

Palm Ash as a Pozzolanic Material for Portland Cement Pastes

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Abstract

The effect of the substitution of palm ash (PA) on the physico-chemical and mechanical properties of Portland cement pastes (OPC) was clearly evaluated. Results showed that as the PA content increased, the fineness as well as the heat of hydration of the whole mix increased too. The water of consistency (WC) and set times (ST) decreased with the increase of PA content due to the presence of the water reducing admixture. The bound water content (B_{Wn}), bulk density (BD) and compressive strength (CS) improved and enhanced up to 20 % PA content, and then decreased onward at all hydration periods, while the total porosity decreased and then increased. Above 20 % PA content, all properties were adversely affected. The free lime content (FL_n) of the OPC increased continuously up to 90 days, but decreased with PA content. The FTIR spectra illustrated that there is a large amount of free lime content with P0 (OPC), but it gradually decreased with PA content. The SEM microscopy demonstrated the formation of ettringite phase and aggregates of CSH in addition to free lime. In the case of PA blended cement pastes the ettringite was disappeared completely and well-defined crystals were detected.

Keywords: Opc, Palm Ash, Setting Times, Density, Porosity, Strength, Ftir, Sem.

Introduction

Scope of the problem

The necessity to utilize waste materials either solids, liquids or even gases to decrease the overall energy consumption is becoming increasingly obvious worldwide. The benefits from applying pozzolanic materials as fly ash, rice husk ash, sugarcane bagasse ash, and fuel ash as a partial substitution of Portland cement in cement pastes, mortars and/or concretes are now well established. These pozzolanic materials can improve their workability, strength and durability [1-6]. It is well known that palm trees are the main food crop in tropical and subtropical countries because it plays a vital role in the countrywide economy of countries [7-12]. Palm trees have been the best friend of Egyptians since the dawn of time. They are well known on the banks of the Nile, desert oases in Sinai and along the sea shores. They are the source of dates, where the weather and humidity affect its taste. The coastal palm trees have red and yellow dates that ripen quickly, where the dates are a very delicious seasonal fruit. The Oasis palm trees have fruits that are extra sweet and can be stored all year long. The palm branches (PB) are a solid waste material generally disposed to the landfills or disposal sites so that it now represents a heavy environmental burden. Moreover, the PB creates an environmental nuisance due to the direct disposal on the open areas so that it can form garbage heaps in these areas [1,6,8,13]. To reduce the environmental burden of these PB, its utilization of in cement pastes, mortars or even concrete is a significant aspect. The burning of organic wastes, like PB, produces a considerable amount of ash [12,14,15]. One of the effective ways to reduce the environmental impact is to use it as a mineral admixture for the partial substitution of cement in mortar and/or concrete, which can reduce its production cost, energy conservation, and waste emission [16-20]. Locals have made the best out of palm trees. The palm leaves are used for both shelters and for making fire. A shelter made by palm leaves and wood gives a beautiful earthy feeling. Palm branches ash (PBA) is acquired through the control burning of it. PBA could be used as a partial substitution material in mortars and/or concretes because it contains active amorphous silica, which has pozzolanic characteristics [7-12].

Objective of the current study

In the present work, the authors tried to utilize a larger amount of PBA in the Portland cement pastes as a pozzolanic material than used before. The physical properties, water of consistency, setting times, chemically-bound water and free lime contents, bulk density, total porosity and compressive strength were investigated. The obtained results would be confirmed with FTIR and SEM microscopy.

Experimental and methods

Raw materials

The used raw materials in the current research article are Ordinary Portland cement (OPC Type I- CEM I 42,5R) with a Blaine surface area $3400 \text{ cm}^2/\text{g}$, and palm leaves (PL) as a source of active Nano silica with a fineness of $300 \mu\text{m}$. The OPC was supplied from the Sakkara cement factory, Giza, Egypt, and its commercial name is known as "As mat El-Montez", while the PL sample was provided by a local farm, Egypt. PL was first processed and washed with running water, and also with distilled water, and then let too dry under the sun and open air for some days. The dried PL was subjected for firing at $700 \text{ }^\circ\text{C}$ for two hours soaking to produce what is known as palm leaves ash (PLA). Then, the resulting PLA was screened to pass through 300 am standard sieve. The chemical composition of the OPC and PLA is shown in Table 1. The mineralogical phase composition of the used OPC as calculated from Bogue equations [11,12] is given in Table 2, while the mix composition is illustrated in Table 3. Particles of PLA are amorphous and crystalline, and it is mainly composed of a large percentage of nano-SiO₂ and a lower percentage of nano-Al₂O₃.

Table 1-Composition of the used raw materials, mass %.

Oxide Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	LOI	Specific gravity
OPC	21.78	4.13	3.15	61.11	2.16	2.78	0.11	0.65	0.87	3.14
BA	73.83	7.21	1.95	7.16	1.32	1.47	0.12	1.65	6.91	2.23

Table 2- Mineralogical composition of the used OPC sample, mass %.

