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## Ground Clay Bricks With Blast Furnace Slag In Blended Cements As Ternary Blended System

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### ABSTRACT

This paper study the effect of substitution of two by-products, namely granulated blast furnace slag (WCS), from iron steel company and homra (GCB) from Misr Brick (Helwan, Egypt) by 30 mass% OPC on the physico-chemical and mechanical characteristics of the investigated hardened cement pastes. The required water of standard consistency and setting times were measured. The hydration kinetics as well as physico-chemical and mechanical characteristics of the hardened cement pastes were investigated. Some selected specimens were tested by TGA, DTA and FT-IR techniques to investigate the variation of hydrated products of the prepared blended cements. The results showed that, substitution of OPC by 30 mass% WCS the initial and final setting times were elongated, whereas, increase of the amounts of GCB up to 30%, the setting time accelerates. Addition of 30% WCS ( $S_1$ ) to OPC, reduces the amounts of chemically combined water contents at all curing times. On the other hand, substitution of WCS with 10 mass% GCB, the chemically combined water increases at all curing ages. 30 mass% Homra (GCB) shows the lowest total porosity than these values of total porosity. 30 mass%, GCB the compressive strength increases and shows the maximum values than all hardened blended cement pastes. © 2006 Trade Science Inc. - INDIA

### KEYWORDS

Ground clay bricks;  
Blast furnace slag;  
Ternary blended system.

## INTRODUCTION

With the expected increase in cement production to meet the need of steadily growing world population, and with the urgent need to reduce the amount of energy consumed and CO<sub>2</sub> released in the air, there will be an increasing pressure to reduce cement consumption.

The problem of producing blended cements, namely pozzolanic, and filled pozzolanic cements, has been of considerable scientific and technological interest because such additions increase the chemical resistance to sulphate attack, impermeability, lowering heat of hydration and thermal. The pozzolanic or blended cements are increasing worldwide because they need less energy for production<sup>[1]</sup>.

Blast-furnace slag is a by-product formed in the iron manufacture from the fusion of limestone with ash from coke and the siliceous and aluminous residue remaining from the iron ore after the reduction of iron.

Clay bricks are made from about 70 wt% of naturally clays and 30 wt% of quartz sand mixed with each other by water to give a suitable workability, compressed, left to dry and then fired between 900-1100°C.

In Egypt about 5-10% of the product of clay bricks is considered as a waste product. This solid material consists of vitreous materials and can be considered as a source of Si, Al, Fe and Ca.

The by-products such as condensed silica fume, granulated slag and homra were used for the preparation of blended cements. They help to reduce the cost and conserve energy sources, and the environment.

Physico-chemical and strength development properties of six granulated steel furnace slags<sup>[2]</sup>. The influence of slag proportions, specific surface, and water demand on compressive strength and bulk density of blended cements were studied.

The effect of copper slag on the hydration of cement based materials using semiquantitative X-ray diffraction and TGA/DTA<sup>[3]</sup>. Samples of copper slag and hydrated lime (ASTM type S) were used to test the pozzolanic properties of the slag. The porosity as examined using mercury intrusion porosimetry indicated a decrease in capillary porosity and an increase in the gel porosity. The compressive strength was continually increased for up to 1 year.

Ground granulated copper metallurgical slag (maximum grain size 60 μm) as partial replacement of cement in concrete<sup>[4]</sup>. Coarser slag grains were used in concrete mixtures to replace 10-20% of aggregated. Replacement of cement by copper slag does not improve the strength of standard mortars but better results were obtained when larger copper slag grains were added to concrete mixtures.

The pozzolanic activity of homra by using lime as an activators<sup>[5]</sup>. The hydration characteristics of the hydrates were investigated using TGA and DTA. The results of DTA of the formed hydrates were related to the pozzolanic activity as determined by chemical analysis. The results show the formation of C-S-H, calcium aluminate, sulphoaluminate and gehlcnite hydrates. The quantity of C-S-H and progress of reaction is mainly controlled with C/S ratio.

The effect of substitution of OPC by 0, 10, 20 and 30% homra on the physico-chemical mechanical and mineralogical properties of pozzolanic cement pastes<sup>[6,7]</sup>. The effect of temperature on the phase composition and physico-mechanical properties of 10, 20 and 30% Homra blended cement pastes, the cement pastes were fired for 3 hours without any load from 100 to 600°C by increment of 100°C. The results show that the replacement of OPC by 20% Homra improves the compressive strength by about 25.0%, but at 10 and 30% homra, the strength increases by 4.0 and 8.5% at 600°C.

