Setting, Hardening and Mechanical Properties of Some Cement / Agrowaste Composites - Part I

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Abstract The main objective of this study is to reutilize the barely and rice husks (BH & RH) after its conversion to ashes by firing at 600°C (BHA & RHA) as replacing materials of Ordinary Portland cement (OPC) to prevent or at least to reduce the problems of air pollution and energy consumption. The results showed that the water of consistency and setting times of fresh cement pastes increased gradually by the addition of either BHA or RHA. Generally, all the studied properties are improved and enhanced with curing time up to 90 days. The combined water content, bulk density, flexural and compressive strengths decreased with curing time up to 3 days, whereas the apparent porosity increased. During the later ages from 3 up to 28 days and then decreased onward, these properties increased, while the apparent porosity decreased. These characters improved and increased only with 16 wt.% BHA or RHA content and then decreased. The free lime content of the OPC pastes increased as the curing time proceeded up to 90 days, while those containing either BHA or RHA increased only up to 3 days and then decreased up to 90 days and then reincreased onward. It was concluded that the higher contents of BHA and RHA (20 wt.%) must be avoided due to its outstanding cementing properties. The FT-IR spectra and SEM images appeared a slight improve in the crystals and microstructures of the newly formed phases.

Keywords: *OPC, BHA, RHA, hydration, setting, combined water, free lime, porosity, density, strength, FT-IR, SEM*

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1. Introduction

In Egypt, the rice production is concentrated in a limited agricultural area around the Nile Delta, where nearly about 8 million tons of rice is produced annually. This is creating a large volume of rice byproducts. Often, an uncontrolled burning of rice husk was done for its disposal. Random burning of either rice or even barely husks creates what is known as "Black Cloud" which is very dangerous to the environment. The seasonal and highly localized massive burning usually generated an excessive air pollution that lowers air quality in the surrounding megacity of Cairo. This has become a serious healthy concern for citizens and authorities [1,2,3,4].

Since 2-3 decades, the pozzolanic cements are widely used all over the world. Such cements are employed for their economical, ecological and technological importance, i.e. reduction of energy consumption and CO_2 emission [4,5,6]. These cements reduce the resulting lime during the hydration process and replace it with pore-filling cement hydrates, which are known to improve the ultimate strength, impermeability and durability to the aggressive attack of chemical environments around cement structures. Several pozzolanic materials are used such as natural pozzolans, low and high calcium fly ashes, silica fume (SF), Perlite and Granulated blast furnace slag (GbfS) and also crystalline materials which generally known as fillers. The pozzolanic activity of these materials is mainly associated with their vitreous and/or amorphous structure [5,6,7,8]. Among of these additives is the ash resulted from the controlled combustion of some agricultural wastes such as rice and barley husks [1,2,3]. Burning these husks under a controlled temperature, a highly reactive material-like ash is obtained.

About 20% of the rice and barley paddy are husks, the majority of these husks are either burnt or dumped as a waste [4-8]. RHA and BHA contain high amounts of SiO_2, and their reactivity related to lime depends on a combination of two factors, namely the noncrystalline silica content and their specific surface. The ashes are very light and easily carried by wind and water in its dry state. Prior to 1970 the rice husk ash was usually produced by uncontrolled combustion, and the ash so produced was generally crystalline and had poor pozzolanic properties [9,10,11,12]. In 1973, Mehta had shown that burning rice husks at 600°C produces an ash with an optimum composition for pozzolanic materials [11].

The main advantage of using RHA as a mineral admixture in a concrete is the significant reduction in the permeability of the concrete. Controlled combustion

influences the surface area of RHA, since that time, temperature and environment are considered to produce ash of maximum reactivity [13]. Some of the advantages include improved workability, reduced permeability, increased ultimate strength, reduced bleeding, a better surface finish and reduced heat of hydration [14,15]. Mineral admixtures or pozzolans are used to improve strength, durability and workability in concretes [14,15,16,17].

Cement notation: C: CaO, S: SiO_2, A: Al_2O_3, F: Fe_2O_3, CS: $CaSO_4$, H: H_2O, CH: $Ca(OH)_2$, CSH: Calcium silicate hydrate, CAH: Calcium Aluminate hydrate.

Smoother mixtures are typically produced if the mineral admixture is substituted for sand rather than cement, but highly reactive or cementitious pozzolans can cause loss of workability through early hydration. Very finely divided mineral admixtures, such as silica fume, can have a very strong negative effect on water demand and hence workability, unless high-range water-reducing admixtures are used. The main objectives of this work are the production of the barley and rice husk ashes and its utilization as additives for Ordinary and Slag Portland cements to study their effect on the physicochemical and mechanical properties of its hardened pastes.

2. Experimental

2.1. Raw Materials

The raw materials are Ordinary Portland cement (OPC-1, 32.5 R) with a Blaine surface area of 3.350 m^2/g was delivered from National Cement Company, El-Tibbin, Egypt as well as the barley (BH) and rice husks (RH). The chemical analysis of the OPC cement as well as RHA and BHA ashes using the X-ray fluorescence (XRF) technique is shown in Table 1, while the mineralogical phase composition of OPC as calculated from Bogue equations [17,18] is given in Table 2.

