

Low Heat Blended Cements Containing Nanosized Particles of Natural Pumice Alone or in Combination with Granulated Blast Furnace Slag

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Abstract: The heat of hydration, water of consistency, setting times, free lime and bound water contents, density, porosity and the compressive strength development of the various blended cements containing the natural pumice (NP) and/or granulated blast furnace slag (GbfS) have been experimentally investigated. There are two groups of blended cements were prepared. The first was containing NP alone, while the second was containing both NP and GbfS. The results proved the w/c ratio as well as setting times increased as the NP and/or GbfS contents increased. The bound water contents, density and compressive strength increased as NP or NP with GbfS contents increased, only up to 20 wt. % NP (P4) in the first group, and up to equal amounts of both NP and GbfS (PS4) in the second, and then decreased with further increase. Contrary, the apparent porosity gradually decreased, and then increased. The free lime content of the blank cement increased with hydration time continuously. In presence of NP, the free lime content reduced gradually up to 90 days, while in combination of GbfS, the free lime content at first enhanced up to 3 days of hydration, and then decreased onward. So, both NP and GbfS acted as pozzolanic materials. Moreover, the NP and GbfS could be reduced the heat of hydration of all blended cement pastes when compared to that of the blank. The values of the heat of hydration of Group II were slightly lower than those of the first. Also, the heat of hydration reduced more with increasing the NP and/or GbfS ratios.

Keywords: Blended cements; NP, GbfS; consistency; setting times; density; strength; heat of hydration

1. Introduction

On account of the global warming, the need to reduce energy consumption has been increased worldwide to a large extent, and its impact could be influenced everyone on the planet. High levels of energy are required to produce cement, which always releases large amounts CO₂ and also contributes to the greenhouse gases. Atmospheric levels of CO₂ have been increased by > 30 % over the past 100 years.^[1] Each year, about 120 million tons of the controlled wastes from household, commercial and industrial wastes are disposed of in the landfill sites in many countries causing a rise in landfill costs and environmental problems.^[2]

When the cement powder is being in contact with water, the heat is released. This heat is known as the heat of hydration. The evolved heat of hydration is the result of several exothermic chemical reactions between cement and water. The heat generated due to the hydration of the major cement phases increases the temperature of concrete. Understanding the mechanism of heat generated in the cement is the key to control the temperature of the concrete mass.^[3-6] The physical and/or chemical reactions of the cement after contacting with water determine the setting and hardening properties of the cement pastes and/or concrete. The rate

of the heat of hydration of the cement plays an important role to determine the mechanical properties and durability of cement or concrete. The rate and amount of heat released are greatly depending on the cement type, the chemical composition and physical properties of the cement, the w/c- ratio, and the added supplementary cementitious materials to the cement, such as granulated blast furnace slag (GbfS), silica fume (SF), fly ash (FA), natural pumice (NP), chemical admixtures, curing conditions and atmospheric temperature.^[7-11] Cement hydration at higher environmental temperatures is accelerated at early ages but decelerated thereafter. The heat of hydration and heat reactions of the cement are faster and increase with the increase of water curing temperature. The heat of hydration could be used to characterize the setting and hardening of the cement and also to predict the temperature rise.^[10-15]

Cement and/or concrete structures is the most widely used material in the construction industry for various purposes due to its ability to withstand high loads, its ability to be cast in any shape and its good resistance against wear and tear.^[16-18] Finer cement particles result in faster and more complete hydration. However, an increase in cement fineness and cement content in concrete raises the adiabatic temperature of these structures.^[19-22] In order to save

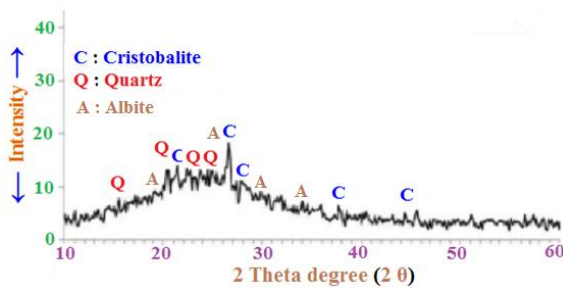


Fig. 1. XRD patterns of the natural pumice pozzolana.

energy and to reduce emission, the cement industry is confronted with extensive press coverage. To save energy and reduce emissions for cement industry, and in addition to improve equipment, it must increase the grind ability of the cement using a grinding agent. Thereby, it could be reduced the power consumption.^[4]