Effect of calcination temperature of clay brick on the pozzolanic activity<sup>[8]</sup>. The calcination at temperatures were 600-1100°C. The performance of mortars was observed to fall into two distinct classes. Mortar containing clays calcined at 600-800°C showed good initial 28 days strength relative to control, but poor long term 90 days strength. Mortar containing calcined clay brick calcined above 800°C but below 1100°C showed poor early strength but good long term strength. The optimum clay firing temperature to give maximum beneficial effect was around 1000°C. In addition it was demonstrated that concrete, containing ground waste of clay brick gives 90 days strength similar to or excess of that of control for replacement up to 20 wt%. It was suggested that the poor long term strength of mortar containing clay brick calcined at 600-800°C, where poz-

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zolan activity derives from the activated clay, was due to the excessive amount of anhydrite present. At higher firing temperature (900-1000°C), where pozzolanic activity almost certainly derives from amorphous glassy phase the amount of residual anhydrite was much lower and does not therefore impair the long term strength development of mortar.

The result suggested that clay brick ground to cement fineness could provide available source of mineral replacement for cement<sup>[9]</sup>.

The work aimed to study the effect of substitution of GCB by WCS on the physico-chemical and mechanical characteristics of the investigated hardened cement pastes. TGA, DTA and FT-IR techniques to investigate the variation of hydrated products of the prepared blended cements.

### EXPERIMENTAL

The materials used in this investigation were ground granulated blast furnace slag (WCS), which provided from iron steel company, Helwan, Egypt, homra (GCB) from Misr Brick (Helwan, Egypt) and ordinary Portland cement (OPC) from Suez cement Company;. The chemical oxide compositions of each starting materials are given in TABLE 1. The surface area determination using Blaine apparatus the results of surface area measurements are shown in TABLE 1. The mix compositions of the investigated pastes are given in TABLE 2.

The dry constituents were mechanically mixed for one hour in a porcelain ball mill using three balls to attain complete homogeneity. After preparation the specimens were kept in airtight containers until the time of cement preparation. The mixing was carried out on the cement powder with the required water of standard consistency. The blended cement was placed on a smooth non-absorbent surface and

a crater was formed in the center. The required amount of water was poured into the crater by the aid of a trowel. The dry cement around the outside of the crater was slightly troweled over the remaining mixture to absorb the water for about one minute. The mixing operation was then completed by continuous vigorous mixing for about three minutes by means of ordinary gauging trowel. At the end of mixing, the paste was directly poured in the moulds. The water of consistency, initial and final setting time of cement pastes was determined using a vicat apparatus<sup>[10,11]</sup>.

The hydrated of cement pastes were stopped using microwave oven. The cement pastes were placed in suitable container (glass dish). The apparatus used was microwave oven (EM-S3555, Sanyo, China, living technology). The glass dish containing the cement specimen placed in a microwaves oven for 10 minutes to remove the free water. After the predetermined, the kinetics of hydration was followed by the determination of combined water contents, the combined water content was estimated on the basis of ignition loss of dried sample heated at 1000°C for 30 minutes minus the weight of water in Ca(OH)<sub>2</sub>. The development of hydration products was followed using DTA, TGA and FT-IR spectroscopy. The total porosity, Bulk density and compressive strength were also measured.

### RESULTS AND DISCUSSION

#### Water of consistency and setting time

The water of consistency, initial and final setting times of blended cement pastes are graphically represented in figure 1. The water of consistency of neat OPC cement pastes was found to be 27%. This ratio tends to decrease with the substitution of 30 mass% slag (WCS) by OPC. This means that the

TABLE 1: Chemical composition of starting materials, mass%

| Oxides           | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MgO  | MnO  | TiO <sub>2</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | BaO  | SO <sub>3</sub> | S-   | L.O.I | Surface Area<br>Cm <sup>2</sup> /g |
|------------------|------------------|--------------------------------|--------------------------------|-------|------|------|------------------|-------------------|------------------|------|-----------------|------|-------|------------------------------------|
| <b>Materials</b> |                  |                                |                                |       |      |      |                  |                   |                  |      |                 |      |       |                                    |
| Granulated slag  | 37.48            | 12.86                          | 0.40                           | 36.70 | 2.45 | 6.24 | 0.72             | 1.84              | 0.71             | 5.31 | 0.01            | 0.75 | --    | 3500                               |
| OPC              | 21.51            | 5.07                           | 4.39                           | 65.21 | 2.00 | 0.15 |                  | 0.23              | 0.29             |      | 0.25            |      | 0.40  | 3100                               |
| Homra            | 74.80            | 14.03                          | 5.04                           | 1.25  | 1.30 | --   | --               | --                | --               | --   | 0.80            | --   | --    | 3000                               |

