37

Utilization of GBFS in The Preparation of Low Cost Cement

H. El-Didamony, M. Heikal[*]**, H. Moselhy**[**]**, M.A. Ali**[***]
*Faculty of Science, Zagazig University, Zagazig , *[*]*Chemistry Department, Faculty of Science, Benha University, Benha,* [**]*Higher Institute of Engineering, El-Sohrouk Academy, El-Sohrouk and* [***]*Faculty of Pharmacy, Badr University in Cairo, Badr City, Egypt.*

GROUNDED blast furnace slag GBFS is one of common supplementary cementitious materials in Portland cement concrete, and is capable of improving the performance of concrete and reducing the costs. There are strong environmental and energy reasons for developing a wide range of pozzolanic cements. The aim of this work is to study the effect of substitution of cement with GBFS by the determination of water of consistency, initial and final setting times, combined water and free lime contents, bulk density, total porosity and compressive strength. The results show that the substitution of GBFS decreases the water of consistency, initial and final setting times, 50 % GBFS increases compressive strength as well as total porosity, whereas the free lime and combined water decrease with the granulated slag content. The hydration products of some GBFS cement pastes were identified by the aid of XRD, DTA and IR techniques.

Keywords: Granulated slag GBFS, Hydration, Compressive strength, Blk density and Total porosity.

Ground granulated slag is one of the most important supplementary cementitious materials in cement paste, and has been widely used in modern concrete because of its several well-known advantages. For instance, GBFS is capable of improving the resistance of concrete to chloride ingress, it can also reduce the total heat generation and peak temperature reached during the early stage of mass concrete structure, which lessens the risk of early-age thermal cracking[1-3]. Power plants using coal or rice husks as fuel and metallurgical furnaces producing pig iron, steel, copper, nickel, lead, silicon and ferrosilicon alloys are major sources of by-products. These by-products must be disposed off in a suitable way. Disposal by dumping represents a resource of waste and causes environmental problems. Exploiting the pozzolanic and the cementitious properties of these materials by incorporating as components of Portland cement concrete, represents high value of applications.

Blast-furnace slag has no cementitious value; but when it is quenched in excess water and then ground, it acquires cementitious value. The process of quenching is called "granulation" and the product is "granulated blast-furnace slag" (GBFS).

Granulated blast-furnace slag (GBFS) is a nonmetallic, rapidly chilled alumino-silicate material that separated from molten iron in the blast-furnace. Granulated slag issues from the blast-furnace as a molten stream at temperatures 1400 –500 °C from reaction of silica and alumina as acidic oxides with calcium and magnesium as basic oxides to form slag in the presence of other oxides of iron, sodium, potassium and sulfides as minor components[4]. Cooling is most often effected by spraying droplets of the molten slag with high-pressure jets of water. This gives a wet, sandy material which when dried and ground is called granulated blast-furnace slag GBFS and often contains over 95% of glass.

The Tunisian blast-furnace slag has been characterized by several physicochemical methods to evaluate its hydraulic reactivity[5]. It has been noted that nearly all the GBFS is glassy, so its use as a replacement of cement is possible. This result has been confirmed by different physical tests applied to pozzolanic cements as specific surface area, normal consistency, setting time, stability to expansion and the minislump.

The replacement of a part of clinker by GBFS has led to the following results:
- an acceptable extension of the setting time, an improvement of the rheological behavior, and a very good stability to expansion,
- an improvement of the compressive strength at 28 days, but with a slight decrease at 7 days.

GBFS is the most useful latent hydraulic material, because the amount produced is very large and its properties are very stable compared with other industrial by-products[6].

Bágel[7] studied the workability and incorporating granulated blast furnace slag and silica fume composite cement mortars. The compressive strength and mercury intrusion were tested for plain Portland cement mortar and/or slag-cement mortar. The results showed that with high portions of GBFS and SF in the binding system, the mortars reached relatively satisfactory level of compressive strength and contributed to the significantly denser pore structure.

The aim of the present work is to establish the optimum composition of slag cement made from granulated blast-furnace slag and OPC. Different blends were prepared from these materials and the physico-mechanical properties were studied. The water of consistency , initial and final setting times, combined water, free lime as well as bulk density, total porosity and compressive strength are determined.