Phase Material	C ₃ S	β -C ₂ S	C ₃ A	C ₄ AF
OPC	43.01	30.00	5.65	9.58

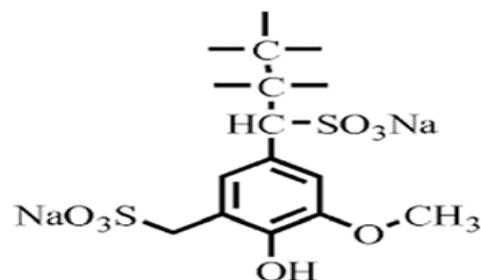
Table 3- The batch composition of cement mixes, mass %.

Batch Material	B0	B1	B2	B3	B4	B5	Fineness, cm ² /g
OPC	100	96	92	88	84	80	3400
BA	----	4	8	12	16	20	6500
Fineness, cm ² /g	3400	3850	4100	4450	4780	5050	

Preparation and methods

There are 6 cement batches from OPC and PA as 100:0, 95:5, 90:10, 85:15, 80:20 and 75:25 having the symbols: P0, P1, P2, P3, P4 and P5, respectively. The blending process of the various cement blends was done in a porcelain ball mill using three balls for two hours to assure the complete homogeneity of all cement blends. During casting, a definite percentage of sodium lignosulphonate as an admixture (Figure 1) was added to the prepared cement mixes so as to avoid the agglomeration of the nanoparticles of the used PA or OPC. Sodium lignosulfonate super plasticizer (SL) was applied due to its higher activity than other conventional ones. Its molecular weight is 534.51, while its molecular formula is $C_{20}H_{24}Na_2O_{10}S_2$. It contains several free carboxylic groups which help greatly to improve cement dispersion [5,9].

Figure 1-The chemical structure of sodium lignosulphonate



The standard water of consistency (WC) as well as setting time (initial and final) of the various cement pastes were directly determined using the Vicar Apparatus [19-21] 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). The cement pastes were then cast using the predetermined water of consistency, molded into one-inch cubic stainless-steel molds ($2.5 \times 2.5 \times 2.5 \text{ cm}^3$) using about 500 g cement mix, vibrated manually for three minutes and then on a mechanical vibrator for another three minutes. The surface of the molds was smoothed using a suitable spatula. Thereafter, the molds were kept in a humidity chamber for 24 hours under $95 \pm 1 \text{ RH}$ and room temperature, demoulded in the next day and soon immersed in water till the time of testing at 1, 3, 7, 28 and 90 days. The bulk density (BD) and total porosity (δ) of the hardened cement pastes [12,15,22] were calculated from the following equations:

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

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

Where, W1, W2 and W3 are the saturated, suspended and dry weights, respectively. The compressive strength (CS) of the various hardened cement pastes [23] was measured as follows:

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

Where L is the load taken, S_a is the surface area. Thereafter, about 10 grams of the broken specimens were first well ground, dried at 105°C for an hour, and then were placed in a solution mixture of 1:1 methanol: acetone to stop the hydration [11,12,14,18]. About 10 grams of the broken specimens from the determination of compressive strength 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 [15,24]. 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 24h, and then the chemically-bound water content (BWn) at each hydration age was determined on the basis of ignition loss at 1000°C for 30 min. soaking [24-26] as follows:

$$\text{BWn, \%} = \frac{W1-W2}{W2} \times 100 \quad (5)$$

Where, BWn, W1 and W2 are bound water content, the weight of sample before and after ignition, respectively. The free lime content (FLn) of the hydrated samples pre-dried at 105°C for 24h was also determined. About 0.5g 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 0.1N HCl was prepared using the following equation: Where, Wn, W1 and W2 are combined water content, the weight of the sample before and after ignition, respectively. The free lime content of the hydrated samples pre-dried at 105°C for 24h was also determined. About 0.5g 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 0.1N HCl was prepared using the following equation:

$$V1 = N \times V2 \times W(7) \times 100/D \times P \times 1000 \quad (6)$$

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 color did not appear on heating. The free lime content [12,17,18,22] was calculated from the following relation:

$$\text{FLn, \%} = (V \times 0.0033/1) \times 100 \quad (7)$$

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

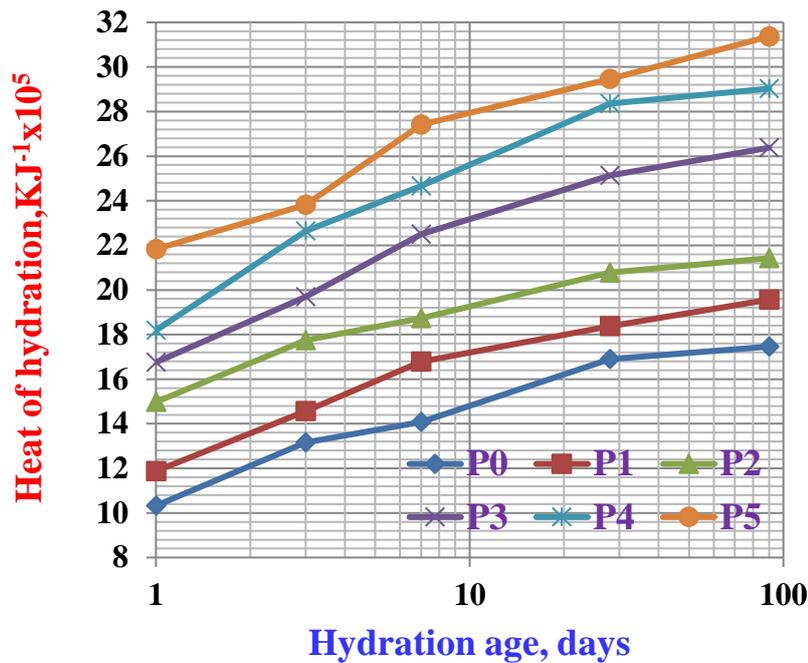
The obtained results were confirmed by infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). The FT-IR spectra were performed by Perkin Elmer FT-IR spectrometer in the range of 4000-500 cm⁻¹ and a resolution of 500 cm⁻¹. The SEM images were done for some selected samples by using JEOL-JXA-840 electron analyzer at accelerating voltage of 30 KV. The fractured surfaces were fixed on Cu- α stubs by carbon paste and then coated with a thin layer of gold.

Results and Discussion

Heat of hydration

The released heat which is due to hydration of the various cement pastes containing PA is graphically represented as a function of hydration age at 1, 3, 7, 28 and 90 days in Figure 2. Results showed that the heat of hydration gradually enhanced as the hydration age-progressed up to 90 days. The same trend was displayed by all cement pastes. This is mainly due to the increase of the rate of hydration of cement paste. This often was accompanied by releasing of heat. Furthermore, the rate of the released heat of hydration increased at early ages up to 28 days as the PA content increased. This is essentially attributed to the fact that the fine PA particles activated the hydration reaction mechanism of C₃S and β -C₂S. At later ages, the rate of hydration reaction as well as the released heat of hydration also increased, but with a lower rate. This is due to the reduction of the activation effect of fine PA particles on the hydration mechanism of β -C₂S [5,11,12,27].

Figure 2-The heat of hydration of the various cement pastes containing BA hydrated up to 90 days.

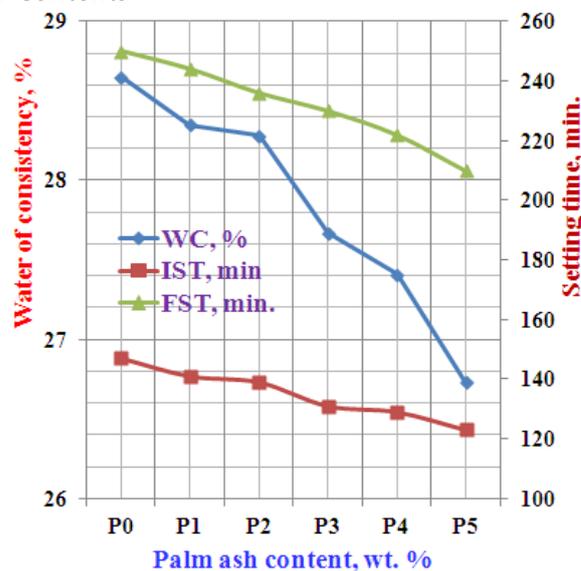


Water of consistency and setting time

Figure 3 indicates the water of consistency and setting times (Initial and final) of all cement mixes. The water of consistency of the pure OPC pastes (P0) was 28.65 %. This ratio was tended to decrease with the various blended cement pastes (P1-P5) gradually as PA content increased, i.e. the higher PA content is the lower water absorption. This is essentially attributed to the fact that the used admixture is a water-reducing agent [5,27]. On the other hand, the initial and final setting times also diminished and decreased with PA content. This is mainly contributed to the spongy nature of PA particles which tends to absorb more water during the mixing process, but the admixture reduced the ability of the PA absorbability [11-14]. Therefore, it can be concluded that the PA acts as an accelerator. Also, the diminishing of the cement portion due to the incorporation of PA is another reason for the set acceleration.