**TABLE 2: Mix composition of the investigated specimens**

| Mix No.        | OPC | Slag | Homra |
|----------------|-----|------|-------|
| OPC            | 100 | -    | -     |
| S <sub>1</sub> | 70  | 30   | -     |
| S <sub>2</sub> | 70  | 20   | 10    |
| S <sub>3</sub> | 70  | 10   | 20    |
| S <sub>4</sub> | 70  | -    | 30    |

water of consistency slightly decreases with the slag cement up to 30 mass% from 27% to 26.7%.

Substitution of WCS by GCB (Homra), the water of consistency increases. Replacement of WCS 10 mass% GCB the water content increases from 26.7% to 28%. Increase the GCB content up to 30 mass%, the water of consistency shows slight increase from 28% to 28.7%. This is due to the amorphous properties of Homra, which absorbs water<sup>[12]</sup>.

The initial and final setting times of OPC were initially equal to 161 min and finally equal to 281 min. Substitution of OPC by 30 mass% WCS the initial and final setting times were elongated to become initial equal to 184 min and final equal to 251 min., due to the amount of OPC clinker which has setting characteristics in comparison with WCS as well as the decrease of the hydraulic properties of WCS<sup>[12]</sup>.

It was shown also that, the initial and final setting time elongated with the substitution of GCB instead of WCS in blended cement containing 30

mass% WCS. Substitution of GCB, the initial and final setting time elongated up to 20 mass% of GCB. Increase of the amounts of GCB up to 30%, the setting time accelerates. This is due to the amorphous properties of GCB (Homra). Also, homra acts as pozzolanic material and filler. The filler acts as nucleating agent which accelerates the hydration characteristics.

### Chemically combined water contents

The chemically combined water contents of OPC and blended cement pastes cured at 3, 7, 28 and 90 days at room temperature under tap water were graphically plotted as a function of curing time in figure 2. The chemically combined water contents increases with curing time. As the hydration proceeds, the amounts of hydration products increase. Addition of 30% WCS (S<sub>1</sub>) to OPC, reduces the amounts of chemically combined water contents at all curing times. This is attributed to the decrease of amount of C<sub>3</sub>S and  $\beta$ -C<sub>2</sub>S phases containing the clinker Portland cement phases, which hydrated to produce CSH, CAH and CH. On the other hand, WCS has less hydraulic properties than the OPC. Also, the WCS consumed some of CH liberated during the hydration of OPC, due to its pozzolanic activity, the decrease of CH affected on the chemically combined water results.

Substitution of WCS with 10 mass% GCB, the chemically combined water increases at all curing

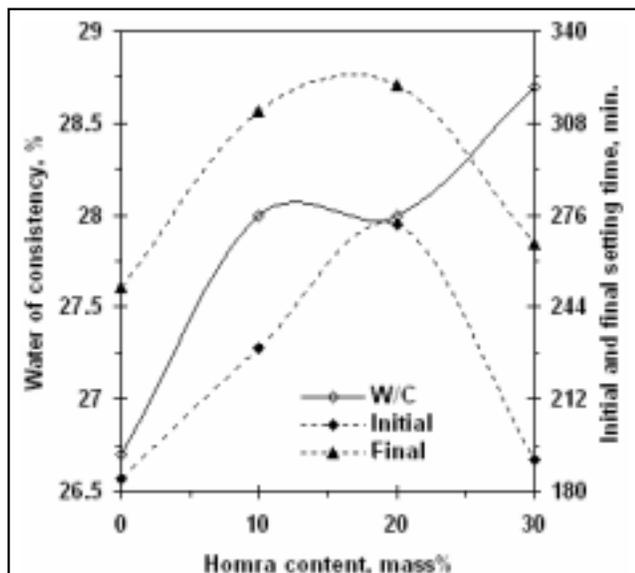


Figure 1: Water of consistency, initial and final setting times of blended cement