Table 1. The chemical composition of the raw materials, wt.%

Oxides	L.O.I	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3
Material										
OPC	2.64	20.12	5.25	1.29	63.13	1.53	0.55	0.3	0.23	2.54
RHA	0.84	77.17	8.83	1.29	1.26	0.11	0.03	1.06	0.11	0.02
BHA	0.73	78.30	9.78	1.42	2.84	0.08	0.05	0.85	0.13	0.03

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

Phases	C_3S	β-C_2S	C_3A	C_4AF
Material				
OPC	46.81	28.43	5.90	12.56

2.2. Physical Properties

The physical properties (19,20) of raw materials are calculated from the following relations:

$$Kb = \left(CaO + MgO / SiO_2 + Al_2O_3\right) \qquad (1)$$

$$Hm = \left(CaO / SiO_2 + Al_2O_3 + Fe_2O_3\right) \qquad (2)$$

$$Sm = \left(SiO_2 / Al_2O_3 + Fe_2O_3\right) \qquad (3)$$

$$Am = \left(Al_2O_3 / Fe_2O_3\right) \qquad (4)$$

$$Lm(100xCaO / 2.8\ SiO_2 + 1.1\ Al_2O_3 + 0.7\ Fe_2O_3) \qquad (5)$$

where, Kb, Hm, Sm, Am and Lm are the basicity coefficient, hydration modulus, silicate modulus, aluminate modulus and lime modulus, respectively.

2.3. Preparation of Cement Pastes

At first, the husks of rice (RH) and barely (BH) were processed and washed separately with running water for few minutes and then washed with distilled water, well dried under sun, burned at 600°C for 8 hrs and then screened to pass through 200 mesh sieve (63 µm). The OPC cement was mixed with 0, 4, 8, 12, 16 and 20 wt.% of RHA and BHA ashes as shown in Table 3. The mixes are taken the symbols of R0, R1, R2, R3, R4, R5 for RHA and B0, S1, B2, B3, B4, B5 for BHA, respectively. The pastes were moulded into one inch cubic stainless steel moulds (2.5 x 2.5 x 2.5 cm^3), vibrated manually for two minutes and on a mechanical vibrator for another two minutes. The surfaces of pastes were smoothed with a spatula and then were kept inside a humidity cabinet for 24 hrs at 23 ±1°C and 100% R.H, demoulded and soon cured under water till the time of testing for bulk density, apparent porosity and compressive strength after 1, 3, 7, 28 and 90 days.

Table 3. Cement mixes containing BHA and RHA, wt.%

Group	Raw materials	OPC	BHA	RHA
	B0	100	---	---
	B1	96	4	---
	B2	92	8	---
BHA	B3	88	12	---
	B4	84	16	---
	B5	80	20	---
	R0	100	---	---
	R1	96	---	4
	R2	92	---	8
RHA	R3	88	---	12
	R4	84	---	16
	R5	80	---	20

2.4. Methods of Investigation

The standard water of consistency (or mixing water) as well as setting times (initial and final) of the prepared cement pastes were directly determined by Vicat Apparatus [21,22]. The water of consistency was determined from the following relation:

$$WC,\% = H / W \times 100 \qquad (6)$$

Where, WC is the water of consistency, H is the amount of water taken to produce a suitable paste and W is the weight of the cement sample (300 g). The initial setting time is the time taken to reach the initial set while the final setting time is the time taken to reach the final set of the paste.

The bulk density and apparent porosity [17] of the hardened cement pastes were calculated from the following equations:

$$B. D, \left(g / cm^3 \right) = W_1 / \left(W_1 - W_2 \right) \times 1 \qquad (7)$$

$$A. P, \% = \left(W_1 - W_3 \right) / \left(W_1 - W_2 \right) \times 100 \qquad (8)$$

Where, B.D, A.P, W_1, W_2 and W_3 are the bulk density, apparent porosity, saturated, suspended and dry weights, respectively.

The compressive strength [23] was measured by using a hydraulic testing machine of the Type LPM 600 M1 SEIDNER (Germany) having a full capacity of 600 KN and the loading was applied perpendicular to the direction of the upper surface of the cubes as follows:

$$Cs = L\left(KN \right) / Sa \left(cm^2 \right) KN / m^2$$
$$x \ 102 \left(Kg / cm^2 \right) / 10.2 \left(MPa \right) \qquad (9)$$

Where, Cs: Compressive strength (MPa), L: load (KN), Sa: surface area (cm^2).