Experimental

The materials used in this investigation were Imported granulated blast-furnace slag supplied by (Kokan Mining Co. LTD, Japan) and ordinary Portland cement (OPC) from Suez Cement Company. The chemical analysis of these raw

materials are shown in Table 1. The X-ray diffraction of granulated slag is seen in Fig. 1. Generally, the granulated slag is nearly completely vitreous with an amorphous hump characteristic of the glass at 28 2θ. This corresponds to a 2θ value of 30.70 2θ consistent with those of the amorphous phase being constituted of network-forming oxides SiO_2 and Al_2O_3.

Different mixes were made by substitution of 70, 60, 50, 40 wt. % OPC by GBFS. The mixes were denoted as A1, A2, A3, and A4 as shown in Table 2.

TABLE 1. Chemical composition of starting materials, (wt%).

Oxides / Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	BaO	SO_3	S^-	L.O.I
WCS	37.48	12.86	0.40	37.70	2.45	1.84	0.93	5.31	0.01	0.75	—
OPC	20.51	5.07	4.39	62.21	2.00	0.23	0.29	—	2.25	—	2.40

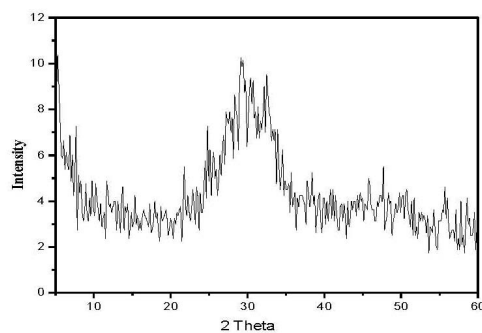**Fig. 1. XRD pattern of imported granulated slag.**

TABLE 2. Mix composition of the prepared cements, (wt %).

Mix No.	OPC	GBFS
A1	30	70
A2	40	60
A3	50	50
A4	60	40

Each dry mix was homogenized on a roller in a porcelain ball mill with four balls for 1 hr to assure complete homogeneity. The water demand for standard consistency and setting time were measured (ASTM Designation: C191, 2008)[8]. The pastes were mixed with the water of consistency and moulded into stainless steel (2×2×2 cm) cubic moulds, cured in a 100 % R.H at 23 ± 1°C for the first 24hr, then demolded and cured under water until the desired curing time such as 3, 7, 28, 90 and 180 days was reached. The compressive strength was carried out on four samples. The procedure described by ASTM Specifications (ASTM Designation: 150, 2007)[9]. Four cubes were used for the determination of compressive strength of the hardened pastes at any given condition. The compressive strength measurements were done on a compressive strength machine of SEIDNER, Riedlinger, Germany, having maximum capacity of 600 KN force. The broken specimens were immersed in water to avoid loss of water filling the pores, and then collected for further testing.

After the predetermined curing time, the hydration of the paste was stopped by the removal of free water. About 10 grams of the crushed paste, after compressive strength testing, were ground and dried at 70°C for about 3 hr to remove the free water. The resulted dried samples were then stored in desiccators for other physico-chemical measurements. The kinetics of hydration was followed by the determination of the free lime according to BS EN 196-2:2013[10]. The portlandite content of cement paste can be thermally determined. 0.5 g of the hardened cement was placed in a porcelain crucible and introduced into a cold muffle furnace. The temperature was increased up to 390 then to 550°C at heating rate of 3 C/min. The loss of weight occurring between 390 and 550 °C with soaking time of 15 min is equal to the weight of water of calcium hydroxide. Therefore, the free lime can be calculated [11] . The combined water content was determined by the ignition loss of the dried paste at 850 ºC for 20 minutes based on ignited weight basis minus the loss of the anhydrous blend [12] . The compressive strength was determined up to 180 days. The bulk density and total porosity, ξ, was calculated by weighing the saturated sample as (W1), then suspended in water (W2) and finally dried weight after drying at 105°C for 24 hr,

$$(W3) \text{ bulk density} = \boxed{\frac{W1}{w1\text{-}w2}} \text{ g/cm}^3 \text{ , The total porosity} = \boxed{\frac{W1\text{-}w3*}{w1\text{-}w2}} 100$$