To improve the characteristics of the cement, supplementary cementitious materials are quite common today in cement and/or concrete industry.^[5-7] Pozzolanic reactions are known to take place at later stages involving a low rate of hydration.^[9,10] The partial substitution of Portland cement with one or more of these supplementary cementitious materials such as Gbfs does not only improve the mechanical and durability properties of cement or concrete, but also reduces the development of heat of hydration.^[10,11] As the fineness of the Gbfs increases, the total surface area of the cement as a whole increases too. This results with an increased rate of hydration. This is mainly due to the pozzolanic reactions of Gbfs with the generated free lime, $\text{Ca}(\text{OH})_2$ coming from the hydration of calcium silicate phases of the cement (C_3S and $\beta\text{-C}_2\text{S}$).^[13] Recently, there has been increased interest to use a natural pozzolan like perlite, pumice and an artificial pozzolan like fly ash (FA), silica fume (SF) and granulated slag (Gbfs) as supplementary cementitious materials.^[14-18]

Natural pumice (NP) is a fine natural pozzolan containing glass shards, mineral phases and a small amount of volcanic rock. The essential minerals in NP are feldspar, quartz and biotite.^[18-21] Gbfs is a glassy granular material that is formed when molten blast-furnace slag is rapidly chilled by immersion in water. Gbfs is a non-metallic product consisting of silicates and alumino-silicates of calcium and other bases, developed in a molten condition simultaneously with iron in a blast furnace. Gbfs has been used for many years as a supplementary cementitious material in Portland cement pastes and/or concrete, either as a mineral admixture or as a component of blended cement.^[22-24]

The heat of hydration decreases proportionally with the content of slag in the cement blends. The use of high contents of slag in the cement is very common and represents a suitable alternative to produce low heat Portland cement.^[25-28] Low heat cements are not allowed to evolve more than 270 J of heat per gram of cement in the

Table 2. Mineralogical composition of the OPC and Gbfs

| Phase Materials | C_3S | C_2S | C_3A | C_4AF |
|-----------------|----------------------|----------------------|----------------------|-----------------------|
| OPC | 65.78 | 8.67 | 8.24 | 11.71 |
| Gbfs | 60.51 | 7.63 | 8.15 | 11.94 |

first 7 days after mixing with the water. These cements are used more particularly for mass concrete structures, which, if made with ordinary cement, might undergo an excessive rise in temperature, causing stress and cracking.^[28-31]

As all chemical reactions are nearly followed by releasing of a heat, the hydration of blended cements can be quantified by their heat of hydration. Also, the pozzolanic reactions of pumice/slag blended cements are known to take a vital action at later stages involving a low heat rate. So, the bound water and free lime contents, density, apparent porosity and strength development were investigated. The obtained results could be confirmed by measuring the heat of hydration.

2. Experimental Section

2.1. Raw materials

The used raw materials in the present research are Ordinary Portland cement (OPC Type I- CEM I 42,5R), granulated blast furnace slag (Gbfs) and natural pumice rock (PC) as a source of nanosilica having the blaine surface area or fineness 3400, 5455 and 6650 cm^2/g , respectively. The blaine surface area was conducted by the "Air Permeability Apparatus". The OPC sample was supplied from El-Amrya cement factory, Alexandria, Egypt, while Gbfs sample was supplied by Iron and Steel Company, Helwan, Egypt. The pumice sample was collected from the northern coast of the Mediterranean Sea at El-Ariesh, North Sinai, Egypt.^[32] The natural pumice rock was collected from excavations in North Sinai, Egypt which it is parallel to the coast line. Pumice could be considered to be more or less similar to a glass. This is attributed to that it has no crystal texture. It is often formed during volcanoes, i.e. volcanic eruptions when the molten lava was shot in the air. During its cooling, it solidifies into what is known as pumice. Pumice is an unusual light rock due to the many air bubbles inside it. It varies in density according to the thickness of the solid material between the bubbles. Therefore, samples of pumice always float in water. Then, Both Gbfs and PC samples were subjected to crushing and well grinding till reach to nano-grain size particles. The resulting nano-slag and pumice materials were screened to pass through 300 μm standard sieve. The chemical analysis of the OPC, Gbfs and PC as taken from X-ray fluorescence technique (XRF) is listed in Table 1, while the mineralogical constituents of both OPC and Gbfs as determined from Bogue equation are tabulated in Table 2. The XRD patterns of the natural pumice (PC) were shown in Fig. 1.

Table 1. Chemical analysis of the OPC, Gbfs and PC raw materials, mass %.

| Oxide Material | SiO_2 | Al_2O_3 | Fe_2O_3 | CaO | MgO | MnO | SO_3 | Na_2O | Ti_2O | K_2O | LOI |
|----------------|----------------|-------------------------|-------------------------|--------------|--------------|--------------|---------------|-----------------------|-----------------------|----------------------|------|
| OPC | 20.12 | 4.25 | 1.29 | 63.13 | 1.53 | 0.36 | 2.54 | 0.55 | 0.19 | 0.30 | 2.64 |
| NP | 53.89 | 11.31 | 2.82 | 12.57 | 6.94 | 0.17 | 0.13 | 2.36 | 0.12 | ---- | 3.74 |
| Gbfs | 40.95 | 11.77 | 1.78 | 32.91 | 2.17 | 2.42 | 3.51 | 1.52 | ---- | 0.76 | 0.43 |

