CRONICON
OPEN ACCESS

CHEMISTRY
Research Article

# Quaternary Cement Composites Containing Some Industrial By-products to Avoid the Environmental Pollution

**HHM Darweesh[1]* and MR Abo-El-Suoud[2]**

[1] *Department of Refractories, Ceramics and Building Materials, Egypt*

[2] *Department of Botany, National Research Centre, Cairo, Egypt*

***Corresponding Author:** HHM Darweesh, Department of Refractories, Ceramics and Building Materials, Egypt.

**Received:** September 15, 2015; **Published:** November 04, 2015

## Abstract

Seven Quaternary cement composites were prepared from ground granulated blast furnace slag (GGBS), fly ash (FA), silica fume (SF), rice husk ash (RHA) and Homra (H) waste materials by replacing equal ratios (7 wt. %) of any three types of these wastes at the expense of OPC (M0-M6). The results showed that the incorporation of 7% of any three types of these wastes with OPC pastes increases its standard water of consistency as well as setting time, chemically-combined water content and bulk density, but decreases the free lime content and the total porosity. The compressive strength of the hardened Portland cement pastes was greatly improved and enhanced at all curing ages up to 90 days. The free lime contents of mixes (M1, M2 and M3) are increased up to 3 days of hydration and then decreased onwards, while those of mixes (M4, M5 and M6) increased up to 7 days and then decreased, i.e. the pozzolanic property started to appear after 3 days with M1-M3, whereas with M4-M6 after 7 days. The cement composite M3 exhibited the highest and best results while that of M6 recorded the lowest. The resulting CSH with the cement composites (M1-M6) on hydration are the same with the OPC pastes, but with modified and improved crystals and morphologies, particularly those of M3. Large amounts of CSH and a lower amount of free lime Ca $(OH)_2$ evidently could be detected in the hardened cement pastes by FTIR spectra as well as SEM micrographs.

***Keywords:*** *Slag; Fly ash; Silica fume; Rice husk ash; Homra; wastes; CSH; Strength; Free lime; Combined water; IR; SEM*

## Introduction

Due to not only the high consumption of energy but also to the high price of energy, most countries had done their best to save-wise its use. The cement industry is one of the most consuming energy either by its thermal or electrical forms. This will be carried out by developing new technologies for manufacturing or by the reduction of energy consumption [1-11]. This can also be made by increasing the recycling or reutilization of these harmful industrial byproducts to produce another types of cement at least to avoid the environmental pollution with these wastes and to keep the environmental balance on the other hand [12-16]. Some of the commonly used supplementary waste materials are silica fume, granulated blast furnace slag, fly ash, rice husk ash, homra, cement bypass dust, natural or synthetic zeolite and perlite. Unfortunately, most of those wastes are dumped into the environment without any commercial return. As a result, environmental pollution is increased by time [17-19].The current annual production of cement kiln dust (CKD), fly ash (FA) and granulated blast furnace slag (GGBS) all over the world is about 2500, 450 and 100 million tons annually, respectively. Only about 25 million tons which represents about 6 mass % of the total available fly ash is being used as a pozzolanic material in blended cement, mortar or concrete mixtures. The utilization amount of granulated blast furnace slag as a cementitious material is quite low because in many countries like Egypt, only small quantity of the produced slag is available in the granulated form, which is having the cementitious property. The silica fume (SF) is an artificial ultrafine amorphous glassy solid sphere of silicon dioxide with high surface area (20-22 $m^2/g$) and water demand forming during the manufacture of silicon and its alloys as ferrosilicon [20-24]. Also, Homra is the broken waste of the fired building bricks. These wastes often pollute the environment and represent a heavy load on it.

The use of pozzolanic cements is increasing worldwide because they need less energy for production, less effort and lesser costs. Furthermore, these cements can withstand against sulphate, chloride and sea water attack for longer periods [25-27]. Studies on the individual specific characteristics of these waste materials, their combination and their influence on the properties of cement pastes, mortars or even concrete are very necessary for their adequate and effective use. When siliceous byproducts such as granulated slag, fly ash, silica fume, homra and rice husk ash are mixed with Portland cement and let to hydrate in water, they can react and hydrate with cement portion. This can produce a more pore, more discontinuous and impermeable structure than that of the hydrated Portland cement pastes [23, 25, 28]. So, the objectives of this study is to investigate the influence of GGBS, FA, SF, RHA and H waste materials on the specific properties of Portland cement pastes.

## Experimental

### Raw Materials

The raw materials used in the study are Ordinary Portland cement (OPC Type I- CEM I 42,5R), granulated blast furnace slag (GGBS), fly ash (FA), rice husk ash (RHA), Homra (H) and silica fume (SF) as mineral admixtures. The OPC and GGBS with Blaine surface area 3300 and 4450 $cm^2/g$, respectively are obtained from Tourah Portland Cement Company, while SF sample with a surface area of 22 $m^2/g$ was provided by Ferrosilicon alloys Company, Edfo, Egypt. The FA sample having the specific surface area of 5850 $cm^2/g$ was obtained from the Toshki project which was previously imported from abroad. The H sample was taken from a local brick-making plant. To obtain the RHA, the rice husk (RH) was processed and washed with running water for few minutes and then washed with distilled water, well dried under sun and open air, burned at 600°C for 8 hrs and then screened to pass through 200 mesh sieve (63 µm).The chemical composition of the starting raw materials is shown in Table 1, while the mineralogical phase composition of OPC as calculated from Bogue equations [29] is given in Table 2.