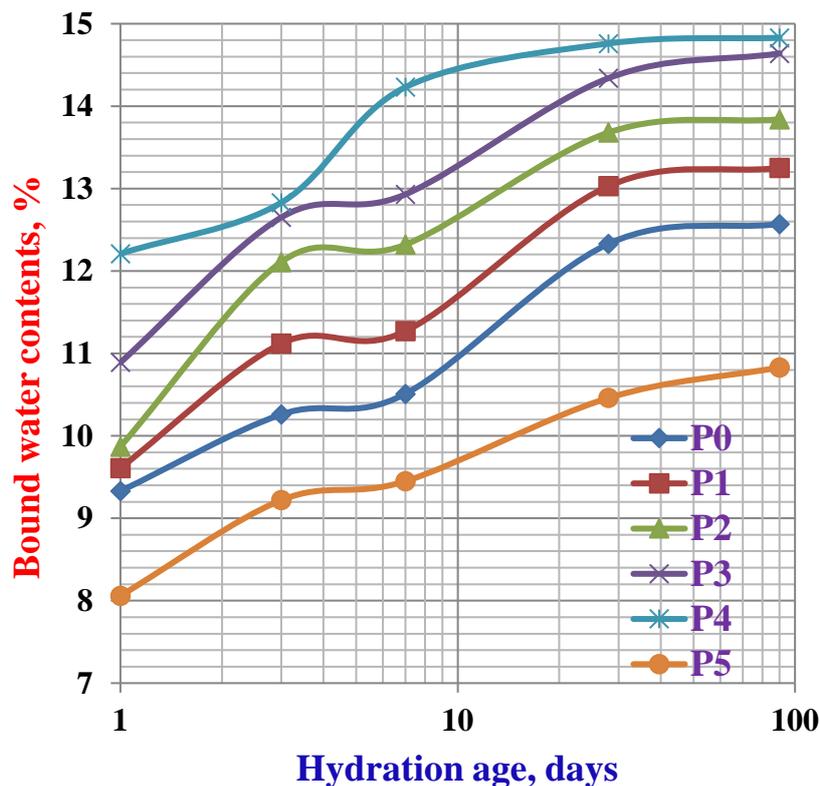
Figure 3- Water of Consistency and Setting Time of Cement Blends Containing BA Cured Up To 90 Days.

Chemically-Bound Water Contents



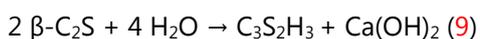
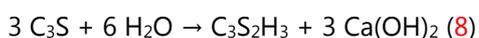
The chemically bound water contents of the different cement pastes containing PA are shown in Figure 4. The bound water content increased as the hydration age proceeded up to 90 days. This is principally contributed to the hydration of the main cement phases, especially C_3S , C_3A and C_4AF at early ages of hydration up to 28 days, whereas β - C_2S often hydrates at later ages from 28 days onward [9,11,12]. The bound water contents slightly increased as the PA content increased up to 20 %, and then suddenly decreased sharply with a further increase of PA almost at all curing ages, i.e. the cement blends P1, P2, P3 and P4 are slightly higher than that of the pure OPC (P0). This is primarily due to the pozzolanic reactivity of PA through which the constituents of PA can react with the $Ca(OH)_2$ resulting from the hydration of C_3S at the early stages of hydration and β - C_2S at later stages to produce additional CSH. Whereas, the bound water contents of P5 was becoming lower than with the control mix (P0). The lower values of bound water may be due to the unburned carbon existed in PA, and to the dilution of PA [11-14,28-32]. Accordingly, it can be concluded that the optimum addition of PA does not exceed 20 % because the higher amounts of PA is undesirable due to its adverse effect, i.e. the higher quantity of PA must be avoided because it may hinder the hydration of cement phases.

Figure 4-Chemically Bound Water Contents of Cement Blends Containing BA Cured Up To 90 Days.



Free lime contents

Figure 5 indicates the free lime contents of the various cement mixes containing PA hydrated up to 90 days. The free lime contents of the pure OPC (P0) gradually increased with the hydration ages indicating an enhancement in the rate of hydration [11,12]. As the PA content increased in the cement, the free lime content was slightly decreased up to 90 days and became lower than that of the control (P0). The increase of free lime content as in P0 is due to the normal hydration process, while the decrease is due to the pozzolanic reaction mechanism between PA constituents and the resulting $Ca(OH)_2$ coming from the hydration of C_3S at early ages and β - C_2S at later ages of hydration as follows: -



The obtained results proved that the PA acts as a pozzolanic material, and therefore the higher the amount of PA, the higher is the pozzolanic activity [28-32].