Table 3. Mix composition of the first group composed of OPC and NP (PC).

| Mix Materials | Group I (PC) | | | | | |
|---------------|--------------|-----|-----|-----|-----|-----|
| | NP0 | NP1 | NP2 | NP3 | NP4 | NP5 |
| OPC | 100 | 95 | 90 | 85 | 80 | 75 |
| NP | 0 | 5 | 10 | 15 | 20 | 25 |

Table 4. Mix composition of the second group composed from OPC, NP and Gbfs (PS).

| Mix Materials | Group II (PS) | | | | | | |
|---------------|---------------|-----|------|------|------|------|------|
| | PS0 | PS5 | PS10 | PS15 | PS20 | PS25 | PS30 |
| OPC | 100 | 95 | 90 | 85 | 80 | 75 | 70 |
| NP | 0 | 5 | 5 | 10 | 10 | 15 | 20 |
| Gbfs | 0 | 0 | 5 | 5 | 10 | 10 | 10 |

2.2. Preparation and methods

The blended cements were prepared using one type of cement (OPC), one type of a natural pozzolan (NP) and an artificial pozzolan (Gbfs). So, there are two blended cement mix groups composed from OPC, NP and Gbfs. The first is PC and was composed of OPC and NP as 100:0, 96:5, 90:10, 85:15, 80:20 and 75:25 having the symbols: NP0, NP1, NP2, NP3, NP4 and NP5, respectively. The second is PS and was composed of OPC, NP and Gbfs as 100:0:0, 95:5:0, 90:5:5, 85:10:5, 80:10:10, 75:15:10 and 70:20:10 having the symbols PS0, PS1, PS2, PS3, PS4, PS5, PS6 AND PS7, respectively. The composition of the cement blends of the first group is illustrated in Table 3, whereas that of the second group is shown in Table 4, respectively.

The blending process of the various cement batches was firstly done in a porcelain ball mill using three balls for two hours to assure the complete homogeneity of all cement batches. The standard water of consistency^[4,33] and setting times^[4,34] of the various cement pastes were directly measured using Vicat Apparatus. The water of consistency could be calculated from the following relation:

$$WC, \% = A / C \times 100 \quad (1)$$

Where, A is the amount of water taken to produce a suitable paste, C is the amount of cement mix (300 g). During mixing, the correct predetermined w/c-ratio (water of consistency) was poured into the cement portion inside the mixer step by step, and then the mixer was run for 5 minutes at an average speed of 10 rpm in order to have perfect homogenous pastes. Before casting of cement cubes, the moulds were delt with a thin film of a motor engine oil to facilitate the release of the cement cubes from the moulds during the de-moulding process. The cement pastes were then moulded into one inch cubic stainless steel moulds (2.5 x 2.5 x 2.5 cm³) using about 500 g from the cement powder batch, vibrated manually for three minutes, and then on a mechanical vibrator for another three minutes to remove all air bubbles tapped inside the cement pastes. The moulds were filled to the top surface and smoothed with a flat stainless steel trowel or a suitable spatula to obtain a flat and smooth surface.^[4,35-38] After casting of samples, they were covered with a wet sheet during the first 24 hours to prevent moisture loss. The moulds were then kept in a humidity chamber for 24 hours under 95 ± 1 relative humidity (RH), and room temperature (23 ± 1), demoulded in the following day and soon cured by the total immersion in water at an ambient laboratory temperature till the time of testing for heat of

hydration, bulk density, apparent porosity, compressive strength, combined water and free lime contents at 1, 3, 7, 28 and 90 days. This is necessary for the cement cubes as it facilitates the proper hydration of cement phases.

The bulk density (BD) and apparent porosity (AP) of the hardened cement pastes^[35-37, 39] were calculated from the following equations:

$$B.D, (g/cm^3) = W1 / (W1 - W2) \times 1 \quad (2)$$

$$A.P, \% = (W1 - W3) / (W1 - W2) \times 100 \quad (3)$$

Where, W1, W2 and W3 are the saturated, suspended and dry weights, respectively. The compressive strength (CS) of the various hardened cement pastes^[40,41] was measured and calculated from the following relation:

$$CS = L (KN) / Sa (cm^2) KN/m^2 \times 102 (Kg/cm^2) / 10.2 (MPa) \quad (4)$$

Where, L is the load taken, Sa is the surface area. Thereafter, about 10 grams of the broken specimens were first well ground, dried at 105°C for 30 min. and then were placed in a solution mixture of 1:1 methanol: acetone to stop the hydration.^[6,25,36,37,39,42] The kinetics of hydration in terms of chemically bound water and free lime contents were also measured. About one gram of the sample was first dried at 105°C for 24 hours and then the bound water content^[6,36-38,40,42-44] at each hydration age was determined on the basis of ignition loss at 1000°C for 30 minutes soaking where about 10 grams of the broken specimens from the determination of compressive strength were first well ground, dried at 105°C for 30 minutes and then were placed in a solution mixture of 1:1 methanol: acetone to stop the hydration.^[5,17,44] The kinetics of hydration in terms of chemically bound water and free lime contents were also measured. About one gram of the sample was first dried at 105°C for 24 hours, and then the chemically-bound water content (CBn) at each hydration age was determined on the basis of ignition loss at 1000°C for 30 minutes^[5,44] from the following equation:

$$CBn, \% = W1 - W2 / W2 \times 100 \quad (5)$$

Where, CBn, W1 and W2 are combined water content, weight of sample before and after ignition, respectively.

The free lime content (FLn) of the hydrated samples pre-dried at 105°C for 24 hours was also determined. About 0.5 g sample + 40 ml ethylene glycol → heating to about 20 minutes without boiling. About 1–2 drops of pH indicator were added to the filtrate and then titrated against freshly prepared 0.1N HCl until the pink color disappeared. The 0.1 N HCl was prepared using the following equation:

$$V1 = N \times V2 \times W \times 100 / D \times P \times 1000 \quad (6)$$

Where, V1 is the volume of HCl concentration, V2 is the volume required, N is the normality required, W is the equivalent weight, D is the density of HCl concentration and P is the purity (%). The heating and titration were repeated several times until the pink colour did not appear on heating. The free lime content^[11,15,17,44-46] was calculated from the following relation:

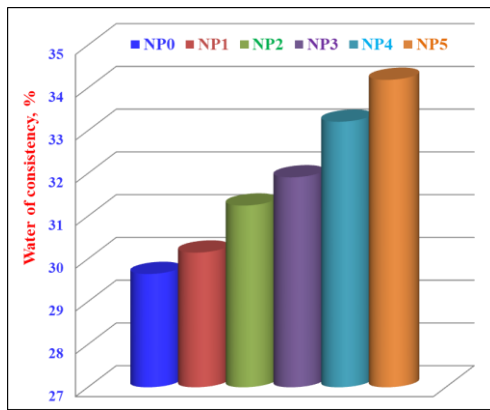


Fig. 2. Water of consistency of the first group (PC) containing NP alone.

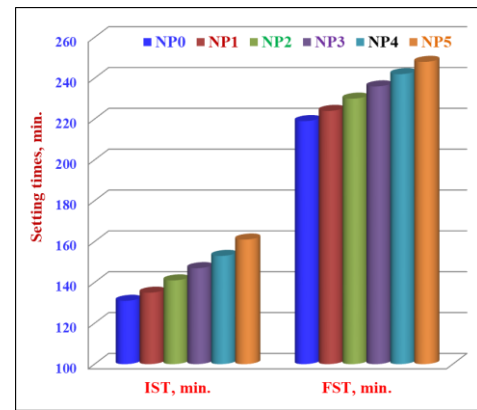


Fig. 4. Setting times of the first group (PC) containing the NP alone.

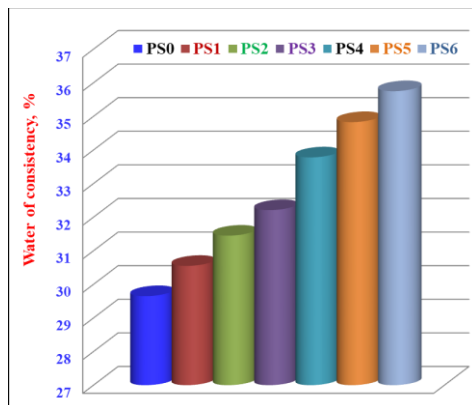


Fig. 3. Water of consistency of the second group (PS) containing NP in combination with Gbfs.

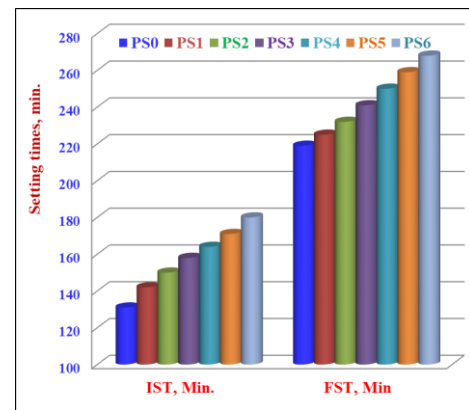


Fig. 5. Setting times of the second group (PS) containing NP in combination with Gbfs.

$$Fl_n, \% = (V \times 0.0033/1) \times 100 \quad (7)$$

Where, Fl_n and V are the free lime content and the volume of 0.1 N HCl taken on titration, respectively.