| Materials Oxides | OPC | GGBS | FA | SF | H | RHA |
|---|---|---|---|---|---|---|
| LOI | 0.51 | 0.43 | 1.76 | 0.63 | ---- | 0.84 |
| $SiO_2$ | 22.14 | 38.21 | 49.49 | 9436 | 58.22 | 81.17 |
| $Al_2O_3$ | 4.86 | 10.45 | 25.75 | 1.09 | 28.25 | 9.83 |
| $Fe_2O_3$ | 4.13 | 1.27 | 9.96 | 1.26 | 8.16 | 1.29 |
| CaO | 62.32 | 37.70 | 5.81 | 1.02 | 0.79 | 1.26 |
| MgO | 2.17 | 2.05 | 2.44 | 0.45 | 0.46 | 1.84 |
| MnO | 0.36 | 3.50 | ---- | ---- | ---- | 0.11 |
| $Na_2O$ | 0.65 | 1.61 | 1.24 | 0.07 | 1.46 | 0.03 |
| $K_2O$ | 0.36 | 0.71 | 2.02 | 0.49 | 1.32 | 1.06 |
| $SO_3$ | 1.89 | 3.50 | 0.54 | 0.33 | ---- | 0.02 |
| $TiO_2$ | ----- | 0.24 | 0.43 | 0.02 | 0.61 | 0.13 |
| Undetermined | ---- | 0.33 | 0.56 | 0.28 | 0.63 | 2.42 |
| Blaine surface area, $cm^2/g$ | 3300 | 4450 | 5850 | 19 x $10^4$ | 4650 | 5350 |

***Table 1:*** *Chemical composition of the investigated raw materials, mass %.*

| Phase Material | $C_3S$ | β-$C_2S$ | $C_3A$ | $C_4AF$ |
|---|---|---|---|---|
| OPC | 46.81 | 28.43 | 5.90 | 12.56 |

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

***Citation:*** HHM Darweesh and MR Abo-El-Suoud. "Quaternary Cement Composites Containing Some Industrial By-products to Avoid the Environmental Pollution". *EC Chemistry* 2.1 (2015): 78-91.

| Materials Mixes | OPC | GGBS | FA | SF | RHA | H | Blaine surface area of mixes, $cm^2/g$ |
|---|---|---|---|---|---|---|---|
| M0 | 100 | ---- | ---- | ---- | ---- | ---- | 3300 |
| M1 | 79 | 7 | ---- | 7 | 7 | ---- | 4100 |
| M2 | 79 | 7 | 7 | ---- | ---- | 7 | 4250 |
| M3 | 79 | 7 | 7 | 7 | ---- | ---- | 4600 |
| M4 | 79 | ---- | 7 | ---- | 7 | 7 | 3550 |
| M5 | 79 | 7 | 7 | ---- | 7 | ---- | 3475 |
| M6 | 79 | ---- | ---- | 7 | 7 | 7 | 3400 |

***Table 3:*** *The composition of mixes, wt. %and their blaine surface areas,* $cm^2/g$.

**Preparation and Methods**

The blending proportions of the various cement mixes are shown in Table (3), taking into account that the combination of GGBS and/or FA and/or SF and/or RHA and/or H was used at the total dosage of 21 wt. % replacing the same amount of cement in order to keep the weight of the essential binding material (OPC) the same. The blending process of the various cement blends was done in a porcelain ball mill for two hours using three balls to assure the complete homogeneity of all blends. The standard water of consistency as well as setting time of the various cement pastes were directly determined using Vicat apparatus [30, 31] from the following relation:

$$W.\ C, \% = A / C \times 100 \qquad (1)$$

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, moulded into one inch cubic stainless steel moulds (2.5 x 2.5 x 2.5 $cm^3$) using about 500g cement mix, vibrated manually for two minutes and then on a mechanical vibrator for another two minutes. The moulds were placed in a humidity chamber for 24 hours, de moulded in the following day and then cured in water till the time of testing 1, 3, 7, 28 and 90 days. The bulk density and apparent porosity [1, 12, 13, 15, and 29] of the hardened cement pastes were first calculated from the following equations:

$$B.\ D, (g/cm^3) = W^1/(W_1–W_2) \times 1 \qquad (2)$$

$$A.\ P, \% = (W_1 – W_3)/(W_1–W_2) \times 100 \qquad (3)$$

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 [32] 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:

$$Cs = L\ (KN)/Sa\ (cm^2)\ KN/m^2 \times 10^2\ (Kg/cm^2)/10.2\ (MPa) \qquad (4)$$

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

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 [14, 33]. The kinetics of hydration in terms of chemically combined 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-combined water content at each hydration age was determined on the basis of ignition loss at 1000°C for 30 min. [4, 16, and 33] as follows:

$$Wn, \% = W_1\text{-}W_2/W_2 \times 100 \qquad (5)$$

***Citation:*** HHM Darweesh and MR Abo-El-Suoud. "Quaternary Cement Composites Containing Some Industrial By-products to Avoid the Environmental Pollution". *EC Chemistry* 2.1 (2015): 78-91.

Where, Wn, $W_1$ and $W_2$ 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 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 colour disappeared. The 0.1N HCl was prepared using the following equation:

$V_1 = N \times V_2 \times W\ (7) \times 100/D \times P \times 1000$ (6)

Where, $V_1$ is the volume of HCl concentration, $V_2$ 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 [5, 13, 15, and 16] was calculated from the following relation:

Free lime, % = $(V \times 0.0033/1) \times 100$ (7)

Where, V is the volume of 0.1 N HCl taken on titration.

The phase composition of cement pastes were further investigated by infrared spectroscopy (FT-IR). The FT-IR spectra were performed by an FT-IR spectrometer in the range of 400-4000 $cm^{-1}$ and a resolution of 4 $cm^{-1}$ (Nexus 670, Nicolet, USA).

## Results and Discussion

Generally, the surface area of fly ashes (FA), granulated slag (GGBS), fly ash (FA), silica fume (SF), Homra (H) and rice husk ash (RHA) is one of the most important characters having a crucial influence on the specific properties of both fresh and hardened cement pastes, mortar or even concrete. Hence, the water demand and workability of Portland cement blended with these materials essentially depend on their finenesses, shape, and morphology and particle size distribution [9, 15, and 34]. On the other side, the particle size and crystalline/amorphous ratio play a vital role in their reactivity towards lime. This is mainly due to the pozzolanic reactivity that can take place on the surfaces of particles. Furthermore, the glassy content of these materials is greater for the finest fractions, which in turn affects largely the rate of their pozzolanic reactivity [13,25, and 35].