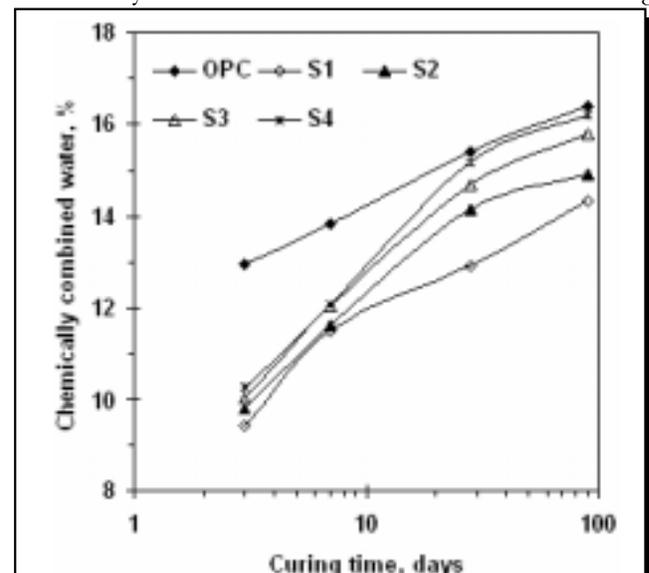


Figure 2: Chemically combined water content of blended cement cured up to 90 days

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ages. As GCB (Homra) content increases the chemically combined water content increase. GCB (Homra) shows higher pozzolanic activity than WCS, it reacted with CH to form CSH and CAH, which precipitated in the pore system of hardened cement pastes. The rate of pozzolanic reaction of WCS is very slow due to the formation of acidic surface film as a small amounts of  $\text{Ca}(\text{OH})_2$  is released into the solution. As the hydration reaction proceeded, more CH present, which removes this film and continued the hydration<sup>[13]</sup>. The increase of pozzolanic activity of Homra is also due to the nucleating effect.

### DTA and TGA

Figure 3 shows DTA thermograms of OPC, S1, S3 and S4 cured at 90 days. The thermograms show five endothermic peaks located at 80, 110, 163, 487 and 735°C. The endothermic peaks located below 200°C are attributed to the dehydrated of interlayer of calcium silicate, calcium aluminate and calcium sulpho-aluminate hydrates. The endothermic peak at 487°C is due to the decomposition of  $\text{Ca}(\text{OH})_2$ . The last endothermic peak located at 735°C due to decarbonation of calcium carbonate. It is clear that the addition of GCB increases the peak area of CSH and CAH. Also, peak at 487°C decreases due to consumption of lime, this is due to the high pozzolanic activity of Homra.

Figure 4 shows weigh loss of decomposition of hydrated phases from TGA thermograms of OPC and WCS S1 (70% OPC + 30%) and S2 (70% OPC + 20% WCS + 10% GCB) cured at 90 days. TGA thermograms of OPC, S<sub>1</sub> and S<sub>2</sub> cured at 90 days.

The thermograms show three temperature ranges up to 390°C due to the decomposition of CSH, CAH and hydrogarnt. The second peak due to the decomposition of CH located at 400-520°C, the last endothermic peak locates at 650-800°C due to decomposition of  $\text{CaCO}_3$ .

The peak located up to 390°C, shows an increase in the decomposition of the hydration products concern with this temperature ranges for the blended cement pastes (S<sub>1</sub> and S<sub>2</sub>) than OPC pastes. On the other hands, the loss of the two other peaks showed that OPC pastes has higher than blended cement pastes, this is due to pozzolanic reaction of WCS