Results and Discussion

Water of consistency and setting time

The results of water of consistency and setting times of slag cement pastes are shown in Fig. 2. The substitution of GBFS by Imported OPC increases the water of consistency of cement pastes. This may be due to the lower hydraulic properties of Imported GBFS in comparison with OPC. The OPC is hydraulic cement which needs more water of mixing than GBFS cement pastes therefore the water of

consistency increases with OPC content. The elongation of initial and final setting times with the decrease of the GBFS content is mainly attributed to the low hydraulic properties of GBFS. This elongates the initial and final setting times of cement paste. The decrease of initial and final setting times of cement pastes at 50% OPC is mainly attributed to the increase of OPC on the expense of GBFS.
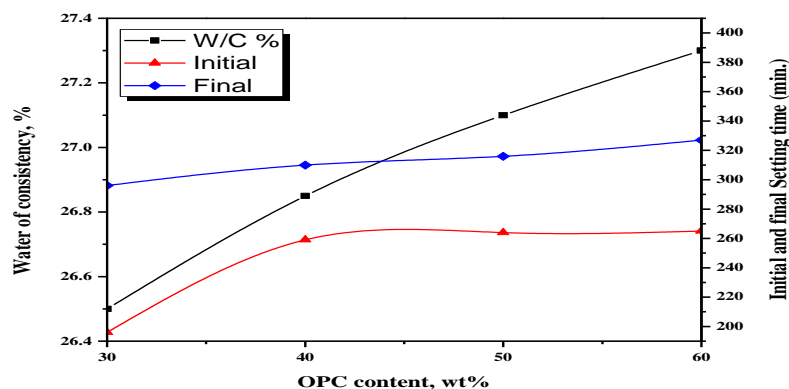

Fig. 2. Water of consistency and setting time of slag cement pastes.

Combined water content

   The combined water contents of hydrated GBFS cement pastes are graphically represented as a function of curing time in Fig. 3. The combined water contents increase gradually with curing time up to 180 days for all cement pastes. This is due to the continuous hydration and accumulation of hydration products as C-S-H and AFt & AFm. GBFS reacts very slowly with water but without setting [13] . The results also show that the combined water contents of GBFS cement pastes decrease with slag content. This is mainly due to the slow hydration reaction of slag grains at early ages. As the amount of OPC increases, the combined water content increases. This may be attributed to the formation of large amounts of C-S-H with OPC content.
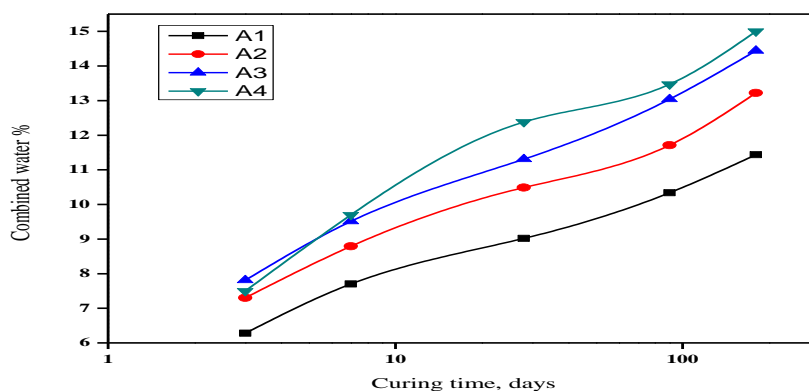

Fig. 3. Combined water contents of granulated slag cement pastes up to 180 days.