### Water of Consistency and Setting Time

The water of consistency as well as setting times (initial and final) of the pure OPC paste (M0) compared with those of other cement pastes (M1-M6) are graphically represented as a function of cement mixes in Figure 1. The water of consistency of the OPC pastes (M0) tends to increase with the incorporation of GGBS, FA, SF (M1); GGBS, SF and RHA (M2); SF, RHA and H (M3), GGBS, FA and RHA (M4); FA, RHA and H (M5); SF, RHA and H (M6). This is mainly attributed to the increase of the specific surface area or fineness of the cements due to the high surface area of the added waste materials which is certainly responsible for high water demand [13,16, and 27]. The combination of SF, H and RHA (M3) exhibited the highest value of water of consistency. This may be due to the high surface area of SF, H and RHA in comparison with other waste materials [1,25]. In a general sense, the combination of three pozzolanas together recorded a lower amount of water of consistency than those of the pure OPC pastes due to the lesser fineness of the OPC than the other mixes [15,27].

On the other hand, the setting time of the corresponding cements displays the same trend as water of consistency, i.e. the initial and final setting times are elongated. The pure OPC pastes (M0) shows the lowest values of both initial and final setting times (120 and 241 min) due to its lowest amount of the water of consistency (28%). As the water of consistency increases, the initial and final setting times are elongated and the vice versa. The presence of the very fine pozzolanas shows a greater setting times (initial and final) than those of the OPC cement pastes. This is essentially attributed to the presence of very fine active pozzolana, in addition to higher mixing water. These two factors are responsible for the elongation of both setting times [36, 37].

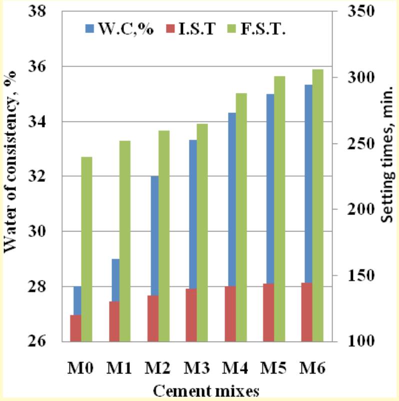

***Figure 1:*** *Water of consistency and setting time of the pure OPC pastes (M0) and the various cement pastes (M1-M6).*

**Chemically-Combined Water Content**

Figure 2 illustrates the chemically combined water contents of the pure OPC pastes (M0) and the various cement pastes (M1-M6) as a function of cement mixes. Generally, the combined water content of the various cement pastes increases gradually with curing time up to 90 days. This is mainly due to the gradual and continuous formation of hydration products from the chemical reactions between the different phases of OPC with water to form CSH and sulphoaluminate hydrates. This is often responsible for the increase of combined water contents [5,10 and 15]. Moreover, the GGBS, FA and SF can react with the released Ca $(OH)_2$ from the hydration of $C_3S$ and β-C2S to form additional amounts of hydration products as CSHs and calcium aluminosilicate (CAHs) hydrates. This causes further increase in the combined water contents of the hardened cement pastes [1,12 and 14]. M3 containing GGBS, FA and SF exhibited the highest values of combined water, whilst M6containing SF, RHA and H achieved the lowest values at all curing times up to 90 days. The decrease of combined water contents of M6 is mainly due to the sluggish rate of hydration of RHA as well as H. On the other side, the increase of combined water contents of M3 is mainly attributed to the high hydraulic properties of GGBS, FA and SF. It can be noticed that the blended cement pastes of M4 (FA, RHA, H), M5 (FA, RHA, GGBS) and M6 (SF, RHA, H) recorded lower values of combined water than those of OPC at all hydration ages (Figure 2), while the cement pastes of M1 (GGBS, SF, RHA) and M2 (GGBS, FA, H) show higher values of combined water than OPC pastes at all hydration ages (Figure 2). This is due to the high hydration characteristics of SF, FA, H and GGBS to the evolved Ca (OH) 2 and higher water demand of SF in comparison to OPC pastes [14-16].

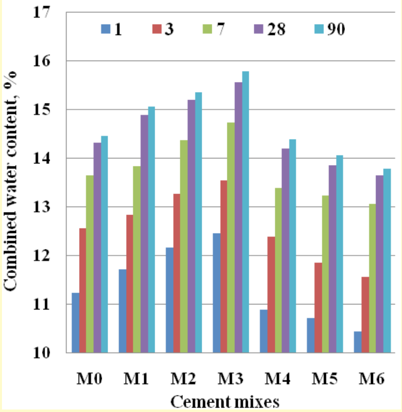

***Figure 2:*** *The combined water content of the pure OPC pastes (M0) and the various cement pastes (M1-M6) cured up to 90 days.*

***Citation:*** HHM Darweesh and MR Abo-El-Suoud. "Quaternary Cement Composites Containing Some Industrial By-products to Avoid the Environmental Pollution". *EC Chemistry* 2.1 (2015): 78-91.