The flexural or bending strength [24] was carried out using three point adjustments system (Figure 1), WAM-VEB THÜRIHGER INDUSTRIEWERK, testing machine - model RAUENSTEIN WPM, Berlin. The beam load was applied perpendicular to the axis of the sample. The flexural strength was determined from the following equation:

$$\delta = 3 / 2 \left(F.S / W.T^2 \right) KN / cm^2$$
$$x102 \ Kg / cm^2 / 10.2 MPa \qquad (10)$$

Where, δ is flexural strength (MPa), F is the loading force (KN), S is the span (cm), W and T are width and thickness of the sample (cm).
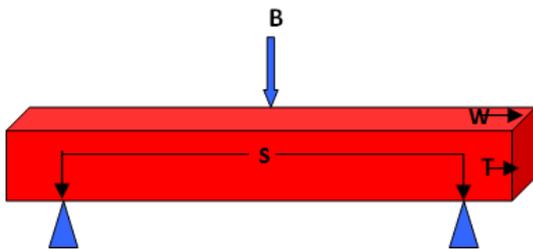
Figure 1. Schematic diagram of the bending strength, B: beam, S: span, W: width and T: thickness

After measuring the mechanical strengths, the hydration of the cement pastes at each interval must be stopped using a mixture of methyl alcohol and diethylether. Then, the chemically-combined water content at each hydration age was determined on the basis of ignition loss [17,21] as follows:

$$Wn, \% = W1 - W2 / W2 \ x100 \qquad (11)$$

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

The free lime content of the hydrated samples pre-dried at 105°C for 24 hours was also determined [25,26,27]. 0.5 g sample + 40 ml ethylene glycol → heating to about 20 min. (without boiling). Add 1-2 drops of ph. ph. indicator to the filtrate and then titrate against freshly prepared 0.1 N HCl till the pink colour disappears. The 0.1 N HCl was prepared using the following equation:

$$V1 = N \ x \ V2 \ x \ W \ x \ 100 \ / \ D \ x \ P \ x \ 1000 \qquad (12)$$

where, V1 is the volume of conc. HCl, V2 is the volume required, N is the normality required, W is the equivalent weight, D is the density of Conc. HCl and P is the purity%. Repeat heating and titration several times till the pink colour does not appear on heating. Calculate the free lime content from the following relation: CaO% = (V x 0.0033/1) x100, where V is the volume of 0.1 N HCl taken on titration.

The phase compositions of some selected samples were investigated using infrared spectroscopy (IR) and scanning electron microscopy (SEM). The IR spectra were performed by Pye-Unicum SP-1100 in the range of 4000-400 cm^{-1}. The SEM images of the fractured surfaces, coated with a thin layer of gold, were obtained by JEOL-JXA-840 electron analyzer at accelerating voltage of 30 KV.

3. Results and Discussion

3.1. Composition of Raw Materials

The chemical composition of the starting raw materials, OPC, BHA and RHA is shown in Table 1. It shows that the cement is composed mainly of CaO (64.63%) and SiO_2 (20.12%) with reasonable amounts of Fe_2O_3 (1.29%), little ratios Al_2O_3 (5.25%), MgO (1. 53%), SO3 (2.54%), Na2O + K2O (0. 85%), free lime (1.09%) and ignition loss (2.64). Due to ASTM-Standards [28], the used cement is the Type I-Ordinary Portland cement (OPC),. The table also illustrates that the two ash samples BHA and RHA are composed mainly of silica (SiO_2); 77.17 and 78.30%, respectively. They possess higher amounts of alumina (Al_2O_3); 8.83 and 9.78, but little amounts of Fe_2O_3; 1.29 and 1.42. There are another constituents in variable amounts e.g. MgO (0.11, 0.08), Na2O (0.03, 0.05), K2O (1.06, 0.), Ti2O (0.11, 0.13) and SO_3 (0.02, 0.03), respectively. The ignition loss of the two ash samples is less than 2%. When the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ is $\geq$ 70%, the material could be considered as a pozzolanic material. On this basis, the sum of SiO_2, Al_2O_3 and Fe_2O_3 of BHA and RHA is 89.5 and 87.29%, respectively, i.e. > 70%. So, the used two ash samples are pozzolanic in nature and the pozzolanicity of BHA is slightly higher than that of RHA. So, they can be used successfully as a partial substitution for Ordinary Portland cement (OPC) to produce blended cement.

3.2. Physical Properties

The physical properties of the OPC, BHA (B1-B5) and RHA (R1-R5) are listed in Table 4, while the relationship between the blaine surface area or fineness of the various cement batches and its densities is plotted in Figure 2. As it is clear, the OPC has a higher Kb and Hm whereas Lm is much higher than those of BHA or RHA, but Sm and Am of BHA or RHA are much higher than those of the OPC. Figure 2 showed that as the fineness of starting raw batches increased, the density decreased. This indicates that BHA or RHA are siliceous and have no hydraulic properties in nature. The data shown in Table 5 indicate that either BHA or RHA are conformed the specifications of ASTM Standards to be used as mineral admixtures for cement pastes, mortars or even concretes [28,29,30,31].

Table 4. The physical properties of raw materials, wt.%

Property	Kb	Hm	Sm	Am	Lm	S. Area, cm²/g	density, g/cm³
Materials							
CEM-I	2.55	2.196	2.331	1.55	97.91	3350	2.8897
BHA	0.033	0.032	6.991	6.89	1.23	1100	2.4866
RHA	0.018	0.014	7.625	6.84	0.558	1000	2.3781