Free lime content

The free lime contents of hydrated slag cement pastes are graphically represented as a function of curing time in Fig. 4. The results show that the free lime content increases with the increase of the amount of C_3S and β-C_2S, which are the main source of free lime during the hydration of cement pastes. On the other side, the rate of consumption of the free lime of slag cement pastes increases with the amount of GBFS in the GBFS cement blends. This is associated with the hydration reaction of the GBFS and the free lime released from clinker hydration in addition to the decrease of clinker portion in the cement blends. Pozzolanic cement pastes with high content of GBFS show slow rate of liberation due to its lower hydraulic properties and its consumption of free lime.
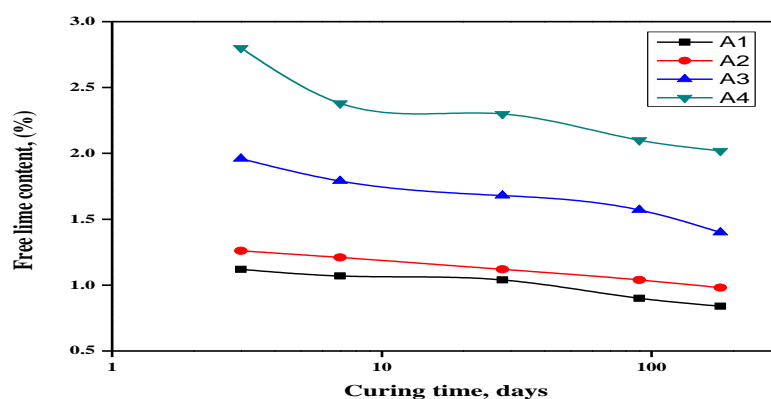

Fig. 4. Free lime contents of slag cement pastes up to 180 days.

Figure 5 shows the XRD diffractograms of the hardened GBFS cement pastes made of mix A_3 (50% OPC + 50% GBFS) cured at 3 and 180 days. It is found that the intensity of characteristics lines for calcium hydroxide (CH) (4.92 Å, 2.62 Å, 1.92 Å and 1.79 Å), decreases with curing time. This is due to the continuous consumption of $Ca(OH)_2$ with GBFS in pozzolanic reaction. Also, the peaks of unhydrated phases of β-C_2S and C_3S decrease with curing time due to the continuous hydration of β-C_2S and C_3S. The $CaCO_3$ (CC) is also detected and overlapped by CSH at 3.03 Å.
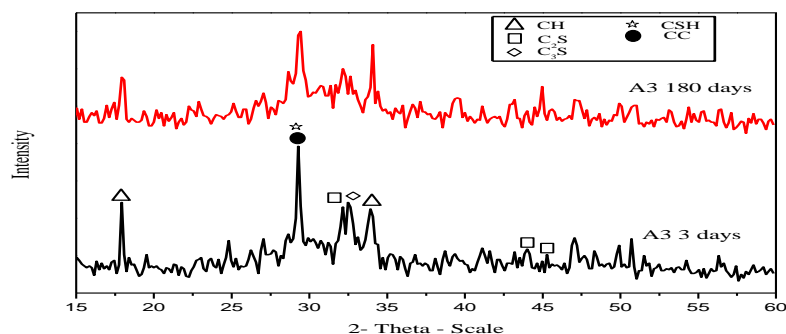

Fig. 5. X-ray diffraction patterns of hardened cement pastes with (50% OPC + 50% GBFS) immersed in tap water up to 180 days.

Figure 6 shows the FTIR spectra of hydrated GBFS cement pastes as a function of curing time. It is clear that the intensity of the band at 3640 cm^{-1} related to OH$^-$ group increases with curing time up to 180 days. This is due to the increase of liberated lime from OPC cement phases.

The broad band near 3436 cm^{-1} due to stretching band $v_1 + v_2$ of H_2O increases with curing time. In addition, the band at 1643 cm^{-1} is related to the bending v_2 of H_2O and indicates the formation of CSH [14]. The band at 985 cm^{-1} due to that CSH increases from 3 days up to 180 days. The absorption band at 1433 cm^{-1} is due to the presence of v_3 CO_3^{-2} as well as 877 cm^{-1} (v_2) that formed from carbonation of $Ca(OH)_2$.
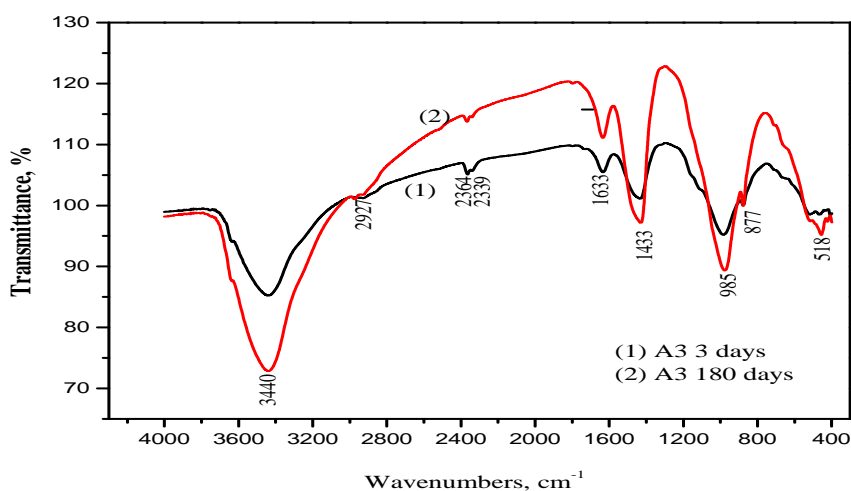