### Free Lime Content

The free lime contents of the pure OPC pastes (M0) and the various blended cement pastes (M1-M64) are plotted as a function of curing time in Figure 3 and as a function of cement mixes in Figure 4. It is well known that when the cement powder becomes in contact with water, the hydration process starts immediately and accompanied by the evolution of what is known as free lime, Ca (OH) 2 as follows:

$3C_3S + H_6 \rightarrow C_3S_2H_3 + 3Ca\,(OH)_2$ (8)

$2C_2S + H_4 \rightarrow C_3S_2H_3 + Ca\,(OH)_2$ (9)

Figure 5 shows that the free lime content of the OPC pastes (M0) increases with curing time up to 90 days, whilst those of the other blended cement pastes decrease gradually after the 3rd and 7th days of hydration. The free lime contents of M1, M2 and M3 increase only up to 3 days and then decreased whilst those of M4, M5 and M6 increased up to 7 days and then decreased onward. This means that the pozzolanic reactivity started after 3 with M1, M2 and M3 or after 7 days of hydrations with M4, M5 and M6. The continuous increase of the free lime of M0 is mainly due to the rapid hydration of C3S at early ages of hydration and the hydration of β-$C_2S$ at later ages [15,27,35]. The decrease of free lime contents of 1$M_1$-M6 is essentially attributed to the pozzolanic reactions that can occur between the active silica of GGBS and/or FA and/or SF and/or H and/or RHA with the released Ca $(OH)_2$ from the hydration of Portland $C_3S$ and β-C2S [35,37]. The cement pastes of M6 containing recorded the highest values of free lime at all curing ages up to 90 days. This is mainly attributed to the slow rate of hydration of H, RHA in comparison with SF, while the cement pastes of M3 (GGBS, FA, SF) shows the lowest values also at all curing ages. This means that the SF and RHA have the higher capability to react with the released free lime than the other pozzolanic materials [16,28,35-37]. Hence, the cement pastes incorporated of the three pozzolanic waste materials show the lower values of free lime contents at all curing times if compared the pure OPC pastes. This is in a good agreement with the values of combined water.

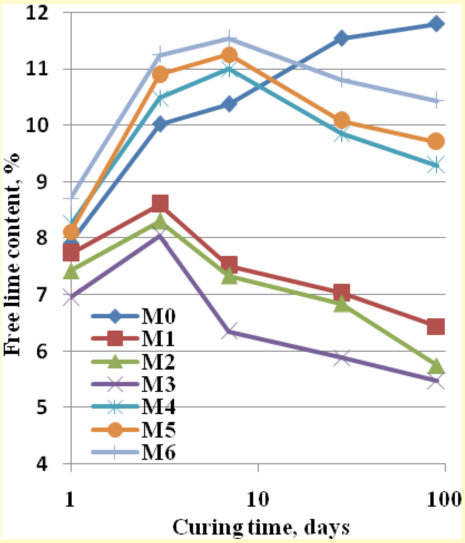

***Figure 3:*** *The free lime contents of the pure OPC pastes (M0) and the various cement pastes (M1-M6) as a function of curing time to 90 days.*

***Citation:*** HHM Darweesh and MR Abo-El-Suoud. "Quaternary Cement Composites Containing Some Industrial By-products to Avoid the Environmental Pollution". *EC Chemistry* 2.1 (2015): 78-91.

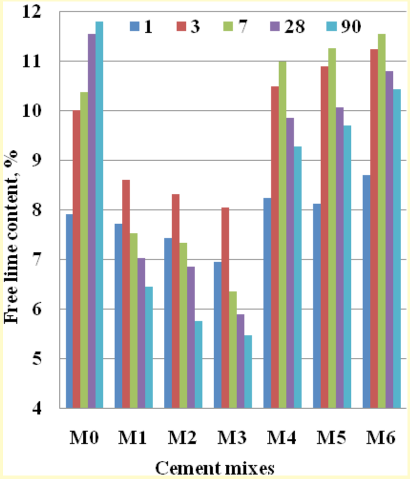

***Figure 4:*** *The free lime content of the pure OPC (M0) and the various cement pastes (M1-M6) as a function of cement mixes.*

### Bulk Density and Total Porosity

The bulk density and total porosity of the pure OPC pastes (M0) and the various blended cement pastes (M1-M6) are represented as a function of cement mixes in Figure 7,8 and 9,10, respectively. It is obvious that the bulk density increases gradually, while the total porosity decreases with curing time up to 90 days for all cement pastes ($M_0$-$M_6$). This is mainly due to the continual deposition of the formed hydration products resulting from the normal hydration process of the OPC phases and also to the chemical reactions of the pozzolanic ingredients (waste materials) with the liberating Ca $(OH)_2$ from the afore process into the available pore structure of the hardened cement pastes [15,38,39]. It is clear from Figure 7,8 and 9,10 that M1, M2 and M3 exhibited the highest values of Bulk density and the lowest of porosity at all curing days of hydration. On contrast, M4, M6 and M6 achieved the lowest values of bulk density and the highest of porosity at all curing times up to 90 days. The increase of bulk density and the decrease of porosity are mainly attributed to the high hydraulic properties of GGBS, FA and SF compared with other waste materials (RHA and H). On the other side, the decrease of bulk density and the increase of porosity of M4-M6 is mainly due to the sluggish rate of hydration of RHA and H as mentioned before [38-40]. It can be also noticed that the quaternary cement composites of M4 (FA, RHA, H), M5 (FA, RHA, GGBS) and M6 (SF, RHA, H) recorded lower values of bulk density and higher values of porosity than those of OPC at all hydration ages, while those of M1 (GGBS, SF, RHA), M2 (GGBS, FA, H) and M3 (GGBS, FA, SF) show higher values of bulk density and lower values of porosity than OPC pastes at all hydration ages. Moreover, M3 recorded the best results for both bulk density and porosity (Figs. 7, 8 and 9, 10). This is due to the high pozzolanic action of SF, FA and GGBS when existed together to the evolved Ca $(OH)_2$ if compared to OPC and other cement composites [4, 11, 14, 15, and 41]. The highly pozzolanic reactions of these admixtures with the released Ca $(OH)_2$ from the hydration of $C_3s$ and β-$C_2S$ to form additional CSHs and/or CAHs which deposited or precipitated into the pore system. This in turn decreases the total porosity and enhances the bulk density, in addition to the filling action of these admixtures and the good compaction of samples during moulding [22, 23, 42, and 43]. Consequently, the incorporation of the three admixtures together (M3) is more effective than the combination of any other three admixtures as in $M_1$, $M_2$, $M_4$, $M_5$ or $M_6$.