Table 5. The Conformity of the BHA and RHA to ASTM-C618-01

Character	Of control		
1- (SiO₂+Al₂O₃+Fe₂O₃) Content,%	89.50	87.29	Min. 70%
2- SO₃ content,%	0.03	0.02	Max. 4%
3- L.O.I	0.73	0.84	Max. 10%
4- Fineness, retained on 45 µm sieve,%	≈24	≈25	Max. 34%
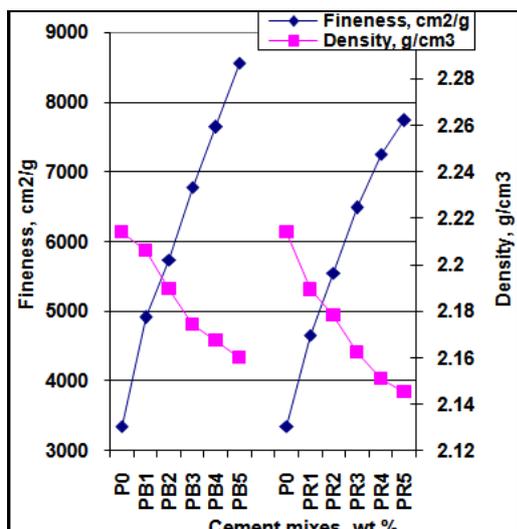
Figure 2. Relationship between the blaine surface area and density of the OPC, BHA (PB0-PB5) and OPC/RHA (PR0-PR%) cement mixes

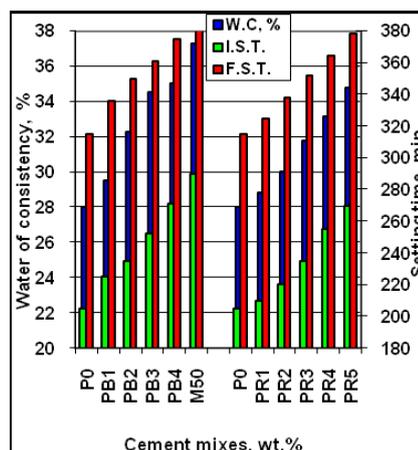## 3.3. Water of Consistency and Setting Times
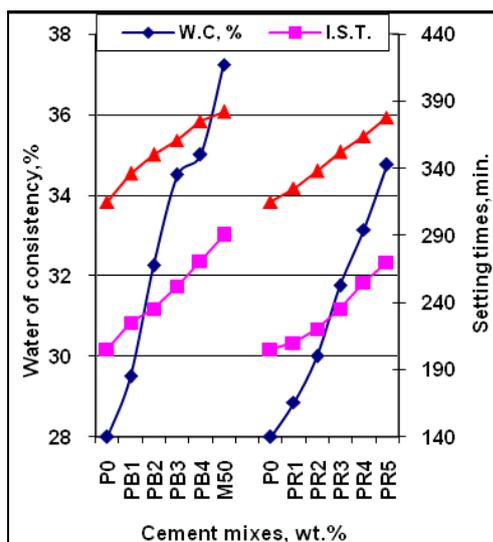
Figure 3. Water of consistency and setting times of cement pastes with BHA and RHA

The water of consistency as well as setting times are represented as a function of BHA (B1-B5) and RHA (R1-R5) content in Figure 3 and Figure 4. It is obvious that the water of consistency of OPC pastes is increased with the increase of BHA and RHA contents. This is mainly due to the higher blaine surface area of the two ash specimens (10 and 11 m²/g) than the OPC (3100 cm²/g) in addition to the hygroscopic nature of the two ash samples which consumes relatively higher amounts of mixing water. These observations are limited to that observed with other several researchers [30,31,32].

The setting times (initial and final) of the OPC pastes (B0 or R0) are also increased gradually as the BHA (B1-B5) or RHA (R1-R5) contents increased. These values are in a good agreement with several studies [4,14,17,33,34,35,36].

Figure 4. Water of consistency and setting times of cement pastes with BHA and RHA

3.4. Combined Water Content

The combined water content (CWn) of the OPC (P0) cement paste mixed with 4, 8, 12, 16 and 20 wt.% of BHA (B1-B5) and RHA (R1-R5) are plotted as a function of curing time up to 90 days in Figure 5. Generally, the CWn of all cement mixes increased continuously with curing time up to 90 days. The Wn of the control mix (P0) are gradually increased sharply with curing time up to 28 days due to the rapid normal hydration process and then slightly increased up to 90 days due to the fact that about 75% of the hydration was completed at the first 28 days and the rest 25% behaved as a slight increase up to 90 days. The cement phases C_3S, C_3A and C_4AF are responsible for the early hydration up to 28 days while $β–C_2S$ for the older hydration from 28 days onwards [17,18].
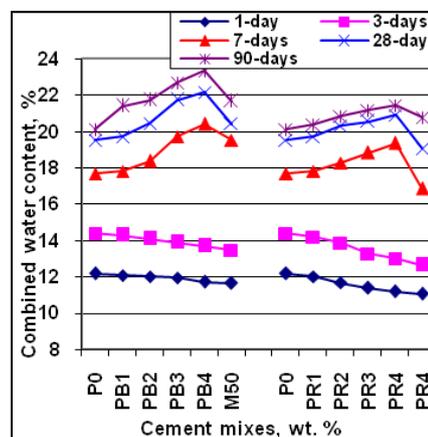
Figure 5. Combined water content of cement pastes with BHA and RHA cured up to 90 days

On the other side, the CWn of cement pastes containing either BHA (B1-B5) or RHA (R1-R5) are decreased up to 3 days compared with those of the blank, i.e. the values of CWn are lower than those of the blank, but then started to increase up to 28 days and then redecreased again (Figure 5), i.e. after the first 3 days of hydration, the CWn enhanced with the increase of BHA or RHA contents only up to 16 wt.%, i.e. the optimum content of both agrowastes is 16 wt,%. This is essentially due to the pozzolanic reactivity of the two used agrowastes are the maximum [4,25,34], and then decreased due to the fact that the higher amounts of the agrowastes prevent or hinder the hydration of cement phases to some extent, and so it affected adversely on it [27,35,36,37]. Moreover, the values of CWn are slightly higher with BHA than with RHA. As a result, it can be concluded that the higher amounts of either agrowastes must be avoided.

