

Characteristics of Blended Portland Cement with the Libyan Steelmaking Slag

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Abstract: The present study has been carried out to improve the characteristics of ordinary Portland cement (OPC) by adding various amount of granulated blast furnace slag (GBFS). Eleven blends of slag cement were prepared namely 100, 95/5, 90/10, 85/15, 80/20, 75/25, 70/30, 65/35, 60/40 and 50/50 mass% of Portland cement and granulated Libyan blast-furnace slag respectively. The physical properties of cement pastes were studied including normal consistency, setting time, total porosity, bulk density and compressive strength. The increase in the amount of GBFS increases the required water of normal consistency. The setting time of Portland slag cement paste was extended with increase in slag cement. Hydration phases and hydration mechanism were investigated by means of XRD, SEM and DTA tests.

Key words: Physical properties • Size effect • Building materials • Cement • Compressive strength

INTRODUCTION

The utilization of by-products from various sectors of industry is a present-day concern involving the problem of energy and pollution. The furnace slag is the by-product released from blast furnace. GBFS is explained as the glassy granular material formed when molten blast furnace slag is quickly cooled as by immersion in water [1-3]. The main chemical composition includes CaO, SiO₂ and Al₂O₃. In addition, it contains very little MgO, FeO and a small amounts of sulfides such as CaS, MnS and FeS. High proportions of CaO, Al₂O₃ and MgO are advantageous to the activity of slag while the viscosity increases with high content of SiO₂. It is easy to form CaSiO₃ and the high silicate glass decreases the activity of slag.

Ground GBFS cement is hydraulic cement produced during the reduction of iron ore to iron in a blast furnace. Molten slag is tapped from a blast furnace, rapidly quenched with water (granulated), dried and ground to a fine powder. The rapid quenching “freezes” the molten slag in a glassy state, which gives the product its cementations properties and become one of the most popular cementitious materials used in concrete [4]. Currently, slag cement is used to produce blended cement

that complies with water at room temperature [5]. The hydraulic activity of slag depends on its chemical composition, glass content, particle size distribution and surface morphology [6, 7]. Mehta [8] reported that a coating film of aluminosilicate forms on the surface of slag grains within a few minutes of exposure to water, which inhibits further hydration. Blast furnaces slag, with a high content of glassy phase, possesses potential cementations ability and forms C-S-H gel after reacting with calcium hydroxide [9, 10]. It can therefore be used as a partial substitute for cement [11, 12].

MATERIALS AND METHODS

The materials used in this investigation are ordinary portland cement (OPC) and B.F. Slag cement. Such cement was laboratory prepared using commercially produced OPC. Clinker provided by Derna Cement Manufactory (cement Libya) in addition to naturally occurring gypsum rock was be used as setting regulator. Also, a representative sample of granulated blast furnace slag (GBFS) was obtained from the Libyan steelmaking. This sample was employed for the preparation of blast furnace slag cement. The starting materials were thoroughly homogenized separately and a representative sample from

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Table 1: Chemical analysis of the starting materials, (W_i in %)

Materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	L.O.I.
GBFS	18.80	9.13	2.86	40.89	11.39	-
OPC	22.49	5.48	2.99	61.97	1.41	1.63
Clinker	22.66	5.61	2.99	65.89	1.41	0.46
Limestone	1.07	0.25	0.20	54.86	0.20	42.92
Gypsum	37.64	9.81	5.19	20.75	2.22	21.45

Table 2: Specific surface area of the starting materials

Material	Specific surface area (cm ² /g)
OPC	3400
GBFS	4400

Table 3: Mix composition of the prepared mixes, (W_i in %)

Group	C ₀	C ₅	C ₁₀	C ₁₅	C ₂₀	C ₂₅	C ₃₀	C ₃₅	C ₄₀	C ₄₅	C ₅₀
OPC	100	95	90	85	80	75	70	65	60	55	50
GBFS	00	05	10	15	20	25	30	35	40	45	50

each was subjected to chemical analysis technique supplemented with XRF method. The chemical composition of OPC and GBFS are given in Table 1. The ground materials were also subjected to surface area determination using the Blain Air Permeability apparatus and the obtained result are given in Table 2.

The dry constituents were mechanically mixed for one hour in a porcelain ball mill using two balls to attain complete homogeneity. The samples were kept in air tight containers until the time of past preparation. Eleven groups were prepared from ground GBFS and OPC. The mix composition of the prepared mixtures is shown in Table 3.