The heat of hydration of the prepared blended cement pastes has been experimentally investigated to confirm the obtained results.^[47]

3. Results and Discussions

3.1. Water of consistency

The water of consistency of the blended cement pastes of the Groups I and II are represented in Figs. 2 and 3, respectively. The experimental results showed that to produce a suitable cement pastes with a good workability for each group, the water of consistency gradually increased as the added NP ratio alone (Group I) and/or both NP and Gbfs ratios (Group II) increased in the cement blend. This is mainly due to that either NP or Gbfs is too greedy for water to a large extent.^[4,6,14,48,49] Moreover, the fineness of the whole cement blend enhanced as the content of both NP alone (Group I), and/or together with Gbfs (Group II) increased. This reflected by the continual increase of mixing water.^[5-7,27,36-38] It can be inferred that the water of consistency of the blended cements of the Group II is higher than those of the first one.

3.2. Setting times

The setting times (initial and final) of the various blended cement pastes of Groups I and II are shown in Figs. 4 and 5, respectively. It is worth noting that the same trend was displayed in setting times of the two groups as in case of water consistency, and also is due to the same reasons previously mentioned. In addition, the very low temperature of the atmosphere during casting of the samples helped to increase the times of setting.^[4,5,7,38,48,49]

3.3. Chemically-bound water contents

The bound water contents of the various blended cement pastes of the two groups (I and II) are shown in Figs. 6 and 7, respectively. Generally, the bound water contents of the various cement blends increased as the hydration time proceeded up to 90 days. This is mainly due to the occurrence of the hydration process between the major cement phases (C_3S , β - C_2S , C_3A and C_4AF with water.^[4-8] The bound water contents of the Group I containing different ratios of PC (Fig. 6) are slightly higher than those of the blank (NP0) at all hydration times up till 20 wt. % PC (P4), and then decreased with further increase of PC (NP5). The increase of bound water is essentially attributed to the pozzolanic reactions that took place between the constituents of NP and the free lime, $Ca(OH)_2$ released from the hydration of calcium silicate phases of the cement (C_3S and β - C_2S) with water as follows:-

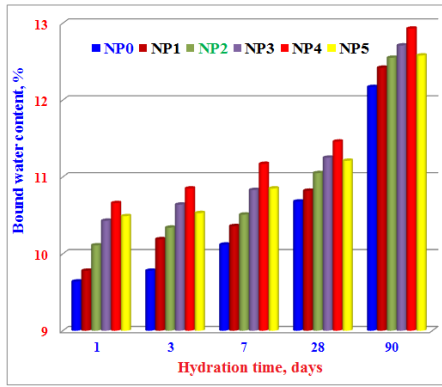


Fig. 6. Bound water contents of the first group (PC) containing NP alone.

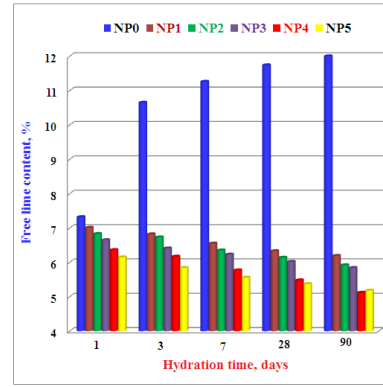


Fig. 8. Free lime contents of the first group (PC) containing NP alone.

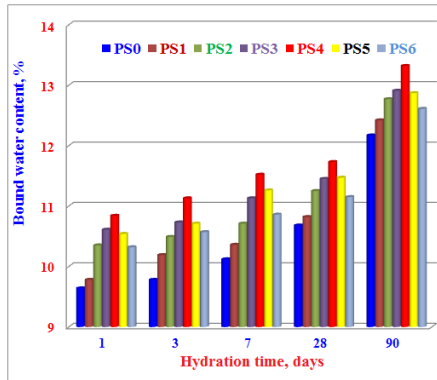


Fig. 7. Bound water contents of the second group (PS) NP in combination with Gbfs.

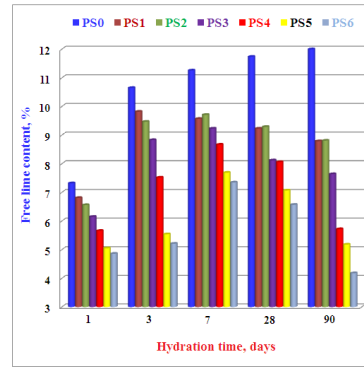
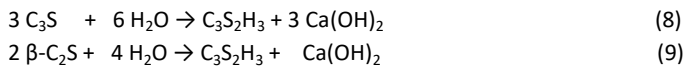


Fig. 9. Free lime contents of the second group (PS) containing NP in combination with Gbfs.