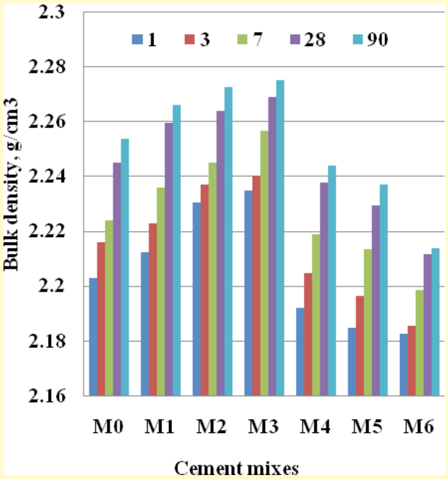

***Figure 5:*** *The bulk density of the pure OPC pastes (M0) and the various cement pastes (M1-M6) cured up to 90 days as a function of cement mixes.*

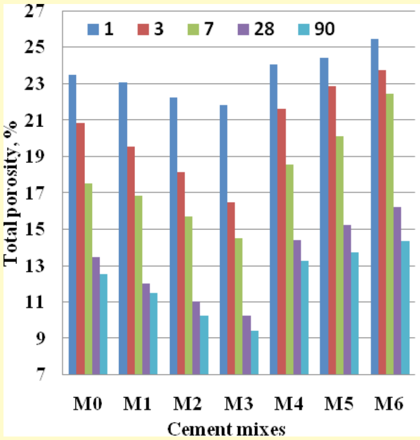

***Figure 6:*** *The apparent porosity of the pure OPC pastes (M0) and the various cement pastes (M1-M6) cured up to 90 days as a function of cement mixes.*

**Compressive Strength**

The compressive strength results of the pure OPC pastes (M0) and the various blended cement pastes (M1-M6$_4$) cured up to 90 days are graphically plotted as a function of cement mixes in Figure 7. Generally, as the curing time proceeds up to 90 days, the compressive strength increases gradually. This is mainly due to the continual deposition of the formed hydration products, which fill the pore structure. Hence, the total porosity decreases while the bulk density increases. This often reflected positively on the compressive strength [4,5,7, 10 and 15]. The compressive strength values of M$_1$ (GGBS, SF, RHA), M$_2$ (GGBS, FA, H) and M3 (GGBS, FA, SF) are higher than those of the OPC pastes at all curing ages up to 90 days. This is due to the high rate of pozzolanic reactivity of SF, FA and GGBS together to the resulting Ca (OH)$_2$ from the normal hydration process. The continuous and gradual deposition of the formed additional CSHs from the pozzolanic reactivity of these ingredients with the released Ca (OH)$_2$ which fill the open pores and therefore, the strength improves and enhances [5,15,43,44], whilst those of M4 (FA, RHA, H), M5 (GGBS, FA, RHA) and M6(SF, RHA, H) are lower up to 90 days due to the higher water demand of SF, H and RHA. At all, there are no large differences in the compressive strength values of M1-M3 or even M4-M6 compared with those of OPC pastes. The main constituents of FA are $SiO_2$ and $Al_2O_3$ which can react with the resulting Ca $(OH)_2$ from the hydration to form Hydrogarnet phase as follows:

$$SiO_2 + Al_2O_3 + 3\ CH + xH \rightarrow C_3\ AS_2Hn \qquad (10)$$

The constituents of GGBS can also react with the raw gypsum in the presence of water to produce ettringite ($C_3A.\ 3CaSO_4.\ 32H_2O$) and CSH (Equation 11) or can react with a part of the free lime Ca $(OH)_2$ to form ettringite and CSH (Equation 12), particularly during the later ages of hydration [5,15,45,46] as follows :

$$C_{16}S_{13}A + CS^{-} + H \rightarrow C_3A.3CS^{-}.H_{32} + 13CSO_3.H_x \qquad (11)$$

$$C_6S_5A + 2CH + nH \rightarrow C_3A.3CS^{-}.H_{32} + 5CS\text{-}O_3.Hx \qquad (12)$$

Hence, there is a continuous and gradual consumption of the evolved Ca $(OH)_2$ leading to a decrease in the free lime content followed by a decrease in the total porosity and an increase in the bulk density. Accordingly, an increase in the compressive strength was obtained [5,15,47-49]. The compressive strength values of the hardened cement pastes of M3 (GGBS, FA, SF) are higher than those of M1 and M2 or even M0. This is mainly due to fact that the SF has a highly pozzolanic reactivity because it is so voracious to Ca (OH) 2 that if it found the free Ca $(OH)_2$, it greatly reacts with it soon. Furthermore, the SF improves the workability of cement pastes and increases the rate of hydration of $C_3S$ at early ages as well as $\beta$-$C_2S$ at later ages [5,15 and 50]. The reactivity of FA is much lower than that of SF and higher than GGBS. This means that the combination of FA with SF (M3) is more effective than SF with GGBS (M1) or FA with GGBS (M2) or even any of RHA (M1) and H (M6).The early pozzolanic reactions, the filling effect and the plasticizing action of these waste materials, especially SF which could be contributed to the higher strength development and workability improvements of the fresh cement pastes or even concrete [7,18]. This tends to improve the hydration of $C_3S$ due to the formation of a retarding layer on the surface of $C_3S$ grain at early time which is converted more rapidly in the lower $Ca^{2+}$ and OH- ions solution into a second less retarding layer [5,14,23 and 51]. Consequently, the formation of CSH in the presence of SF would be more effective in filling pores of the matrix than other additives. This is because the presence of little amount of SF as in M1 and M3 accelerates the hydration reactions of OPC pastes either by providing nucleation sites for Ca $(OH)_2$ or by reacting with $Ca^{2+}$ ions which affects the nature of the resulting CSHs [5, 14, 52]. However, the larger amounts of SF could be avoided because it has a high surface area which tends to increase water demand in blended cements or concrete, which in turn creates a more pore structure [49-53]. Therefore, from the economical point of view, the amount of SF must be limited because its price is too high to be accepted for the cement or concrete users.