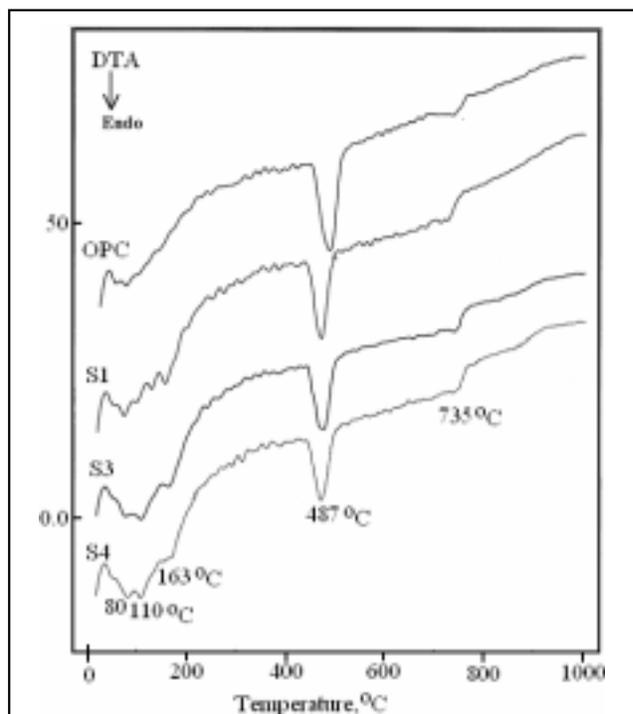


Figure 3: DTA thermograms of OPC, S1, S3 and S4 cement pastes cured at 90 days

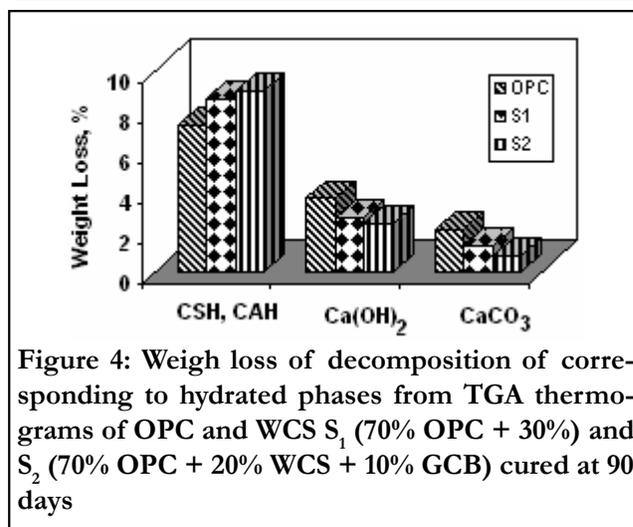


Figure 4: Weigh loss of decomposition of corresponding to hydrated phases from TGA thermograms of OPC and WCS S<sub>1</sub> (70% OPC + 30%) and S<sub>2</sub> (70% OPC + 20% WCS + 10% GCB) cured at 90 days

and GCB consumed CH in the pozzolanic reaction, hence the residual lime decreases as show from TGA thermograms. The loss on weight at 600-800°C decreases with the pozzolana content, i.e. the OPC pastea is more carbonated due to the increase of  $\text{Ca}(\text{OH})_2$  in comparison to the pozzolanic cement pastes. This is also, due to the decrease of OPC content.

### FT-IR spectra of hydrated cement pastes

Figure 5 shows FT-IR spectra of hydrated cement pastes containing OPC, S<sub>1</sub>, S<sub>3</sub> and S<sub>4</sub> cured up to 90

days. FT-IR spectroscopy is a very important tool to identifying the hydrated and unhydrated products in the cement. The fundamental modes of vibration are stretching and bending modes in the region 4000-400  $\text{cm}^{-1}$ . The vibration frequencies of these modes for the species under study very depends on parameters such as molecular structure, chemical bonding, crystal structure, impurities in solid solution.

CSH hydrated shows band at 972  $\text{cm}^{-1}$  as  $\text{V}_3\text{SiO}_4$ <sup>[4]</sup>, at tacks the form of a tetrahedron, while it reported the raman spectra of CSH(I) a bending vibration frequency around 670  $\text{cm}^{-1}$ . The main hydrated products are  $\text{C}_2\text{SH}_2$  and CSH types were detected from  $\text{V}_3(\text{Si-O})$  absorption band at 972  $\text{cm}^{-1}$  and calcium hydroxide from  $\text{V}_3\text{O-H}$  absorption band at 3644  $\text{cm}^{-1}$  and bending vibration band at 1642  $\text{cm}^{-1}$  as well as the sharp band at 3644  $\text{cm}^{-1}$  due to O-H in  $\text{Ca}(\text{OH})_2$ , which liberated from the hydration processes. The absorption band at 1428  $\text{cm}^{-1}$  due to the presence of carbonate in specimens as well as band at 876  $\text{cm}^{-1}$ . The bands due to amorphousness of quartz also appear at 785 and 771  $\text{cm}^{-1}$ . Si-O bond

give characteristics bonds due to bending vibration at 464  $\text{cm}^{-1}$ . Also the band due to 3644, 1642, 1428 and 876 decrease due to increase the content of GCB due to the pozzolanic reaction whereas band 3494, 1642 and 972  $\text{cm}^{-1}$  due to formation of CSH and  $\text{CAH}$ <sup>[5]</sup>. The band 3644  $\text{cm}^{-1}$  due to  $\text{Ca}(\text{OH})_2$  increase in  $\text{S}_4$  which containing 30 mass% homra higher than those containing 10, 20 and 30 mass% slag due to the effect of homra in comparison with slag.

