelerate CSH gel formation as a result of increased crystalline $Ca(OH)_2$ amount and hence increase the bulk density of the cement pastes. In addition, NFnano-particles are able to act as nano-fillers and recover the pore structure of the pastes by decreasing harmful pores leading to a more compact and dense structure higher than neat OPC pastes [27].

Table 4: Bulk density of OPC and OPC admixed with 1, 2 and 3% NF prepared at different temperatures cured up to 90 days

Time, days Mix	**Bulk density, g/cm^{3}**			
	3	**7**	**28**	**90**
OPC	2.2301	2.2549	2.2802	2.2983
(a) NF prepared at 275^{o}C				
1% NF	2.2475	2.2806	2.2956	2.3084
2% NF	2.2443	2.2658	2.2877	2.2981
3% NF	2.2429	2.2617	2.2845	2.2975
(b) NF prepared at 600^{o}C				
1% NF	2.3047	2.3053	2.3106	2.3117
2% NF	2.2741	2.2834	2.2954	2.3037
3% NF	2.2722	2.2785	2.2924	2.3001
(c) NF prepared at 800^{o}C				
1% NF	2.2949	2.3051	2.3151	2.3196
2% NF	2.2860	2.2943	2.2993	2.3082
3% NF	2.2777	2.2788	2.2988	2.3031

Cement pastes admixed with 1mass% NF give higher bulk density than that containing 2 and 3mass%. As the amount of NF increases up to 3%, this amount is higher than that required for combination with the liberated lime during the hydration, thus leads to excess silica leaching out [27]. The increase of leached silica is due to the alkali-acidic reaction forming soluble silicates with low density. This may be also due to that the increase of the NF content increases the water of consistency [30]. The increase of bulk density of admixed cement pastes at the early hydration period can be attributed to the acceleration of the hydration reaction. In addition, the NF interaction with the liberated portlandite leads to the formation of hydration product similar to Al-etttingite as Fe-ettringite with a reasonable hydraulic character [51]. Therefore, more hydration products are formed which improve the cement microstructure.

It can be concluded that 1mass% NF fired at any temperature such as 275, 600 and 800^{o}C admixed with OPC pastes gives higher bulk density comparable to 2 , 3mass% NF and the blank OPC.

3.1.8. Compressive strength

The compressive strength of the OPC pastes and admixed with 1, 2 and 3 mass% NF fired at 275, 600 and 800^{o}C hydrated up to 90 days is is tabulated in table 4. It is clear that 1% NF shows the optimum content which gives the higher compressive strength at later ages. As the amount of NF increases up to 3% the compressive strength decreases due to the fact that the quantity of NF in the paste is higher than that required for combination with the liberated lime, leading to excess silica leaching out caused a decrease in strength. This leaching decreases the amount of CSH tobermorite-like gel which is the main source of compressive strength. It may be due to the defects generated in dispersion of nanoparticles that caused weak zones [27,52].

It can be concluded that 1.0 mass% NF fired at 275, 600 and 800°C admixed with OPC gives the highest compressive strength of all cement pastes. Also, all cement pastes admixed with 1, 2 or 3 mass% NF show higher strength values than those of OPC pastes. The decrease of compressive strength with the NF content may be due to the increase of the leaching of silicate forming CFSH with low strength. The increase of NF content leads to increase water of consistency and the total porosity then the compressive strength diminishes.

Ginebra et al., [53] reported that the particle size can greatly affect the hydration kinetics of cement paste. Their findings indicate that a reduction in particle size can lead to a more rapid setting and hardening of the cement paste due to stronger electrostatic attractive forces and a greater specific surface. Other studies have shown that the compressive strength of cement mortars admixed with SiO_2 and Fe_2O_3 nanoparticles were higher than those of the plain cement mortars [54]. The rate of pozzolanic reaction is proportional to the amount of surface area available for reaction.

The increase of compressive strength in the presence of n-Fe_3O_4 especially in the early ages of hydration can be attributed to the acceleration by the Fe_3O_4 nano-particles. In addition the interaction of n-Fe_3O_4 with liberated $Ca(OH)_2$ leads to formation of ettringite-ferrite phase and/or mono sulphate ferrite hydrates[38,51]. As consequence hydration of cement is accelerated and larger amounts of hydration products are formed which improve the cement microstructure. Therefore, the Fe_3O_4 nano-particles act as nuclei for the deposition of the formed cement hydration products leading to resort of acceleration of the hydration process [28].

4. Conclusions

From the above findings it can concluded that :

1. The water of consistency of NF admixed cement pastes increases with NF content prepared at 275, 600 and 800 °C. On the other hand, there is slight effect on the initial and final setting times with NF content.
2. All admixed cement pastes give higher combined water contents than those of neat OPC pastes up to 90 days. The combined water contents increase with NF content due to the increase of water of consistency.
3. The results of DTA
4. It was found that 1 mass% NF prepared at 275°C decreases the crystallinity of portlandite at 3 days but the crystallinity increases at 90 days. The enthalbies of OPC pastes admixed with 3 mass% NF increase with firing temperature at 90 days.
5. Cement pastes admixed with 1.0 mass% NF prepared at 275, 600 and 800°C show higher bulk density as well as compressive strength and lower total porosity up to 90 days. Also, 1.0 mass% NF nanoparticles prepared at 275°C admixed cement pastes give reasonable results as compared with OPC and admixed pastes with NF prepared at 600 and 800°C.

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