Fig. 6. FTIR spectroscopy of A3 (50% OPC + 50% GBFS) cured at 3 and 180 days under tap water.

Bulk density and total porosity

The bulk density and total porosity of GBFS cement pastes cured up to 180 days are shown in Fig. 7 and 8, respectively. The bulk density of the hardened cement pastes increases and the total porosity decreases with curing time due to the filling of some pores by hydration products. The bulk density decreases and the total porosity increases with slag content. This is mainly due to the decrease of GBFS density in addition to the low rate of hydration which forms hydration products with high bulk densities such as C-S-H gel. A4 40/60 GBFS : OPC gives the higher bulk density, *i.e.* increases with OPC content. The C-S-H formed from slag cement paste gives lower bulk density than that of Portland cement. The decrease of total porosity at later ages is mainly due to the higher pozzolanic reaction of GBFS with CH at later ages [13].
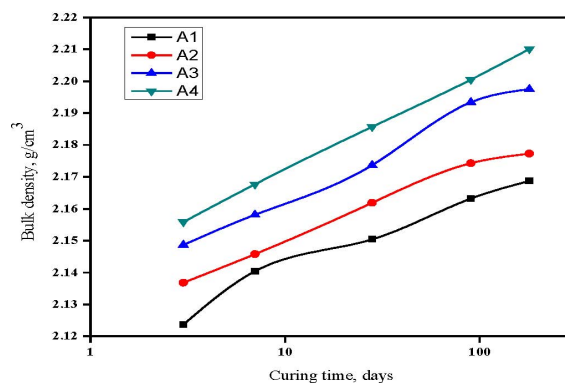
H. El-Didamony *et al.*

Fig. 7. The bulk density of imported GBFS rich cement pastes with curing time.
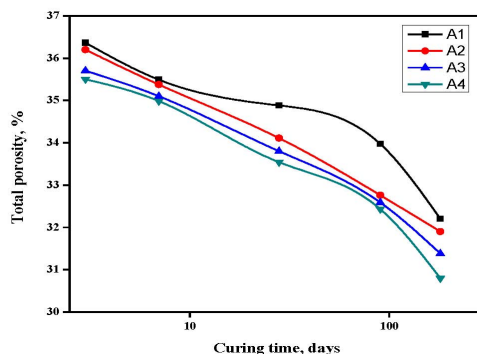

Fig. 8. The total porosity of imported GBFS rich cement pastes with curing time.

Compressive strength

The results of compressive strength of GBFS cement pastes cured up to 180 days are graphically plotted in Fig. 9. It is clear that the compressive strength increases with curing time for all GBFS cement pastes. As the hydration proceeds, more hydration products and cementing materials are formed. This leads to increase the compressive strength of hardened cement pastes. The hydration products possess a large specific volume than unhydrated cement compounds. Therefore, the accumulation of the hydrated products will fill a part of the originally filled spaces which leads to decrease the total porosity and increase the compressive strength of the cement paste. The compressive strength decreases with GBFS content. This is due to the lower β- C_2S and C_3S content in slag cement blends, which is responsible for the formation of CSH and CH upon hydration that accelerates also the hydration of GBFS. Therefore, the compressive strength decreases at early ages of hydration but at later ages of hydration (180 days), the GBFS cement pastes contribute strongly to the developed compressive strength. These results of compressive strength are compatible and in agreement with the total porosity, bulk density, and combined

water of GBFS cement pastes. Pozzolanic cement admixed with 40 and 50 wt% GBFS shows higher strength values at later ages due to the increase of pozzolanic activity of GBFS at later ages.