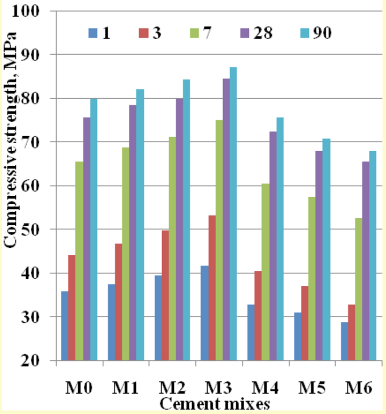

***Figure 7:*** *The compressive strength of the pure OPC pastes (M0) and the various cement pastes (M1-M6) cured up to 90 days as a function of cement mixes.*

**Ft-Ir Spectroscopy**

The infra red spectroscopy (FT-IR) of the pure OPC pastes (M0) and the optimum cement pastes (M3) are shown in Figure 8 and 9, respectively. The sharp absorption band at 3644-3641 cm-1 is related to the free $OH^-$ group coordinated to $Ca^{+2}$, i.e. Ca $(OH)_2$ or free lime. The intensity of this peak increased gradually with hydration time up to 90 days. This is contributed to the continuous hydration of $C_3S$ and $C_2S$ (Figure. 8), while increased only up to 3 days and then decreased (Figure 9). The intensity of the broad absorption band at 3450-3425 $cm^{-1}$, which was ascribed to the $OH^-$ group associated to $H^+$ bond that related to the symmetrical stretching frequency of water. The intensity of this peak which is characteristic to the chemically-combined water content, increased continuously up to 90 days (Figure 8 and 9). The two absorption bands at 2960 and 2860 $cm^{-1}$ are due to $-CH_2$ and $-CH_3$ from the residual organic mixture. The two absorption bands at 1645-1640 $cm^{-1}$ and 1430-1422 $cm^{-1}$ are related to the main silicate band involving Si-O stretching vibration bands of CSH, while the band at 1122-1112 $cm^{-1}$ may be due to CAH. The intensity of the two absorption bands at 990-980 $cm^{-1}$ and 874 $cm^{-1}$ characterizing $CO3^{-2}$ and $SO4^{-2}$ is irregular due to the rate of carbonation or sulphonation of CSH and/or CAH, where the vibrations of $CO3^{-2}$ are smaller than those of $SO4^{-2}$. Also, the intensity of the absorption bands of Si-O, CAH, $CO3^{-2}$ and $SO4^{-2}$ are slightly higher with cement composites (M1-M6) than those of the OPC.

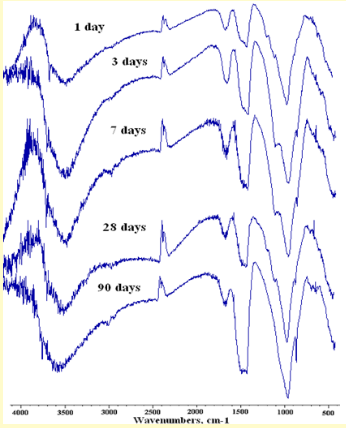

***Figure 8:*** *The IR spectra of the pure OPC pastes (M0) hydrated up to 90 days.*

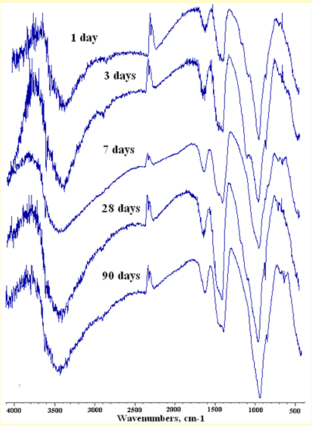

***Figure 9:*** *The IR spectra of the optimum mix (M3) hydrated up to 90 days.*

***Citation:*** HHM Darweesh and MR Abo-El-Suoud. "Quaternary Cement Composites Containing Some Industrial By-products to Avoid the Environmental Pollution". *EC Chemistry* 2.1 (2015): 78-91.

### Sem Microscopy

The SEM micrographs of the hydrated OPC pastes of M0, M3 and M6with two magnification powers of 10 µm - X2000 as well as 10 µm - X3500 are shown in Figure 10. It is clearly seen from Figure 10 that very low crystalline CSH phase and relatively large crystalline aggregates of Ca $(OH)_2$ or Portlandite are present which could be easily distinguished from other hydration products. Also, needle-like crystals of ettringite as well as globules of carbonates are observed. The same hydration products as those formed with the pure OPC pastes are also occurred but with variable morphologies and crystallinity. This is essentially attributed to the overall chemical composition of these mixes which falls into the same field but with minor differences. This affected the quantities of the hydrated phases (CSH) but their structure did not.

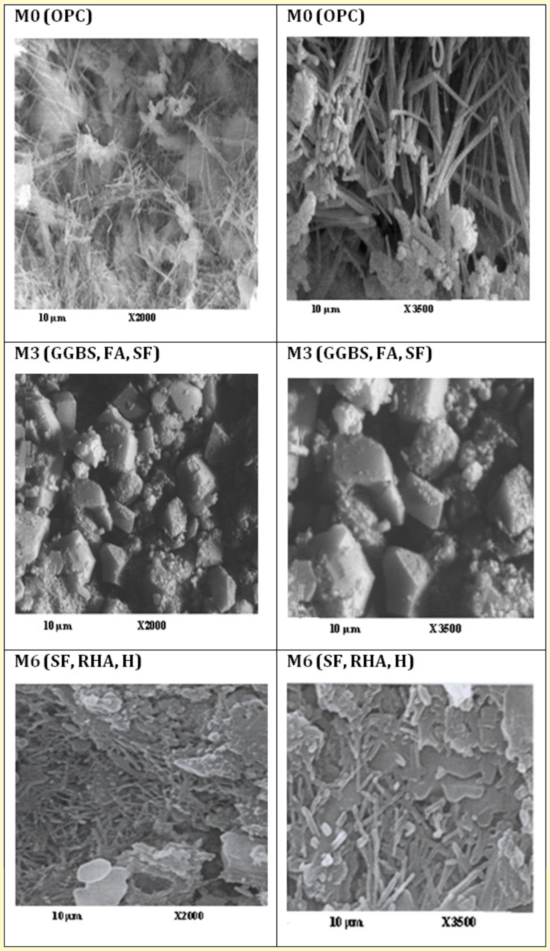

***Figure 10:*** *The SEM spectroscopy of M0, M3 and M6 at 28 days of hydration with magnification power of 10 µm -X2000 as well as 10 µm-X3500.*