Therefore, the bound water contents improved and enhanced more than those of the blank. So, it appeared slightly higher. While the decrease of bound water content is principally contributed to the higher deficiency of the main binding material of the cement, and moreover the higher quantities of NP stood as an obstacle that hindered and ceased the formation of more hydration products.^[35-37,39] As a result, the higher amounts of the additive materials must be rejected.

On the other side, the bound water contents of the Group II containing different ratios of NP and Gbfs (Fig. 7) also increased as the hydration time progressed up to 90 days. This is due to the normal hydration process of the cement phases, and also for the pozzolanic reactivity of both NP and Gbfs.^[5,8,18,20] The combination of NP with Gbfs improved and increased the rate of the hydration process than in case of NP alone. This may be attributed to the increase of pozzolanic reactions due to the presence of the two pozzolanic materials. The cement blend containing equal ratios from NP and Gbfs achieved the best results. So, it was selected to be the optimum cement blend. Furthermore, the results of Group II are slightly higher than those of Group I. This is mainly due to the presence of two pozzolanic materials together.^[8,20,35-37]

3.4. Free lime content

Figs. 8 and 9 illustrate the results of free lime contents of Groups I and II, respectively, which were represented as a function of

hydration time up to 90 days. It is obvious that the free lime content of the pure OPC pastes increased continuously with hydration time. But in presence of NP, the free lime content soon decreased with hydration time since the first moment of contacting with water, where it decreased sharply on the early ages of hydration up to 7 days, and then slightly decreased onward (Fig. 8). In case of NP in combination of Gbfs, the free lime content increased slightly only up to 3 days and then decreased onward (Fig. 9). The increase of free lime content is mainly due to the normal hydration of the calcium silicate phases of the cement.^[4,6,8,17,20] The decrease of free lime contents is essentially contributed to the pozzolanic reaction by the NP and also Gbfs.^[4,6,32] Moreover, the nanoparticle size of NP and/or Gbfs is another factor to activate the action of these materials to reacted with the free lime, which in turn reduced the free lime content.^[27,30]

3.5. Bulk density and total porosity

The bulk density of the various blended cement pastes of the two groups (I and II) are graphically plotted in Figs. 10 and 11, respectively. As a general sense, the bulk density of the various blended cement pastes of Group I increased with the hydration ages up to 90 days. This is mainly due to the normal hydration process of the main cement phases.^[4-6,49,50] Also, as the NP content increased in the cement blends, the bulk density increased too, but up till the cement blend containing 20 wt. % NP (NP4), and then decreased suddenly. The increase of the bulk density with the increase of NP addition is essentially contributed to the pozzolanic action of NP with the resulting Ca (OH)₂ that is coming from the hydration process of

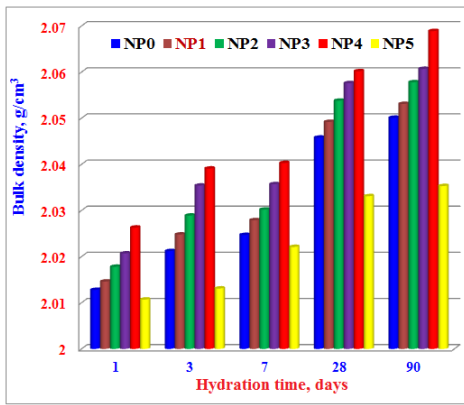


Fig. 10. Bulk density of the first group (NP) containing NP alone.

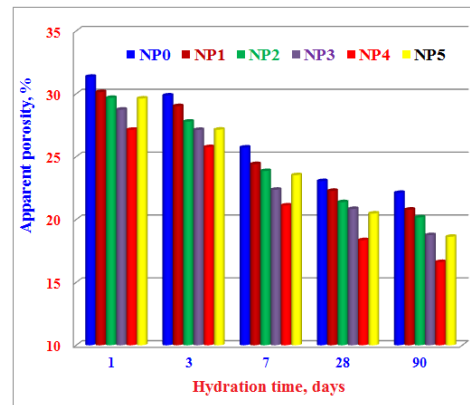


Fig. 12. Apparent porosity of the first group (PC) containing NP alone.

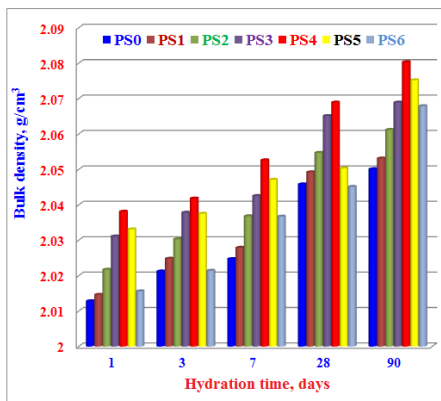


Fig. 11. Bulk density of the second group (PS) containing NP in combination with Gbfs.