Thermo-gravimetric analysis

The hydration products of the GBFS rich cement pastes can be investigated from the DTA of the hydrated cement pastes.
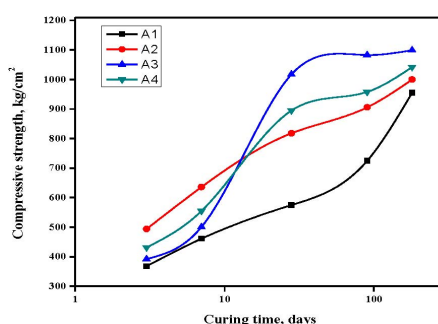

Fig. 9. The Compressive strength of imported slag rich cement pastes up to 180 days.

Figure 10 illustrates the DTA thermograms of Mix A3 with 50 wt% GBFS at 3 and 180 days. The thermograms show endothermic peaks at 100 °C, 150 °C , 200 °C, 215 °C, 475 °C, 700-900°C in addition to an exothermic peak at 955 °C. The first endothermic peak is characteristic to the decomposition of CSH as well as tobermorite like phase[15] . The second peak at 150–200°C is related to C_2ASH_8. Whereas the endotherms at 215 °C and ≈ 417 °C are represented to the decomposition of calcium aluminate hydrate C_4AH_{13} and hydrogarnet series [16]. The endothermic peak at 427C is due to the decomposition of $Ca(OH)_2$, endothermic peaks at 555–674 C are due to decomposition of calcium carbonate and hydrated aluminates as well as the final stage of C–S–H[13] . Also, the endothermic peaks from 550–960 are related to the decomposition of different forms of carbonates. The exothermic peak at 955 ^{o}C is mainly characteristic to wollastonite which is developed during the process of crystallization of monocalcium silicate (CS). This characteristic exothermic peak is related to the hydrated calcium silicate formed from the hydration of pozzolanic materials such as GBFS activated with $Ca(OH)_2$.

Figure 10 illustrates the presence of C-S-H, CAH, C_2ASH_8 in addition to hydrogarnet series at low temperature range before 450 ^{o}C as hydration products of mix A_3. The thermograms show also the peak of $Ca(OH)_2$ at 456 ^{o}C and the endotherm in the range 700 – 900 ^{o}C due to decomposition of $CaCO_3$ in addition to the exotherm at 955 ^{o}C. It is clear that the amount of hydration products increases with curing time due to continuous hydration of GBFS with the liberated $Ca(OH)_2$. The presence of a detectable endothermic peaks from the dissociation of small amounts of $Ca(OH)_2$ in the hydrated cement pastes is mainly due to the great magnification of the thermograms because the chemical analysis gives low values of free $Ca(OH)_2$.
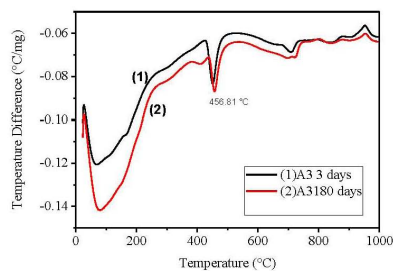
Fig. 10. The DTA thermograms of hydrated GBFS rich cement paste of Mix A3 at 3 and 180 days.
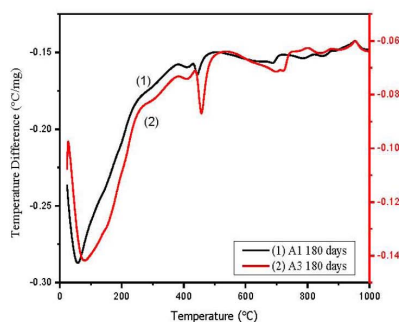

Fig. 11. The DTA thermogram of hydrated GBFS cement paste of A1 and A3 at 180 days.