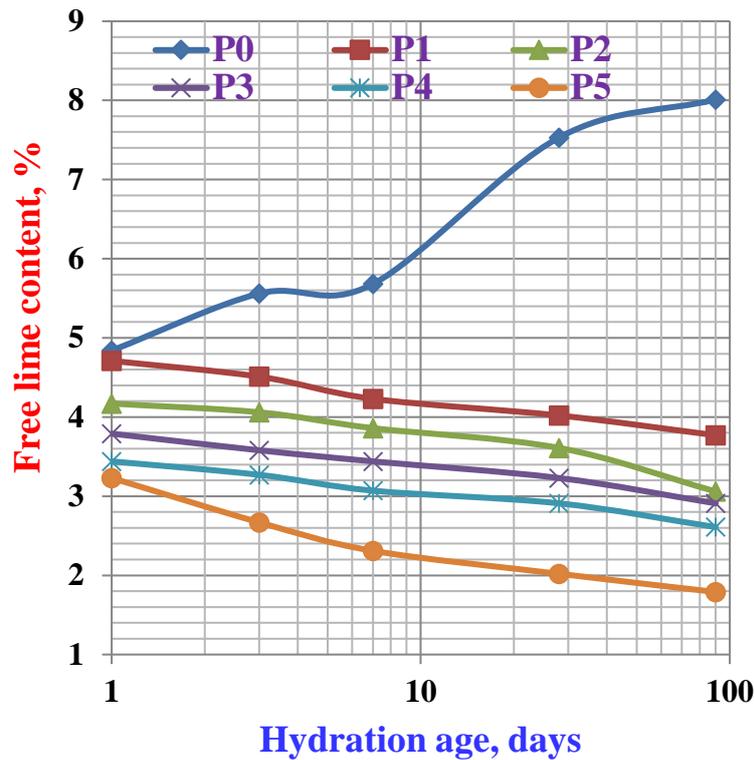


Figure 5- Free Lime Contents Of Cement Blends Containing BA Cured Up To 90 Days.

Bulk Density And Total Porosity

figures 6 and 7 demonstrate the graphs of the bulk density and total porosity of the various cement pastes versus the hydration ages. Generally, the bulk density of the various cement mixes increased as the hydration period progressed up to 90 days, while the total porosity decreased. This is mainly contributed to the fact that: as the hydration ages proceed, the hydration process starts to produce CSH which soon deposited in the pore structure leading to a decrease in the total porosity. This reflected positively on the bulk density, i.e. the bulk density increased while the total porosity decreased [11,12,33]. The bulk density of the cement mixes containing PA (P1-P4) gradually increased as the PA content increased up to 20 % (P4), whereas the total porosity decreased, i.e. the cement blends P1, P2, P3 and P4 are slightly higher than that of the pure OPC (P0). This is evidently due to the formation of additional CSH from the pozzolanic reactions of PA with the constituents of cement through which the constituents of PA can react with the Ca(OH)_2 resulting from the hydration of C_3S at early stages of hydration and $\beta\text{-C}_2\text{S}$ at later stages to produce addition CSH [7,19-21].

The addition of more than 20 % PA, the BD suddenly was decreased, while the total porosity increased at all hydration ages. This is principally due to the decrease in the main binding material of the OPC, and also the higher quantity of PA may obstruct and hinder the hydration process, i.e. it affects negatively and decrease the rate of hydration accompanied by a decrease of BD [9,12,13,22,18,29]. Hence, the increase of total porosity and the decrease of BD resulted with the incorporation of large amounts of PA affected the amount of the used OPC. As a result, it was not sufficient for inducing the reaction with silica from PA.

Figure 6- Bulk Density of Cement Blends Containing BA Cured Up To 90 Days.