## Conclusion

Blending three waste materials of GGBS, FA, SF, RHA and H in combination with OPC to form quaternary cement composites increases its water of consistency and setting time of the fresh cement pastes. The chemically combined water content, bulk density and compressive strength of the hardened cement pastes were also increased with curing time up to 90 days. On contrast, the free lime content and the total porosity of the hardened cement pastes decreased at all curing ages. The combination of the three pozzolanic

***Citation:*** HHM Darweesh and MR Abo-El-Suoud. "Quaternary Cement Composites Containing Some Industrial By-products to Avoid the Environmental Pollution". *EC Chemistry* 2.1 (2015): 78-91.

materials GGBS, FA and SF (M3) recorded the most active effect on the specific properties of OPC pastes compared with those of other combinations (M1, M2, M4, M5, and M6). The results showed also that the pozzolanic effect occurs after the third day of hydration with M1, M2 and M3 whist with M4, M5 and M6 occurred after the seventh day (Figure. 5 and 6). Moreover, a larger amount of CSH and a lower amount of free lime could be detected in the hardened cement pastes by FTIR spectra as well as SEM micrographs. The formed CSH with the cement composites (M1-M6) on hydration are the same with the OPC pastes, but with varying modified crystals and morphologies, particularly those of M3. All cement composites are conformed to the following descending order:

M3 >M1 > M2 > M0 > M4 > M5 > M6

From the previous discussion, it is evidently concluded that the optimum quaternary cement composite is that of M3 containing GGBS, FA and SF.

## Bibliography

1. HH Darweesh. "Effect of the combination of some pozzolanic wastes on the properties of Portland cement pastes". iiCL'industriaitaliana del Cemento 808 (2005): 298-311.
2. H El-Didamony., *et al*. "Utilization of some Egyptian byproducts in the preparation of blended cements". *Zement-Kalk-Gips* 48.9 (1995): 502-507.
3. Bui DD., *et al*. "Particle Size Effect on the Strength of Rice Husk Ash Blended Gap-Graded Portland Cement Concrete". *Cement and Concrete Composites* 27.3 (2005): 357-366.
4. S K Agarwal and G Deepali. "Utilization of Industrial Wastes and Unprocessed Micro-Fillers for Making Cost Effective Mortars". *Construction and Building Materials* 20.10 (2006): 999-1004.
5. A Echart., *et al.* "Hydration of the four main Portland cement clinker phases". *Zement-Kalk-Gips* 48.8 (1995): 443-452.
6. BS Journal., *et al*. "Strength Development of Mortars Containing Ground Granulated Blast Furnace Slag: Effect of Curing Temperature and Determination of Apparent Activation Energies". *Cement and Concrete Research* 36.3 (2006): 434-440.
7. EA El-Alfi., *et al*. "Low energy Portland cement clinker. Part 1". iiCL'industriaitaliana del Cemento 809.5 (2005): 376-385.
8. HH Darweesh. "Alkali-activation of slag-rich cement pastes with sodium hydroxide". iiCl'industriaitaliana del Cemento 826.12 (2006): 992-1007.
9. H Binici., *et al*. "The Effect of Fineness on the Properties of blended cements incorporating Ground Granulated Blast Furnace Slag and Ground Basaltic Pumice". *Construction and Materials* 21.5 (2007): 1122-1128.
10. Bouzoubaa N., *et al*. "Development of Ternary Blends High Performance Cement". *ACI Materials Journals* 101.3 (2004): 19-29.
11. Bouzoubaa NB Fournier., *et al*. "Mechanical Properties and Durability of Concrete Made With High Volume Fly Ash Blended Cement Produced in Cement Plant". *ACI Materials Journal* 99.57 (2002): 560-567.
12. HH Darweesh and ZA Nagieb. "Hydration and micro-structure of Portland/CalcinedBentonite Blended Cement Pastes". *Indian Journal of Chemical Technology* 14 (2007): 301-307.
13. HHM Darweesh. "Utilization of Perlite Rock in Blended Cement-Part I: Physicomechanical properties". *Direct Research Journal of Chemistry and Material Sciences* (2014): 2354-4163.
14. MR Karim., *et al*. "Strength of Mortar and Concrete as Influenced by Rice Husk Ash: A Review". *World Applied Sciences Journal* 19.10 (2012): 1501-1513.
15. PC Hewlett. "Lea's Chemistry of Cement and Concrete". 4th Edn., John Wiley & Sons Inc., New York, Toronto, (1998).
16. HHM Darweesh and MR Abo El-Suoud. "Setting, Hardening and Mechanical Properties of Some Cement/Agrowaste Composites - Part I". *American Journal of Mining and Metallurgy* 2.2 (2014): 32-40.
17. MD Safiuddin., *et al*. "Hardened Properties of Self-Consolidating High Performance Concrete Including Rice Husk Ash". *Cement and Concrete Composites* 32.9 (2010): 708-717.
18. P Chindaprasirt., *et al*. "Influence of Fineness of Rice Husk Ash and Additives on the Properties of Lightweight Aggregate". *Fuel* 88.1 (2009): 158-162.