The pastes were directly moulded into (5x5 cm) cubic stainless steel moulds. After moulding, it was manually vibrated for two to three minutes and then on a vibrator for few minutes, to assure the complete removal of air bubbles and voids and to obtain a better compaction of the paste. The surface of the mould was smoothened. The water consistency and initial and final setting time of cement pastes were determined using Vicat apparatus [13]. The specific surface area of granulated slag and OPC were determined using Blaine Permeability apparatus [14].

The bulk density of hardened cubes was carried out before the specimens were subjected to compressive strength determination. It was determined through weighing of the saturate hardened paste submerged in water and in air (saturated surface dry). Each measurement was conducted on 3 similar cubes of the same age. The following equation was used for calculating the bulk density.

$$\text{Bulk density} = \frac{\text{Saturated weight}}{\text{Volume of sample}}$$

$$\text{Bulk density} = \frac{\text{Saturated weight}}{\text{Saturated weight} - \text{Suspended weight}} \times 1 \left(\frac{\text{g}}{\text{cm}^3} \right)$$

$$\text{Volume of sample} = \frac{\text{Saturated weight} - \text{Suspended weight}}{\text{Density of liquid (water)}}$$

After the determination of bulk density and water content specimens, total porosity of the hardened cement pastes, could be calculated from the equation [15].

$$\epsilon = \frac{0.99 \times W_e \times dp}{1 + W} \times 100$$

Where 0.99 is the specific volume of free water in cm³/g, dp is the bulk density of the paste in g/cm³, W_t is the water content of saturated hardened paste and W_e is the free water content of the paste.

The compressive strength was carried out on three samples following the procedure described by ASTM [16]. The measuring instrument used for XRD was a system with Co k α radiation (X= 1,789 Å) at 40 kV and 30 mA. The 2-theta values ranged from 4 to 70 and were recorded in 0.04° steps with a counting time of 10 s per step. The measurement was carried out on a crushed sample passing through a 40µm sieve. The production and consumption of reaction products through the hydration of the original binder products (cement and Mk) was following using XRD.

DTA locates the ranges corresponding to the thermal decomposition of different phases in paste, in which TGA measures the weight loss due to the decomposition. TGA coupled with DAT makes it possible for the hydration reactions to be followed qualitatively, semi quantitatively and quantitatively. Macrostructure and pore size distribution were studied using scanning electron microscope (SEM) (Joel-Jem. T200).

RESULTS AND DISCUSSION

When cements are in contact with water, calcium hydroxide is liberated during the hydration of the activator (portland cement), which reacts with the colloidal acid hydrates to form hydrates calcium aluminates, silicates and hydro garnet. The reactions of tricalcium aluminate and ferrite solid solution phase at very early age of hydration. The results of water of consistency as well as setting time (initial and final) of different mixes are graphically plotted in Figure 1.

The water of consistency of the pure OPC pastes was found to be 25%. This ratio tends to increase with the incorporation of the various (GBFS) until the maximum ratio (50% (GBFS)) (29.5) is reached. This means that the water of consistency of all blended cement pastes increases with GBFS content compared with that of the OPC pastes. The increase of water of consistency varies from one cement mix to another, which depends on the type and amount of the added component. In addition, the incorporation of fine GBFS increases the surface area of the whole cement mix. The cement pastes containing 50% GBFS recorded the highest value of water consistency compared with the other cement mixes. This is mainly due to the high surface area and fineness of GBFS which needs high water requirement to produce suitable pastes. These findings are similar to those of Darweesh [17]. Variations of setting times of the cement in the presence of different concentration of GBFS are shown in Fig. 2. The results show that the setting time decreased in the presence of GBFS; and also decreases with increase in GBFS concentration.

It is a fact that setting time of cement pastes depends, among other factors, on the type of water increase. The initial setting time of GBFS cement pastes is accelerated as the quantity of GBFS added increases. This may be due to the increase of water/cement ratio. Also the final setting time of GBFS cement pastes is accelerated due to the addition of GBFS. The cement pastes containing 50% GBFS exhibited the value of setting times (initial = 130 and final = 265) compared with the OPC pastes (initial = 75 and final = 400 min) and the other cement mixes due to the high amount of mixing water. At early ages of hydration,