### Bulk density

The results of the bulk density of the hardened cement pastes cured under tap water up to 90 days are plotted as a function of curing time in figure 6.

The bulk density of hardened cement pastes depends on the degree of hydration of pastes. As the hydration progresses, the hydration products fill a part of the pore volume, then the bulk density increases and total porosity decreases as shown letter. It is clear that the bulk density of hardened cement pastes increases with curing ages. As the amount of GCB increases the bulk density decreases. This is due to the increase the amount of water of consistency, which increases with GCB (Homra) content as well as the density of GCB is less than WCS. The initial water / cement ration play an important role in the values of bulk density.

The bulk density of OPC at all ages is higher than the bulk density of blended cement pastes. This is attributed to increases the amount of OPC replacement, which decreases the amount of OPC reactive phases. This leads to hindered the degree of hydration of blended cement pastes. Generally, the bulk density of any pozzolanic cement pastes is lower than that of ordinary Portland cement pastes. This is due the decrease of bulk density of pozzolanic cement relation to that of OPC.

### Total porosity

The total porosity of blended cement pastes are graphically plotted as a function of curing time in figure 7. The total porosity of hardened cement pastes decreases with curing time. As the hydration proceeds more hydration products add more cementing materials are formed, these hydrates fill up the open pores, therefore the total porosity decreases.

As the homra content increases up to 10 mass%

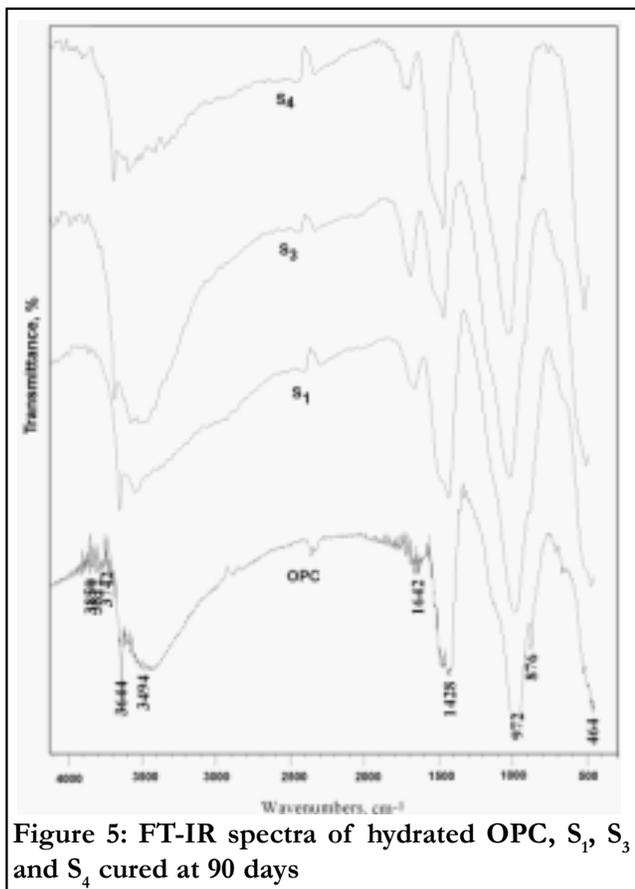
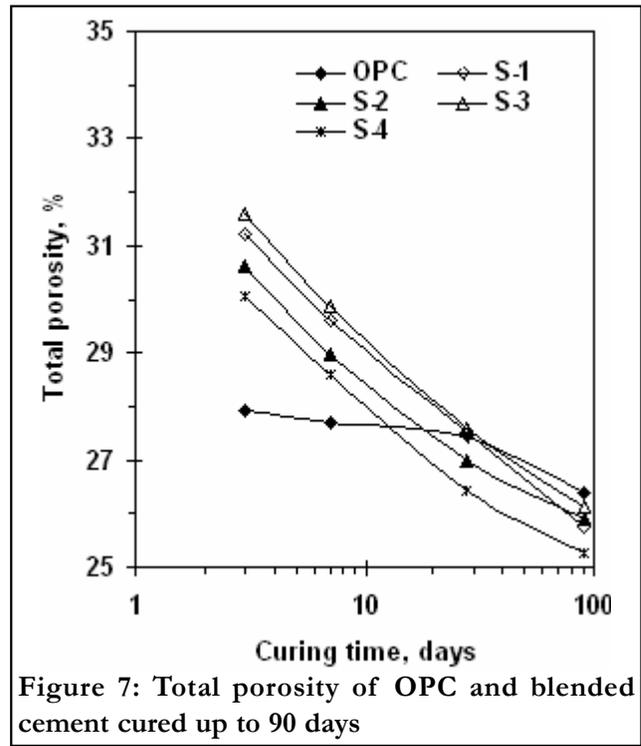
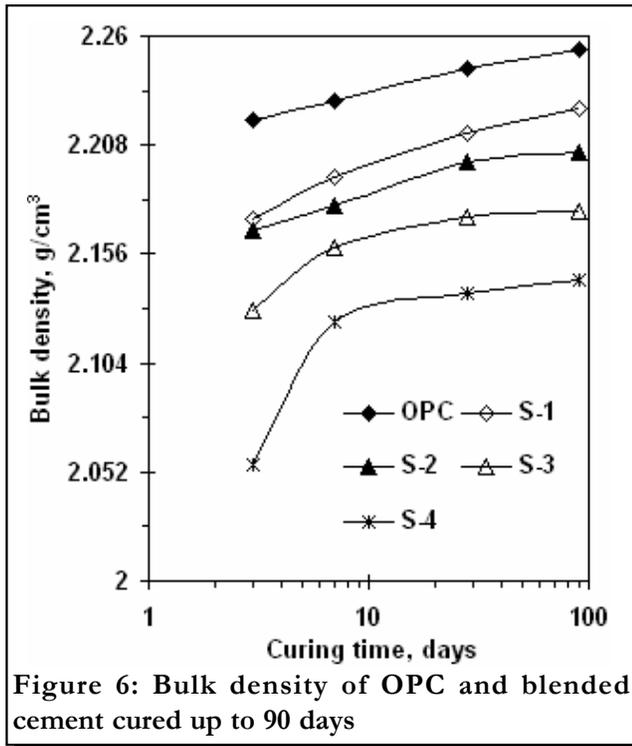