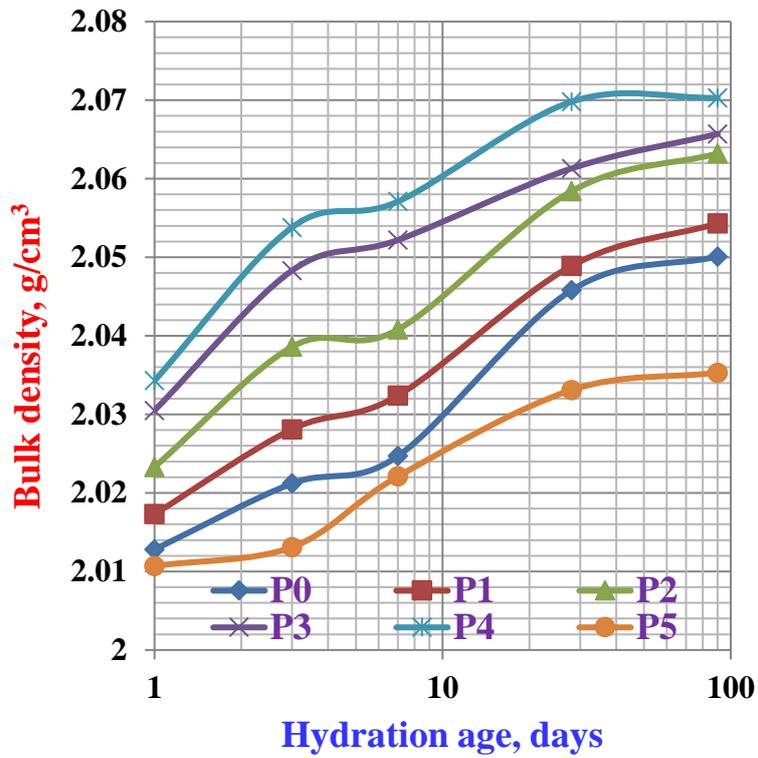
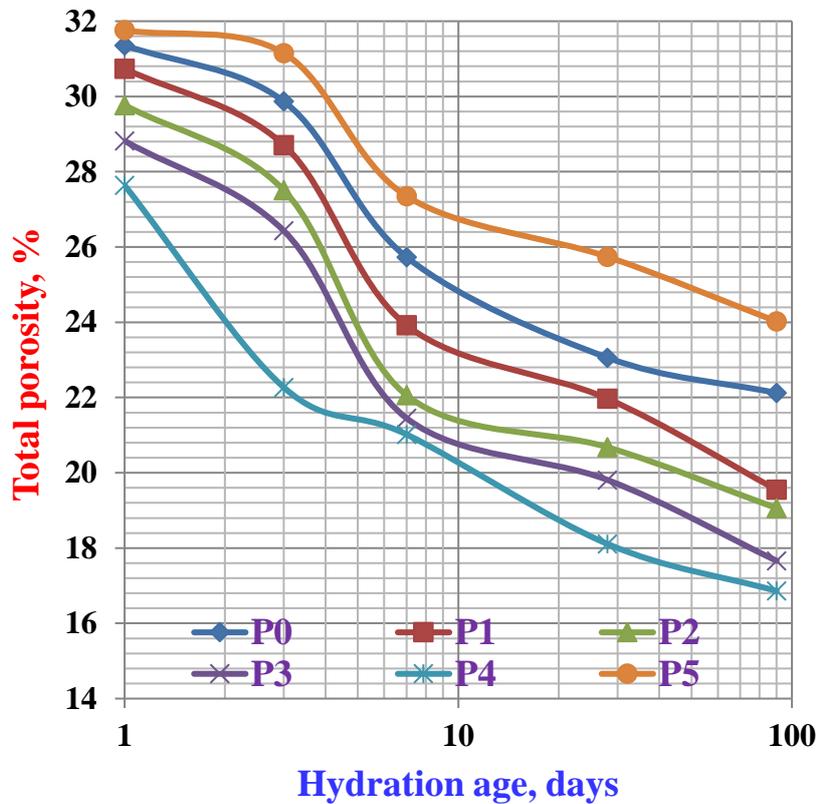


Figure 7-Total Porosity of Cement Blends Containing BA Cured Up To 90 Days.



Compressive strength

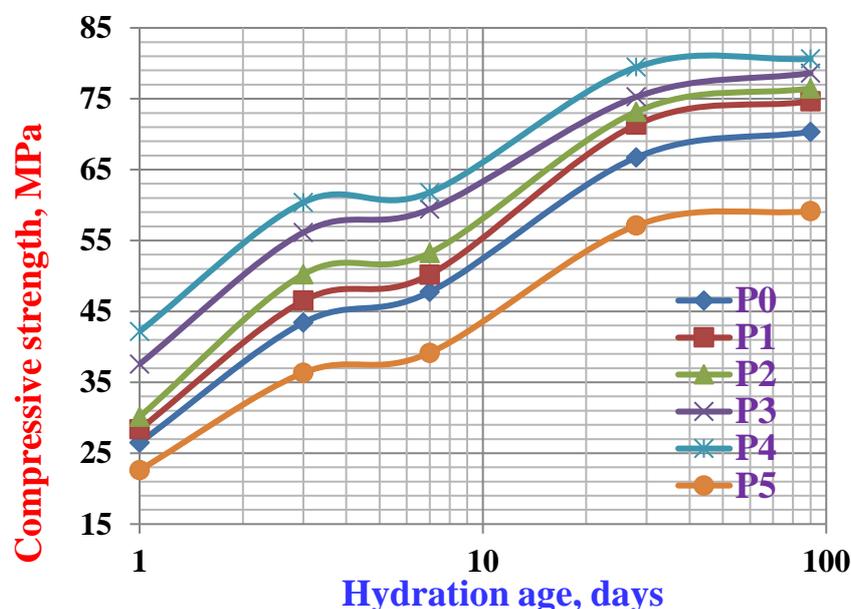


The w/c ratio influences the workability and durability of cement pastes and concrete, which in turn influences its strength, i.e. the decrease of w/c-ratio results in an increase of workability accompanied by an increase in the strength, and the opposite is correct. Figure 8 represents the compressive strength results of the various cement pastes as a function of hydration ages up to 90 days. Generally, the compressive strength improved and increased gradually as the hydration time proceeded till reach 90 days. This is mainly attributed to the formation of CSH, which is due to hydration. These CSH are always precipitated into the pore structure. This results in a decrease in the total porosity and an increase in the bulk density. This may be due to the good dispersion by the used admixture and good compaction of the hardened samples during casting. This in turn was reflected positively on the compressive strength. As a result, the compressive strength improved and increased [15,22,17,33,34]. The compressive strength also enhanced as the PA content increased at all curing ages of hydration. This is essentially due to the formation of additional CSH that is resulting from the pozzolanic reactions of Nano-silica (Nano-SiO₂) and Nano alumina (Nano-Al₂O₃) from PA with the free lime released from the hydration of C₃S and β-C₂S of cement to produce cubic crystals of hydrogarnet (C₃A. S₂. H_n) as follows:-