3.5. Free Lime Content

The free lime content (FLn) of the OPC pastes (P0) mixed with 4, 8, 12, 16 and 20 wt.% of BHA (B1-B5) and RHA (R1-R5) are plotted as a function of curing time up to 90 days in Figure 6. It is generally clear that the (FLn) of the OPC pastes (P0) increased with curing time up to 28 days and then seemed to be nearly constant, whilst those of the other cement blends (B1-B5) and (R1-R5) increased only up to 3 days and then decreased gradually up to 28 days and then started to reincrease again up to 90 days. The increase of the (FLn) of P0 is mainly due to the rapid hydration of C_3S at early ages of hydration and the hydration of β-C_2S at older ages [4,10,11,17,18,19]. The decrease of (FLn) of B1-B5 or R1-R5 is essentially due to the pozzolanic reactions that can take place between the constituents of the added BHA or RHA with the released Ca $(OH)_2$ from the hydration of C_3S and β–C_2S phases of OPC [4,17,18].
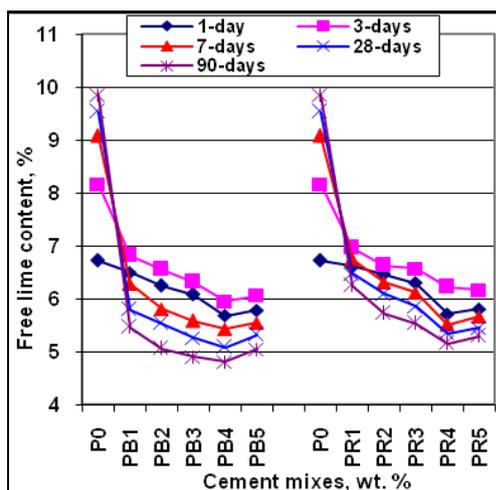

Figure 6. Free lime content of cement pastes with BHA and RHA cured up to 90 days

The (FLn) of B1-B5 and /or R1-R5 during the first 3 days are lower than those of the P0 at all curing ages of hydration. This is attributed to the deficiency of the main hydration material [4,8,11]. On the other side, the cement pastes containing BHA recorded the lowest values of (FLn) than those containing RHA at all curing ages. This is mainly attributed to the higher pozzolanicity rate of BHA than RHA [38,39,40]. Cement pastes of B4 containing 16

wt.% BHA shows the lowest values of (FLn) than OPC mix due to its highest rate of pozzolanity. This indicates that BHA has a higher pozzolanic reactivity than RHA. This is evidently in a good agreement with those of combined water.

3.6. Bulk Density and Apparent Porosity

Figure 7 and Figure 8 show the bulk density (BD) and apparent porosity (AP) of the OPC cement pastes (P0) blended with 4, 8, 12, 16 and 20 wt.% of BHA (B1-B5) and RHA (R1-R5) are plotted as a function of curing time up to 90 days, respectively. Generally, the (BD) increased as the curing time proceeded up to 90 days, while the (AP) decreased. This is mainly attributed to the normal hydration of cement phases and so the continual formation of hydration products which in turn deposited into the pore structure of the cement pastes. Hence, the (AP) gradually decreased and the compactness of samples improved. This means that the (BD) increased [17,36,41]. As the amount of BHA and/or RHA increased, the (BD) slightly decreased only up to 3 days and the (AP) increased. This is attributed to the continuous deficiency of cement which is responsible for the hydration process [17,18] and also, to the relatively lower density of both BHA and RHA compared with OPC. The (BD) slightly increased from 3 to 28 days and the (AP) decreased. This is essentially due to the pozzolanic reactivity of BHA or RHA with the releasing Ca $(OH)_2$ from the hydration of C_3S and β-C_2S phases of the cement [42]. From 28 to 90 days, the (BD) tended to redecrease. The same trend was achieved by all cement blends, i.e. the hydration and the pozzolanic reactions of BHA or RHA may be ceased or nearly completed at 28 days because the change in the (BD) or even the (AP) in the period from 28 to 90 days is intangible [1,2,3,4]. Furthermore, the (BD) of either PB4 or PR4 containing 16 wt.% of both BHA and RHA exhibited the highest and lowest values of (BD) and (AP). The higher amounts of these agrowastes hindered and reduced the hydration of cement phases and affected adversely on it [25,26,34,37]. So, the higher amounts of these agrowasted must be avoided. Hence, it can be concluded that the obtained results of (BD) and (AP) are in accordance with those of combined water and free lime contents.
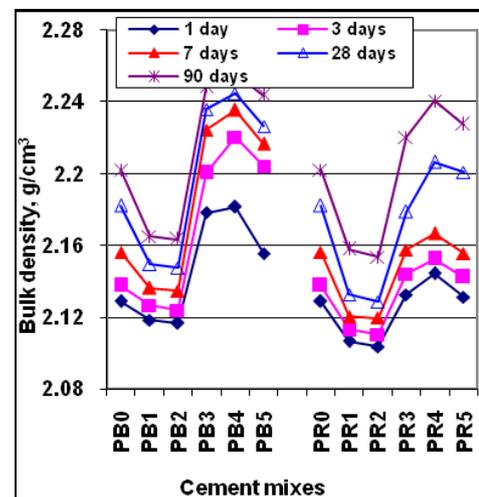