Figure 5: FT-IR spectra of hydrated OPC,  $\text{S}_1$ ,  $\text{S}_3$  and  $\text{S}_4$  cured at 90 days

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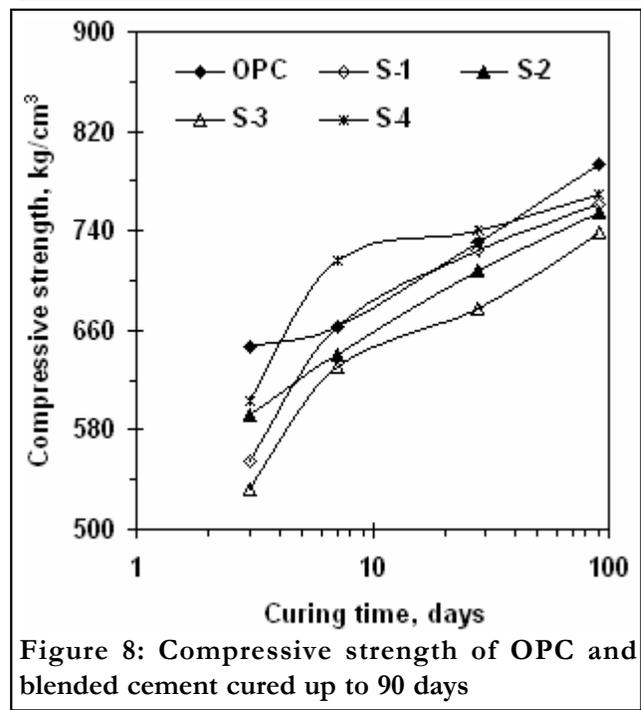
the total porosity decreases. On the other hand when the Homra content increases up to 20 mass% the total porosity increases at 3-7 days. 30 mass% Homra (GCB) shows the lowest total porosity than these values of total porosity there are in a good agreement with those results of compressive strength testing as shown in next figure 8. The total porosity of pozzolanic cement pastes is higher than that of OPC pastes at early ages due to the slow rate of hydration of pozzolana. At later ages the hydration of pozzolana increases due to the activation of  $\text{Ca}(\text{OH})_2$ . Therefore, the total porosity of pozzolanic cement pastes at later ages is lower than that of OPC pastes.

30 mass % Homra shows the lowest values of total porosity, due to the pozzolanic activity than WCS, blended cement pastes as previously discussed.