The decrease of free lime improves the physicochemical and mechanical properties of the hardened cement pastes, and therefore the compressive strength improved and enhanced [3,17,18,34-36]. Moreover, the decrease of w/c ratio due to the presence of Na-lignosulphonate (Figure 1) results in an improvement in the physical and mechanical strength of the hardened cement samples. The compressive strength also increased as the PA content increased only up to 20 %, and then suddenly decreased. The increase of compressive strength is related to the pozzolanic reactivity of PA. This would be led to the segmentation of large capillary pores and nucleation sites due to the continuous deposition of hydration products (CSH from the normal hydration of cement phases and additional CSH from the pozzolanic reactions of PA with the released free lime [30,33-37] The decrease is due to the fact that the replacing of PA at the expense of the essential cementitious material of cement and on the other side the higher amount of PA stands as an obstacle against the normal hydration of cement phases. So, the rate of hydration declined and accordingly, this should be reflected negatively on the compressive strength [3,37,38]. The cement mix of P4 recorded the highest values of compressive strength, while that of P5 exhibited the lowest. On this basis, the cement batch containing 20 % PA is the optimum mix. Hence, the PA does not only improve the various characteristics of the OPC but from an economical point of view, it also reduces the cost of the very expensive OPC production Infrared spectra

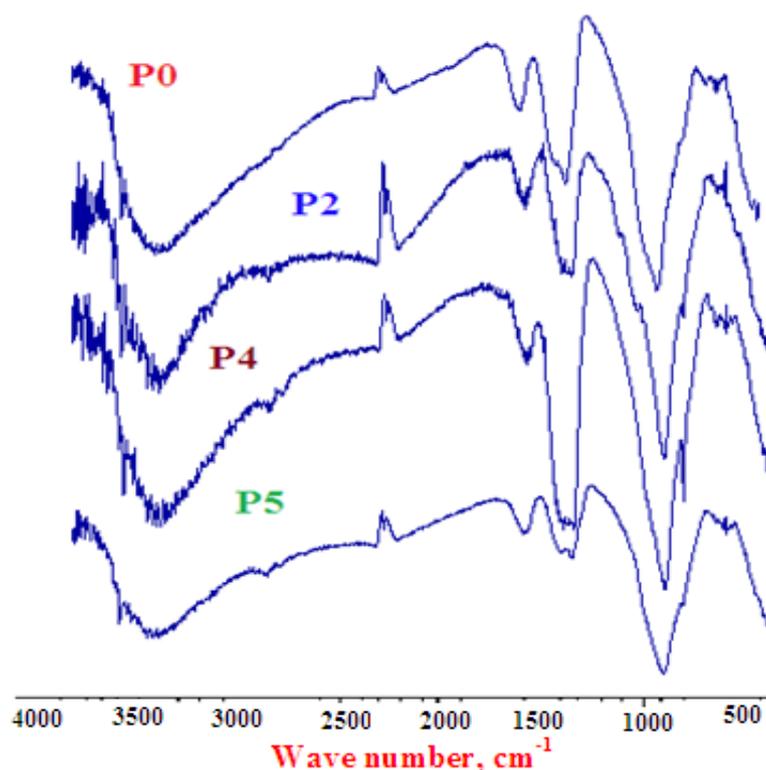
Figure 8-Compressive strength of cement blends containing BA cured up to 90 days.



Infra red spectra

The FT-IR spectra of the OPC (P0) and the various OPC cement pastes containing BA (P1-P5) hydrated up to 28 days are shown in Figure 9. The absorption band at wave number 3644-3648 cm^{-1} is related to the OH^- group coordinated to Ca^{2+} characterizing $\text{Ca}(\text{OH})_2$ or free lime, which was clearly decreased as PA content increased till the lowest with P5. This is responsible for the improvement of physico chemical properties, and particularly the compressive strength. The broad absorption band at wave number 3415-3400 cm^{-1} is due to the OH^- group associated to H^+ bond, i.e. the symmetrical stretching frequency of water. The two absorption bands at 1800-1790 and 1450-1400 cm^{-1} characterizing to CO_3^{2-} and SO_4^{2-} , respectively which are due to carbonation and corporation of CSH and /or CASH, where those of CO_3^{2-} are smaller than those of SO_4^{2-} . The superimposed absorption bands at wave number 1250-780 cm^{-1} are related to the main silicate band involves Si-O stretching vibration bands of CSH, while the band at wavelength 870-867 cm^{-1} is due to CASH. These bands are variable due to the degree of hydration as well as crystallization. The intensity of all absorption spectra was higher in sample P4 containing 20 % PA when compared with those of the other mixes.