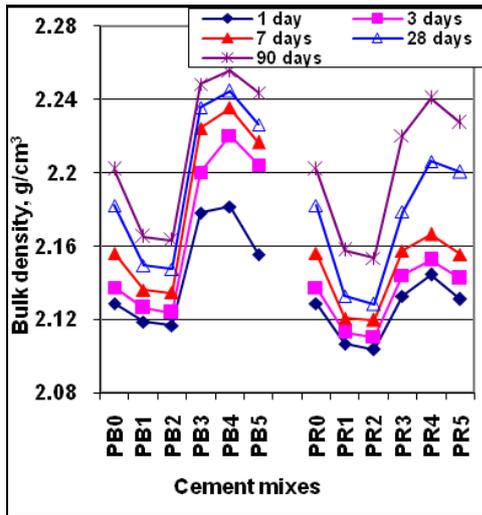**Figure 7.** Bulk density of cement pastes with BHA and RHA cured up to 90 days

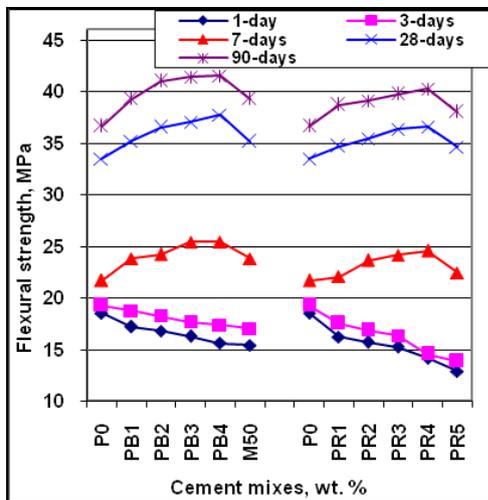**Figure 8.** Bulk density of cement pastes with BHA and RHA Cured up to 90 days

Figure 9. Flexural strength of cement pastes with BHA and RHA cured up to 90 days

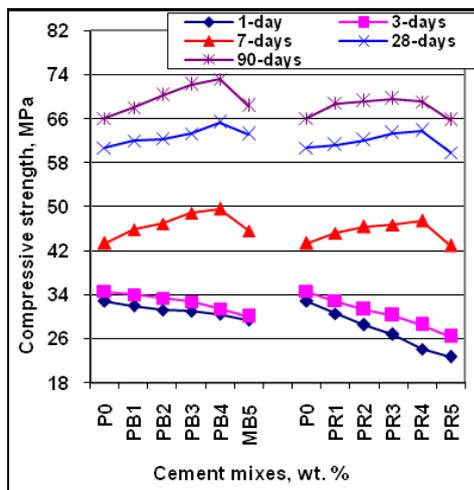## 3.7. Compressive Strength

Figure 10. Compressive strength of cement pastes with BHA and RHA cured up to 90 days

The compressive strength (CS) of the OPC pastes (P0) blended with 4, 8, 12, 16 and 20 wt.% of BHA (B1-B5) and RHA (R1-R5) are graphically represented as a function of curing time up to 90 days in Figure 9. In a general sense, as the curing time progressed, the (CS) gradually improved and increased up to 90 days. This is mainly attributed to the continual deposition of the formed hydration products filling the pore structure. Hence, the total porosity decreased. This evidently reflected positively on the BD and often followed by an increase in the (CS) [4,16-18]. The increase of (CS) from 28 to 90 days is less significant. The (CS) of cement blends containing either BHA or RHA decreased up to 3 days and then increased up to 28 days which then began to redecrease again but still slightly higher than those of the blank. Moreover, the (CS) increased with the increase of BHA or RHA content only up to 16 wt.% and then decreased. This is principally due to the high rate of pozzolanic activity of both BHA and RHA that could consume the resulting $Ca(OH)_2$ from the normal hydration process, where it is higher with BHA than with RHA [1,3,11,17]. So, the optimum BHA or RHA content is 16 wt.%. Furthermore, the (CS) values of cement pastes containing BHA are slightly higher than those containing RHA, i.e. the pozzolanic activity of BHA is more than that of RHA. At all, the results of (CS) are in a well accordance with those of previous tests.