### Compressive strength

The compressive strength of OPC and different hardened blended cement pastes containing different ratios of WCS and GCB (Homra) are graphically represented in figure 8.

It is clear that, the compressive strength values increase with the curing time for all hardened cement pastes up to 90 days. This is mainly due to the increase the amount of hydration products and later accumulation of cementing materials within the



available spaces giving higher strength<sup>[6]</sup>. This was reflected positively on the mechanical properties.

At early ages (3 days), the compressive strength of OPC shows the higher values than the blended cement pastes. This is due to the higher values of water of consistency which leads to increase the porosity of blended cement pastes and accordingly de-

crease the compressive strength and bulk density. The hydration of OPC pastes is higher than the hydration of pozzolanic cement pastes at early ages.

Addition of 10 mass% of GCB (70% OPC + 20% slag, 10% GCB), the compressive strength increases, than blended cement containing 30% WCS (70% OPC + 30% WCS). These results agree with the results of the total porosity. As the amount of GCB increases up to 30 mass%, the compressive strength increases and shows the maximum values than all hardened blended cement pastes.

### CONCLUSIONS

From the all finding it can concluded that:

Substitution of OPC by 30 mass% WCS the initial and final setting times were elongated, whereas, increase of the amounts of GCB up to 30%, the setting time accelerates. This is due to the amorphous properties of GCB (Homra).

Addition of 30% WCS ( $S_1$ ) to OPC, reduces the amounts of chemically combined water contents at all curing times. On the other hand, substitution of WCS with 10 mass% GCB, the chemically combined water increases at all curing ages.

DTA and TGA show that the peak located up to 390°C, due to decomposition CSH and CAH increases for the blended cement pastes ( $S_1$  and  $S_2$ ) than OPC pastes, whereas, the loss of the two other peaks (487 and 600-800°C) showed that OPC pastes has higher than blended cement pastes, this is due to pozzolanic.

As the homra content increases (10 mass%), the total porosity decreases. 30 mass% homra (GCB) shows the lowest total porosity than these values of total porosity there are in a good agreement with those results of compressive strength. 30 mass%, GCB the compressive strength increases and shows the maximum values than all hardened blended cement pastes.

### REFERENCES

- [1] P.C.Hewlett; 'Lea's Chemistry of Cement and Concrete', 4<sup>th</sup> Ed., John Wiley & Sons Inc., New York, (1998).
- [2] M.Tufekci, A.Demirbas, H.Genc; Cem.Concr.Res., **27(11)**, 1713-1717 (1997).
- [3] R.Tixier, R.Devaguptapu, B.Mobasher; Cem.Concr. Res., **27(10)**, 1569-1580 (1997).
- [4] S.Lewowicki, J.Rajczyk; Proc. 13<sup>th</sup> Inter.Confer., on Solid Waste Technology and Management Part 2, 2, Philadelphia, PA, USA, (1997).
- [5] M.Heikal, H.El-Didamony, A.H.Ali; Indian Journal of Engineering and Material Science, **7**, 154-159 (2000a).
- [6] M.Heikal; Cement and Concrete Research, **30**, 1835-1839 (2000).
- [7] M.Heikal, M.S.Morsy, S.A.Abo-El-Enein; 15<sup>th</sup>. Egypt.Chem.Conf., 20-25 Nov., (1999).
- [8] S.Wild, J.M.Khatib, A.Jones; Cem.Concr. Res., **2(10)**, 1537-1544 (1996).
- [9] J.M.Khatib, S.Wild; Cement and Concrete Research, **28**, n1 Jan, 83-92 (1998).
- [10] ASTM Standards; 'Standard Test Method for Consistency of Hydraulic Cement', ASTM Designation: C187-92 (1992).
- [11] ASTM Standards; 'Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle', ASTM Designation, C187-92 (1992).
- [12] H.El-Didamony, M.Heikel, M.M.Shoaib; Silicate Industrial Ceramic and Technology, **65(3-4)**, 39-43 (2000).
- [13] M.Heikal, I.Helmy, H.Didamony, F.Abd El-Raouf; Silicates Industrials, **69(11-12)**, 93-102 (2004).
- [14] J.Bensted; Cem.Concr.Res., **9**, 97 (1979).
- [15] V.Likov, E.Dimitrova, O.E.Petrov; Cem.Concr., **27(1)**, 577-588 (1997).
- [16] A.Echart, H.M.Ludwig, J.Stark, Zemenk-Kalk-Gips, **28(8)**, 443-452 (1995).