The effect of the amount of GBFS in cement paste can be also seen from the DTA thermograms of the hydrated cement pastes of mixes A1 and A3 at 180 days in Fig.13. It is clear that all hydrated cement pastes show the same hydration products in addition to free $Ca(OH)_2$, $CaCO_3$ and the exotherm of the formation wollastonite. It is also seen that the endothermic peaks at the low temperature range due to the decomposition of hydration products increase with the OPC content or decrease of GBFS content. This means that mix A3 with 50 wt% GBFS gives higher values of hydration products as seen from the peak area of the hydrated mixes. As the slag content increases on the expense of OPC the hydration products as seen from the endothermic peaks decrease. This is mainly due to the higher degree of hydration of clinker in comparison to GBFS. On the other side, the hydration products of pozzolanic cement pastes give low

combined water content. On the other side, the peak area of $Ca(OH)_2$ decreases with the GBFS content. The liberated $Ca(OH)_2$ is proportional to the amount of Portland cement clinker or β-C_2S and C_3S which are the main source of free lime. Therefore, the peak area of mix A3 > A1. The exotherm at 955 °C increases with the amount of GPFS has the opposite direction of free $Ca(OH)_2$. The exothermic peak is proportional to the amount of C-S-H gel which is formed from the hydration of GBFS with lime liberated from the hydration of Portland cement clinker.

Figure 12 shows the TG thermograms of GBFS rich cement pastes with 50 wt% GBFS cured at 3 and 180 days. The combined water contents of cement pastes are 9.074 and 13.923 wt% after 3 and 180 days. These losses occurred at nearly 580 °C before the dehydroxylation of $Ca(OH)_2$ and the calcinations of $CaCO_3$. It is clear that the combined water contents increase with curing time. The cement pastes cured for 3 and 180 days , respectively give weight loss 11.54 and 18.42 wt% after firing at about 990 °C. The combined water as determined by chemical method includes the loss of $Ca(OH)_2$ as well as $CaCO_3$. The cement pastes Mix A1 and A3 are seen in Fig. 13. It is clear that the cement is more hydraulic than GBFS and these values are in according with the determined values of combined water.
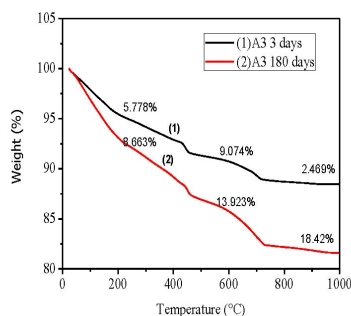

Fig. 12. The TGA thermograms of hydrated GBFS rich cement paste of Mix A3 at 3 and 180 days.
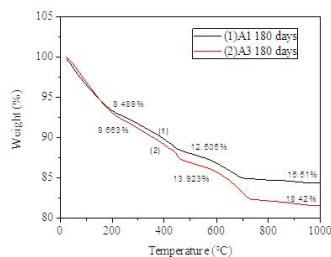

Fig. 13. The TGA thermogram of hydrated GBFS cement paste of A1 and A3 at 180 days.

H. El-Didamony *et al.*

Conclusions

From the above findings it can be concluded that:
1. GBFS decreases the water of consistency and shortens the setting time,
2. GBFS decreases the combined water content at well as the compressive strength at early ages but at later ages 50 % GBFS has the higher compressive strength.
3. The bulk density and the free lime decrease but the total porosity increases with GBFS content.

References

1. **French, W.J.,** Comments on the determination of the ratio of ggbs to Portland cement in hardened concrete. *Concrete,* **25**, 33–36, (1991).

2. **French, W.J.,** Concrete petrography: a review. *Q. J. Eng. Geol*. 24 (1991).

3. **Myers, R.J., Lothenbach, B., Bernal, S.A. and Provis**, **J.L.,** Thermodynamic modelling of alkali-activated slag cements. *Appl. Geochem.* **61**, 233–247 (2015).

4. **Roy, D.M. and Malek, R.I.A.,** *Hydration of Slag Cement. Progress in Cement and Concr.*, first ed., ABI Books Put Ltd., New Delhi India, pp. 48–117 (1993).

5. **Samet, B. and Chaabouni, M.,** Characterization of the Tunisian blast-furnace slag and its application in the formulation of a cement. *Cement and Concrete Research*, (34), pp. 1153–1159 (2004).