The (CS) values were improved and enhanced with the addition of BHA or RHA after 7 days of hydration. This is essentially attributed to the pozzolonic reactivity of these materials which started after the first 3 days of hydtration. The constituents of BHA or RHA could be reacted with $Ca(OH)_2$ evolved during the hydration of the OPC phases (C_3S and β-C_2S), to create new phases which are responsible to improve the specific properties of the hardened cement pastes [31,41,42]. The increase of (CS) is also due to a filler effect beside the higher pozzolanic character of ashes because these ashes are very fine [31,33,43,44]. This means that the higher strength is primarily due to the finer particles of ashes than those of the OPC which causes the segmentation of large pores and increases the nucleation sites for the precipitation of pozzolanic reaction products in cement paste, which in turn increases the pozzolanic reaction and refines the pore structure of the paste. The increase of hydration rate leads to the reduction of $Ca(OH)2$ in the paste. The incorporation of pozzolan such as BHA or RHA reduces the average size and results in impermeable pastes [41-44]. The decrease of (CS) with the increase of ash content at early ages of hydration up to 3 days may be due to the higher deficiency of the OPC, whereas at older ages of hydration is due to the complete consumption of the $Ca(OH)2$ by the pozzolanic reactions with BHA or RHA. Accordingly, the excess contents of ash (>16 wt.%) are not involved in the pozzolanic process as a result of the marked decrease of OPC. Hence, the $Ca(OH)2$ resulting from its hydration was re-increased.
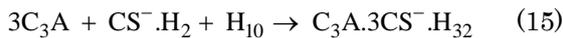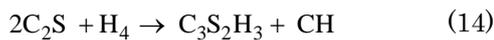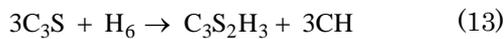
3.8. Flexural Strength

The flexural Strength (FS) of the OPC cement pastes (P0) blended with 4, 8, 12, 16 and 20 wt.% of BHA (B1-B5) and RHA (R1-R5) are graphically plotted as a function of curing time up to 90 days in Figure 10. The (FS) of all mixes displayed the same trend as in CS at all curing ages of hydration but with lower values. The (FS) values of all cement pastes are lower than those of the
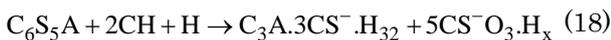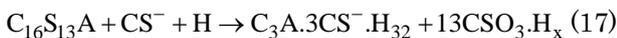
control cement (P0) during the early ages of hydration up to 3 days, but became slightly higher during the later ages (28 and 90 days). The addition of > 16 mass% BHA or RHA to the OPC decreases the (FS) at all curing stages, but still higher than that of the blank. At all, the (FS) values of BHA mixes are slightly more than those of RHA. This is due to that the higher water absorption capacity of RHA than BHA which creates more pore structure and worsens the workability of the pastes. This negatively reflected on the mechanical properties [29-31]. The cement blend containing 16 mass% BHA or RHA (B4 or R4) achieved the highest results of (FS) at all curing periods, but >16 mass% (B5 or R5), the cement blends recorded the lowest values but still higher than that of the blank. So, the high amounts of either BHA or RHA must be avoided when added to OPC.

3.9. Mechanism of Hydration and Pozzolanic Reactions

It is well known that the major phases of the OPC are C_3S, β-C_2S, C_3A and C_4AF which can be hydrated [17,18] as follows:

$$3C_3S + H_6 \rightarrow C_3S_2H_3 + 3CH \qquad (13)$$

$$2C_2S + H_4 \rightarrow C_3S_2H_3 + CH \qquad (14)$$

$$3C_3A + CS^-.H_2 + H_{10} \rightarrow C_3A.3CS^-.H_{32} \qquad (15)$$

$$C_4AF + 2CH + H_{10} \rightarrow 6CAFH_{12} \qquad (16)$$

The constituents of BHA and RHA can react of the raw gypsum in the presence of water to produce ettringite and CSH and moreover can react with a part of the free lime $Ca(OH)_2$ resulting from the hydration of the OPC phases to form ettringite and CSH [4,14,33] as follows :

$$C_{16}S_{13}A + CS^- + H \rightarrow C_3A.3CS^-.H_{32} + 13CSO_3.H_x \quad (17)$$

$$C_6S_5A + 2CH + H \rightarrow C_3A.3CS^-.H_{32} + 5CS^-O_3.H_x \quad (18)$$

On the other side, the main components of both ashes are Al_2O_3 and SiO_2 which can react with a larger part of the resulting $Ca(OH)_2$ from hydration to form cubic crystals of hydrogarnet ($C_3A. S_2.Hn$) [14,33]as follows:

$$A + S + CH + H \rightarrow C_3A. S_2. H_n \qquad (19)$$
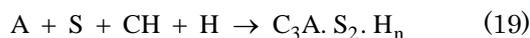
The formation of these new phases is responsible for the strength development along with the whole reaction.