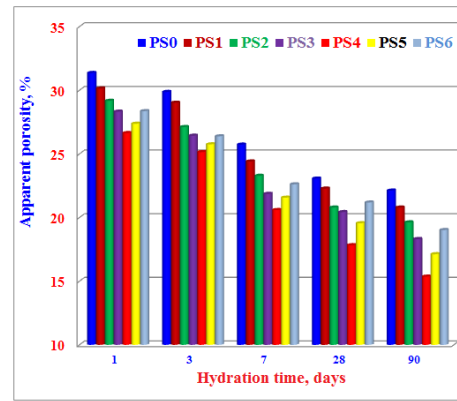


Fig. 13. Apparent porosity of the second group (PS) containing NP in combination with Gbfs.

the major silicate phases of the cement to form additional CSH products. These hydration products often raised the bulk mass of the hardened cement pastes. This is in turn improved and enhanced the bulk density. The decrease of the bulk density is due to the higher lack and deficiency of the main binding material of the cement.

The same trend was displayed with the hardened blended cement pastes of Group II (Fig. 8), i.e. the bulk density was improved and enhanced up to equal ratios of 10 % of both NP and Gbfs (PS4), then decreased and adversely affected with further increase of the two additives. It is good mention that the values of bulk density of Group II are slightly higher than those of Group I at all hydration ages. This is due to the presence of two pozzolanic materials in Group II, while Group I contains only one.^[5,8,20,49]

3.6. Apparent porosity

The apparent porosity of the various blended cement pastes of the two groups (I and II) are shown in Figs. 12 and 13, respectively. It is obvious that the apparent porosity was generally decreased as the hydration ages increased up to 90 days due to the normal hydration of the main cement phases, and also due to the pozzolanic action of the used pozzolanic materials.^[4-7,18,32,48,49] In case of Group I, this trend was continued till the blended cement pastes containing 20 wt % NP (NP4), but with further increase of NP (NP5), the apparent porosity started to increase at all hydration ages up to 90 days, while in case of Group II this trend was continued till the cement blend containing equal amounts of both materials (PS4), and then begins to

increase. The cement blends NP4 and PS4 achieved the lowest apparent porosity. Therefore, they were selected as optimum blends in the two groups. As a result, the higher quantities from any of the additive alone or both together are undesired.^[18,22,26,30,35-37,39]

3.7. Compressive strength

The compressive strength of the various hardened blended cement pastes of the two groups (I and II) are represented as a function of hydration time in Figs. 14 and 15, respectively. The compressive strength enhanced with hydration times up to 90 days as a general trend for all samples. Moreover, the compressive strength also increased more with either NP or together with Gbfs. In the first group, the compressive strength increased only up to 20 PC content (NP4), and then decreased (NP5), while with the second group, the compressive strength enhanced up to equal levels of NP and Gbfs (PS4), and then decreased with further increase of NP and/or Gbfs content (PS5 and PS6). The increase of the compressive strength is mainly due to many factors.^[4-7,15,17,26,30,50] As the hydration proceeded, the hydration process begins forming hydration products which soon deposited in the pore system of the hardened cement pastes. This will decrease the porosity which in turn increases the bulk density.^[32,34-39,48-51] This often reflected positively on the splitting strength, i.e. the splitting strength improves and enhances. Also, the pozzolanic action of the two pozzolanic materials by which it reacted with the free lime to form additional hydration products that precipitated in the pore structure. This decreased the porosity and

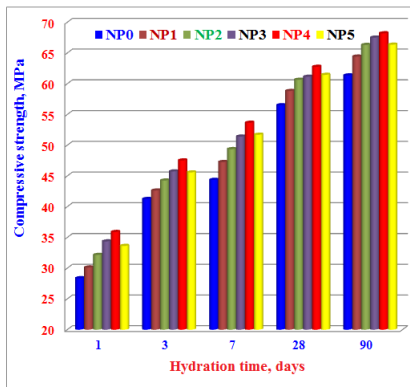


Fig. 14. Compressive strength of the first group (PC) containing NP alone.

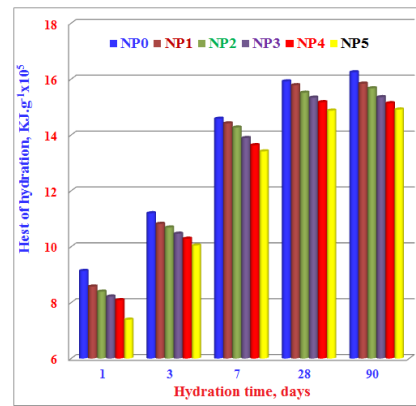


Fig. 16. Heat of hydration of the first group (PC) containing NP alone.