6. **Daimon, M.,** Mechanism and kinetics of slag cement hydration. 7th *Int. Conf. Chem. Cement.* Vol. I, III 2/1 – III 2/8 (1980).

7. **Bágel, L.,** Strength and pore structure of ternary blended cement mortars containing blast furnace slag and silica fume. *Cem. Concr. Res.,* **28** (7), pp. 1011-1022 (1998).

8. **ASTM Designation: C191,** Standard Test Methods for Normal Consistency and Setting time of Hydraulic Cement, *Annual Book of ASTM Standards* (2008).

9. **ASTM Designation, C 150,** Standard Test Methods for Compressive Strength of Hydraulic Cements, *ASTM Standard*, pp. 710–736 (2007).

10. **BS EN 196-2:** Method of testing cement. Chemical analysis of cement (2013).

11. **El-Didamony, H., Mohamed Heikal and Al-Masry, S.,** Effect of delaying addition time of SMF superplasticizer on hydration characteristics of blended cement pastes. *Ceram. Silik*. **56** (3), 245–253 (2012).

12. **Abd-El.Aziz, M.A. and Heikal, M.,** Hydration characteristics and durability of cements containing fly ash and limestone subjected to Caron's Lake water. *Adv. Cem. Res*. **21** (3) 91–99 (2009).

13. **Hewlett, P.C.,** "*Lea's Chemistry of Cement and Concrete*", 4th Ed., John Wiley, Sons Ine., New York (2004).

14. **Perraki Th., Kakali Gl. and Konotolean F.,** The effect of natural zeolite on the early hydration of Portland cement. *Microporous and Mesoporous Materials*, 61, p. 205 – 212 (2003).

15. **Garbev, K.,** June structure, properties and quantitative rietveld analysis of calcium silicate hydrates (C–S–H Phases) crystallized under hydrothermal conditions, *PhD Thesis*, Institut fur Technische Chemie von der Fakultat fur Chemie und Geowissenschaften der Ruprecht-Karls-Universitat Hiedelberg, Germany, (2004).

16. **Taylor**, **H.F.W.,** *Cement Chemistry*, second ed., Thomas Telford Publication, London (1998).

إستخدام خبث الحديد المبرد مائياً فى تحضير أسمنت رخيص التكلفة

حمدى الديدامونى أحمد ، محمد أحمد هيكل* ، حسام مصيلحى** و محمد أحمد على***

قسم الكيمياء – كلية العلوم – جامعة الزقازيق ، *قسم الكيمياء – كلية العلوم – جامعة بنها، **قسم الهندسة الكيميائية – المعهد العالى للهندسة – أكاديمية الشروق و ***كلية الصيدلة – جامعة بدر بالقاهرة – مصر .

يعتبر خبث أفران الحديد ناتج ثانوى عن صناعة الحديد. ويتم إنتاج كميات ضخمة منه كل عام. لذلك فإن إستخدام هذه النفايات فى انتاج الخرسانة يوفر المال ويحافظ على البيئة. وجد أن خبث أفران الحديد يحسن خواص الأسمنت الميكانيكية والفيزيقوكيميائية. هناك العديد من الأسباب الخاصة بتوفير الطاقة والمحافظة على البيئة التى أدت إلى تطوير العديد من الأسمنتات البوزولانية. الهدف من هذا البحث دراسة تأثير إستبدال الأسمنت بخبث أفران الحديد المحبب . تم إجراء إختبارات قياس نسبة ماء الخلط وزمن الشك الإبتدائى والنهائى وتعيين الماء المتحد كيميائياً وكمية الجير الحر والكثافة الكلية والمسامية وقوة تحمل الضغط. من خلال هذه الدراسة أمكن التوصل إلى بعض النتائج نوجزها فيما يلى :-

وجد أن كمية ماء الخلط وزمن الشك الإبتدائى والنهائى وكذلك قوة تحمل الضغط تزداد مع زيادة استبدال خبث أفران الحديد المحبب بالاسمنت البورتلاندى. بينما كمية الماء المتحد كيميائياً وكمية الجير الحر تتناقص مع كمية خبث أفران الحديد المحبب.