3.10. The FT-IR Spectra

The FT-IR spectra of the OPC (P0) and those blended with 16 wt.% BHA (PB4) and RHA (PR4) hydrated up to 90 days, are shown in Figure 11. The sharp absorption band at 3646-3640 cm^{-1} is related to the free OH- group that coordinated to Ca^{+2} ($Ca(OH)_2$ or free lime). The intensity of the broad absorption band at 3454-3428 cm^{-1}, which was ascribed to the OH$^-$ group associated to H$^+$ bond that related to the symmetrical stretching frequency of water, increased in presence of BHA or RHA. The two absorption bands at 1646-1636 cm^{-1} and 1435-1425 cm^{-1} are related to the main silicate band involving Si-O stretching vibration bands of CSH, while the band at 1122-1114 cm^{-1} may be due to CAH. The intensity of the two absorption bands at 998-984 cm^{-1} and 876 cm^{-1} characterizing CO_3^{2-} and SO_4^{2-} is irregular due to the rate

of carbonation or sulphonation of CSH and /or CAH, where the vibrations of CO_3^{2-} are smaller than those of SO_4^{2-}. Also, the intensity of the absorption bands of Si-O, CAH, CO_3^{2-} and SO_4^{2-} are slightly higher with BHA cement mixes. The intensities of the main characteristic peaks were slightly improved with OPC than with BHA or RHAcement pastes.
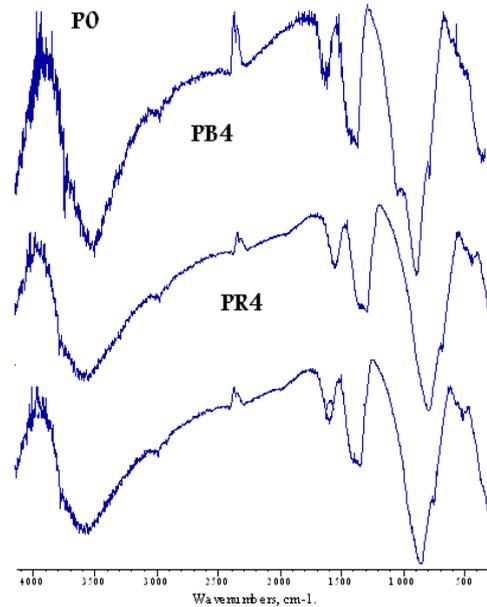

Figure 11. The FT-IR spectra of the OPC (P0) and those blended with BHA (PB4) and RHA (PR4) cured up to 90 days
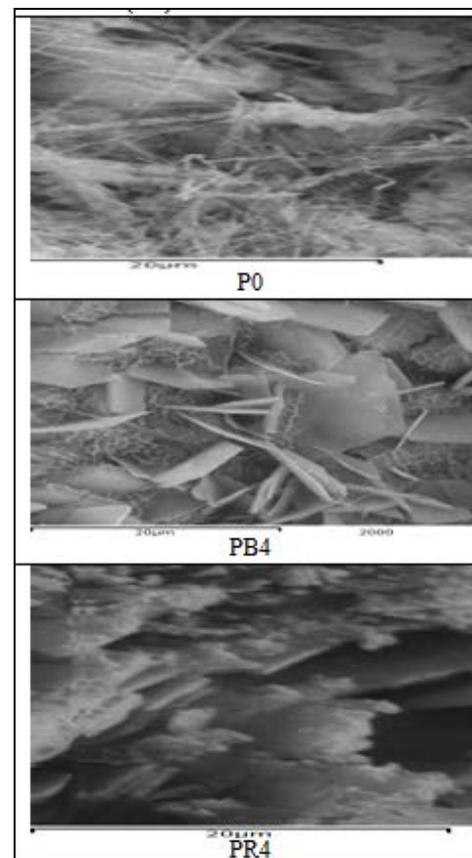
3.11. The SEM Images

Figure 12. The SEM images of P0, PB4 and PR4 cement Pastes cured up to 90 days

Figure 12 illustrates the SEM micrographs of the interfacial layers of the OPC (P0) and the optimum cement pastes blended with BHA (PB4) and RHA (PR4) hydrated in water up to 90 days. It is obvious that the major hydration products are CSH in all samples. Also, the ettringite phase and portlandite or free lime, Ca (OH)$_2$ are clearly shown in the matrix (P0) as needle-like crystals and white granules which reduced or disappeared with the blended cement pastes particularly with mixes PB4 or PR4. This is mainly due to the transformation of ettringite into monosulphate and the pozzolanic reaction of BHA and RHA with the Ca (OH)$_2$. Also, the crystals either BHA or RHA are well-developed when compared with those of the OPC (P0).

4. Conclusion

1. The water of consistency as well as setting times of the OPC cement pastes (P0) increased gradually by the incorporation of either BHA or RHA and it is slightly higher with RHA than with RHA cement mixes.

2. The combined water content (Wn), bulk density (BD) and compressive strength (CS) of the blank increased while the apparent porosity (AP) decreased with curing times up to 90 days, but decreased with either BHA or RHA contents up to 3 days and then started to increase gradually up to 28 days and decreased onward. Moreover, this continued up to 16 wt.% BHA or RHA and then decreased.

3. The free lime content (FLn) of the OPC pastes increased as the curing time proceeded up to 90 days, while those containing either BHA or RHA increased only up to 3 days and then decreased up to 28 days of hydrationand then decreased onwards.

4. Generally, the partial substitution of BHA or RHA to OPC pastes improved the specific cementing properties in the following descending order BHA > RHA which contributed to their pozzolonic character.

5. The higher contents of BHA and RHA (>16 wt.%) must be avoided because it caused adverse cementing properties.6- The FT-IR spectra and SEM micrographs showed a slight improve in the crystals and structures of the newly formed hydration product..

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