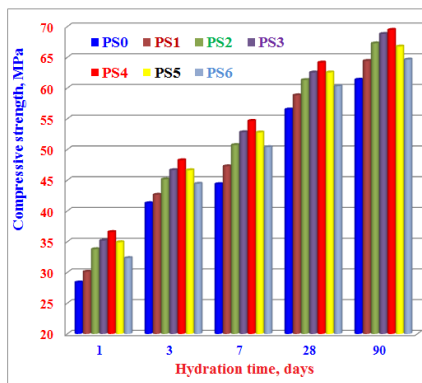


Fig. 15. Compressive strength of the second group (PS) containing NP in combination with Gbfs.

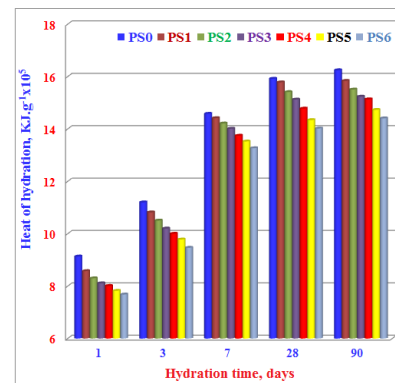


Fig. 17. Heat of hydration of the second group (PS) containing NP in combination with Gbfs.

increased the bulk density. Accordingly, the compressive strength was more improved and enhanced.^[32,48-51] Moreover, the fineness of the cement blends increased with the increase of either NP (Group I) or NP and Gbfs (Group II). So, the rate of hydration increased too, and reflected positively on the mechanical strength^[7,8,15,17,18,27,30,31] On this basis, the optimum NP content is 20 wt % in case of Group I, and 10 wt % from NP and Gbfs in case of Group II.

3.8. Heat of hydration

The heat of hydration of the various blended cement pastes of the two groups (PC and PS) are shown in Figs. 16 and 17, respectively. Results demonstrated that as soon as the various cement powders become in contact with water, the heat of hydration generated immediately. The heat of hydration of all cement pastes was generally increased with the hydration time up to 90 days.^[32,35-37,39,48,49] The same trend was displayed by all cement pastes in both Groups. This is mainly attributed to the increase of the rate of hydration of cement phases. This was accompanied by a gradual generation of heat.^[31,39,45,46] Moreover, the rate of the generated heat of hydration sharply enhanced at early ages from 7 days onward. This is essentially attributed to the activation effect of the hydration reaction mechanism of C_3S by the very fine NP and Gbfs particles. At later ages (28-90 days), the rate of hydration reaction as well as the evolved heat of hydration increased slightly and seemed to be constant. This may be due to the non-activation effect of C_3S and the slight activation action mechanism of $\beta-C_2S$ at later ages.^[3,23,25]

The heat of hydration decreased as the content of NP increased. So, at any hydration time, lower values of heat of hydration were exhibited than those of the previous cement blends including NP0, i.e. the data of heat of hydration of all cement blends of the two Groups were lower than those of the blank (NP0 or PS). This was contributed to the dilution effect of the main binding material (OPC), and the retardation effect of the higher quantity of NP and/or Gbfs at the expense of the OPC portion.^[7,8,18,20,37,48-51] Moreover, the values of heat of hydration of the various blended cement pastes of Group I are little higher than those of Group II. This may be contributed to the presence of two added materials.

4. Conclusions

- i. The surface area or fineness of the cement mixtures increased with the increase nanosized particles of either NP or Gbfs.
- ii. The w/c ratio or consistency as well as setting times increased as the amount of NP or Gbfs increased because these are very insatiable for water.
- iii. The chemically bound water content, bulk density and compressive strength improved and enhanced with increasing NP alone or in combination with Gbfs up only to 20 wt % NP, or with equal amounts of both NP and Gbfs (10 wt % of each), but then decreased with further increase of both.
- iv. The free lime content of the blank increased continuously up to 90 days. In presence of nanoparticles of NP, the free lime content shortened onward continuously, while in combination

- of Gbfs the free lime content enhanced up to 3 days and then decreased onward.
- v. The apparent porosity was generally decreased with the hydration time up to 90 says, but only up to 20 wt % NP (P4) as shown with Group I and up to equal replacement of NP and Gbfs (PS4) as noted in Group II. Then, the apparent porosity started to increase with further substitution of NP or with Gbfs as shown in P5 in group I and P5 and P6 an Group II.
 - vi. In each group, the cement pastes of mixture 20 wt % NP (P4) as in the first group, or 10 wt % of NP and Gbfs (PS4) as in the second group were selected to be of the optimum mixtures.
 - vii. It is good mention that the optimum mixture of the second group containing NP and Gbfs is better than that of the first containing only NP.
 - viii. The heat of hydration continuously decreased with the incorporation of either NP or Gbfs. Therefore, the prepared blended cement pastes are considered as low heat cements.

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Conflicts of Interest

The authors declare no conflict of interest.

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