19. NA Givi., *et al*. "Assessment of the Effects of Rice Husk Ash Particle Size on Strength, Water Permeability and Workability of Binary Blended Concrete". *Construction and Building Materials* 24.11 (2010): 2145-2150.
20. P Chindaprasirt and S Rukzon. "Strength, Porosity and Corrosion Resistance of Ternary Blend Portland Cement, Rice Husk Ash and Fly Ash Mortar". *Construction and Building Materials* 22.8 (2008): 1601-1606.
21. Z Kersener., *et al*. "Mortar composites from waste materials". *Cement Hormigon Spain* 2.943 (2011): 12-19.
22. S Slanicka. "Influence of fly ash fineness on the strength of concrete". *Cement and Concrete Research* 21.4 (1991): 285-296.
23. K Erdogdu and P Turker. "Effects of fly ash particle size on strength of Portland cement fly ash mortars". *Cement and Concrete Research* 28 (1998): 1217-1222.
24. S Rukzon., *et al*. "Effect of grinding on chemical and physical properties of rice husk ash". *International Journal of Minerals, Metallurgy and Materials* 16.2 (2009): 242-249.
25. M Kuroda., *et al*. "Increase of bond strength at interfacial transition zone by the use of fly ash". *Cement and Concrete Research* 30.2 (2000): 253-258.
26. Z Kersener., *et al*. "Alkali-activated slag - rich cement pastes with sodium silicate and water glass". *Cement Hormigon Spain* 4.945 (2011): 18-26.
27. HHM Darweesh. "Setting, hardening and Strength properties of cement pastes with zeolite alone or in combination with slag". *Inter Ceram Germany* 1 (2012): 52-57.
28. P K Mehta. "Studies on the Mechanisms by Which Condensed Silica Fume Improves the Properties of Concrete: Durability Aspect". Proc. Intern. Workshop on Condensed Silica Fume in Concrete Ottawa (1987): 1-17.
29. F M Lea. "The Chemistry of Cement and Concrete". 3rd Edn Edward Arnold Ltd (1970).
30. ASTM –Standards. "Standard Test Method for Normal water of Consistency of Hydraulic Cement". C187-86 (1993): 148-150.
31. ASTM –Standards. "Standard Test Method for Setting Time of Hydraulic Cement". C191-92 (1993): 866-868.
32. ASTM-Standards. "Standard Test Method for Compressive Strength of Dimension Stone". C170-90 (1993): 828-830.
33. R kondo., et al. "kinetics and mechanisn of hydrothermal reaction of Granulated blastfurnace slag". *Bulletin of the chrmical Society Japan* 48 (1975): 222-226.
34. S Slanicka. "The influence of fly ash fineness on the strength of con- crete". *Cement and Concrete Research* 21 (1991): 285-296.
35. El-Didamony H., *et al*. "Characteristics of pozzolanic cement pastes Part I: Physico-mechanical properties". *Silk India* (Cer Sci & Techn) Belgium, 73 Nr. 11-12 (2008): 193-200.
36. HHM. Darweesh. "Hydration, Strength Development and Sulphate Attack of Some Cement Composites". *World Applied science* 23.2 (2013): 137-144.
37. GC Isaia., *et al*. "Physical and Pozzolanic Action of Mineral Additions on the Mechanical Strength of High-Performance Concrete". *Cement and Concrete Composites* 25.1 (2003): 69-76.
38. P H Nicole., *et al*. "Effect of Silica Fume and Rice Husk Ash on Alkali-Silica Reaction". *Materials Journal* 97.4 (2000): 486-492.
39. V Sata., "Influence of Pozzolan from Various By-product Materials on Mechanical Properties of High-Strength Concrete". *Construction and Building Materials* 21.7 (2007): 1589-1598.
40. K Sakr. "Effects of Silica Fume and Rice Husk Ash on the Properties of Heavy Weight Concrete". *Journal of Materials in Civil Engineering* 18.3 (2006): 367-376.
41. S A Rashid., *et al*. "Contribution of Rice Husk Ash to the Properties of Mortar and Concrete: A Review". *Journal of American Sciences* 6.3 (2010): 157-165.
42. GC Isaia., *et al*. "Physical and Pozzolanic Action of Mineral Additions on the Mechanical Strength of High-Performance Concrete". *Cement and Concrete Composites* 25.1 (2003): 69-76.
43. F Massazza. "Properties and Applications of Natural Pozzolans". In: Bensted, J., P. Barnes, 2002. "Structure and Performance of Cement", 2nd Edn., (2002): 326-352.
44. VM Malhotra. "Fly Ash, Slag, Silica Fume and Rice Husk Ash in Concrete: A Review". *Concrete International* 15.4 (1993): 2-28.

45. P K Mehta. “Studies on the Mechanisms by Which Condensed Silica Fume Improves the Properties of Concrete: Durability Aspect”. Proc. Intern. Workshop on Condensed Silica Fume in Concrete Ottawa, (1987): 1-17.
46. P K Mehta. “Advancements in Concrete Technology”. *Concrete Intern* (1999): 69-76.
47. R N Edmonds and A J Majumdar. “The hydration of mixtures of monocalcium aluminate and blastfurnace slag”. *Cement and Concrete Research* 19.5 (1989): 779-782.
48. HH Darweesh. “Characteristics of metakaoline blended cement pastes”. Sil. Ind. (Cer. Sci. & Techn.), Belgium, 72.1-2 (2007): 24-32.
49. J Cabrera and MF Rojas. “Mechanism of Hydration of the Metakaolin-Lime-Water System”. *Cement and Concrete Research* 31.2 (2001): 177-182.
50. P Chindaprasirt and S Rukzon. “Pore Structure Changes of Blended Cement Pastes Containing Fly Ash, Rice Husk Ash and Palm Oil Fuel Ash Caused by Carbonation”. *Journal Materials Civil Engineering* 21.11 (2009): 666-671.
51. M Regourd and B Mortureux. Proc. 4th Intern. Conf. Cem. Microscopy, Las Vegas, (1982): 249.
52. ML Gambhir. “Concrete Technology”. Tata McGraw-Hill Publishing Company, New Delhi, (1993): 79-97.
53. F Deschner., *et al*. “Hydration of Portland cement with high replacement by siliceous fly ash”. *Cement and Concrete Research* 42.10 (2012): 1389-1400.

**Volume 2 Issue 1 November 2015**