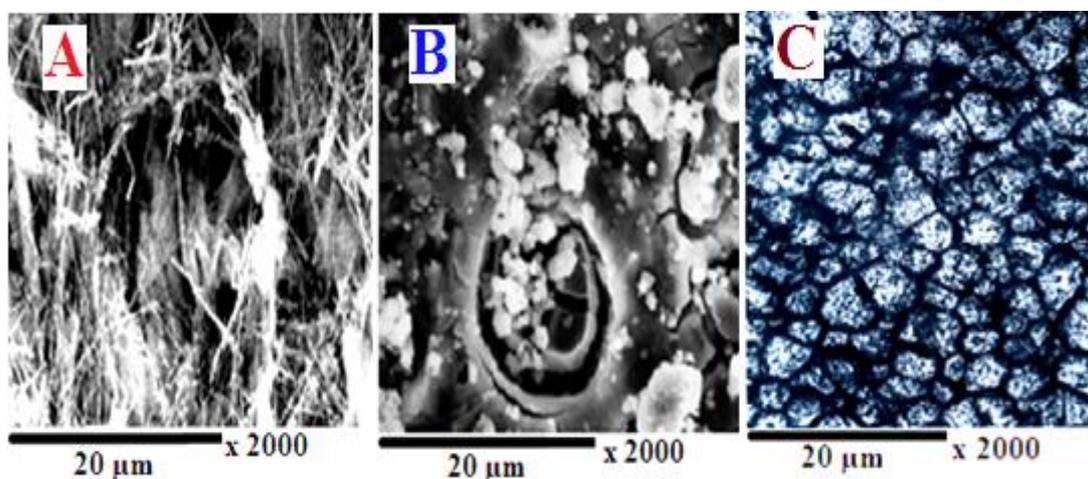
Figure 9- FTIR Spectra of Cement Pastes P0, P2, P4 And P5 Showing the Pozzolanic Reactivity of PA with The $\text{Ca}(\text{OH})_2$ At 28 Days.



SEM microscopy

The SEM images of P0 (A), P4 (B) and P5 (C) hydrated up to 28 days are shown in Figure 10. The ettringite phase is clearly detected in P0 (A), pieces or sheets of CSH are formed with P4 (B), whereas a porous structure and aggregates of CSH are seen with P5 (C). In addition, spots of free lime are detected in all samples with variable rates.

Figure 10-The SEM microscopy of Portland cement blended with PA hydrated up to 28 days (A-formation of ettringite phase, B- CSH, and C-Aggregates of CSH).



Conclusions

The following overall conclusions could be obtained: -

1. The heat of hydration gradually increased with the addition of PA at the expense of the cement.
2. Water of consistency and setting times are decreased, and therefore PA acts as an accelerator. The decrease of water of consistency is due to the presence of the water reducing admixture.
3. The chemically bound water contents increased as the hydration ages have proceeded, and also with the increase of PA only up to 20 %, but then, decreased with a further increase of PA.
4. The free lime content increased up to 90 days with P0 containing no PA, whilst it decreased with cement blends containing PA.
5. The bulk density improved and enhanced as the PA content increased up to 20 %, and then decreased with a further increase of PA, while the total porosity diminished with replacing PA up to 20 %, and then increased onward.
6. The compressive strength significantly improved with increasing the PA content only up to 20 %, and then diminished suddenly at all curing ages of hydration. The increase could be done by increasing the pozzolanic reactions that are leading to reduce of $\text{Ca}(\text{OH})_2$ content which is coming from the hydration of C_3S and $\beta\text{-C}_2\text{S}$ phases of the cement, and by enhancing the precipitation sites of hydration products. The decrease is due to the deficiency of the main binding material of the cement.
7. The addition of 20 % PA to OPC cement could be applied without any adverse effects on its physicochemical and mechanical properties, but on contrast, they improved and enhanced.
8. The FTIR spectra showed the free lime content at the wavelength of 3646 cm^{-1} decreased with the increase of PA content.

9. The SEM images indicated that the ettringite phase, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ is formed due to the hydration of C3A with gypsum in the presence of water. This phase elongated the setting times as in pure OPC (A). This phase was disappeared in the presence of PA and exchanged by CSH (B and C)
10. Na-lignosulphonate admixture is the main reaction responsible for the modification and improving most of the physical, chemical, mechanical and microstructure of the hardened cement pastes.

Acknowledgements

Authors wish to express their deep thanks to NRC for helping to obtain materials, processing, preparing, molding and measuring all of the obtained data of the study.

Compliance with Ethical Standards

Conflict of interest: There is no conflict of interest anywhere.

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