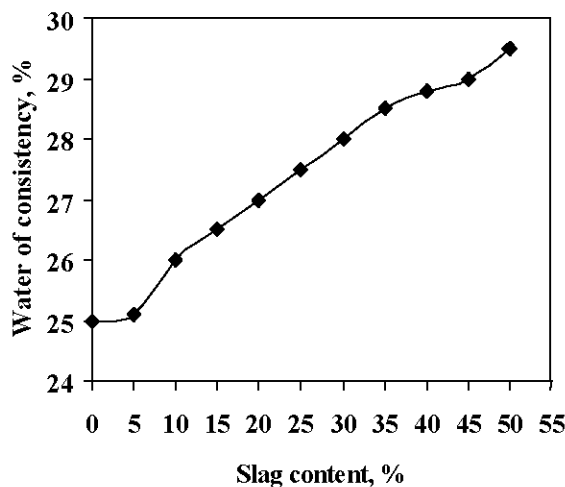


Fig. 1: Water of consistency of OPC pastes without and with GBFS

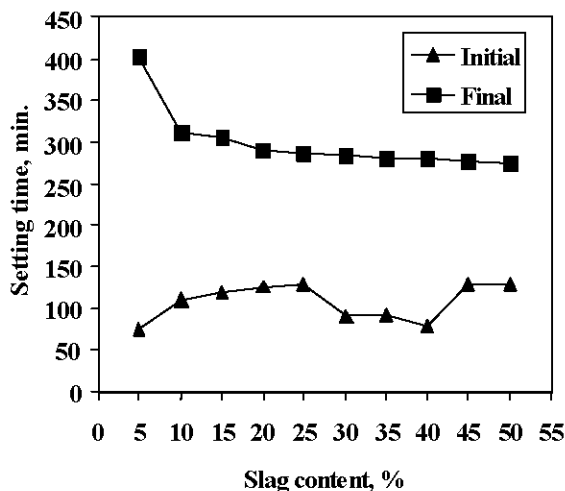


Fig. 2: Variation of setting time of cement in presence of different concentration of GBFS

there is insufficient $\text{Ca}(\text{OH})_2$ to react with the added GBFS. The GBFS grains and hydration products formed coat the cement particles which delay further hydration. Accordingly, the initial and final setting time were elongated. Thus it appears that GBFS acts as a retarded for cement hydration. Also the initial and final setting times are accelerated; this may be due to increase in the amount of excess alkali's in the GBFS which act as a good activator for the hydration of GBFS. Alkaline activation of blast furnace slag disintegrates the network structure of slag and silicate and aluminates ions are taken in the solution [18].

The results of bulk density of the hardened cement pastes made with 0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50% (GBFS) by weight of cement and hydrated for 1, 3, 8, 28 and 90 days are given in Figure 3.

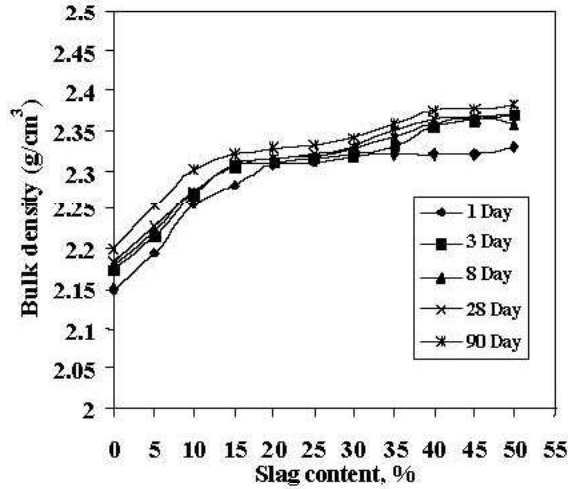


Fig. 3: Effect of GBFS on bulk density of OPC pastes

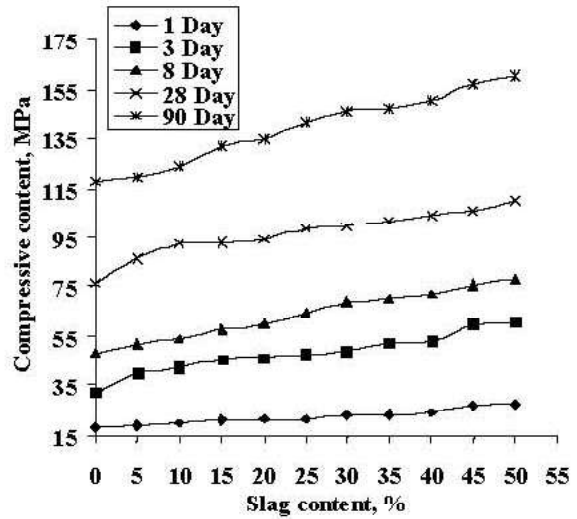


Fig. 4: Effect of GBFS on compressive strength of OPC

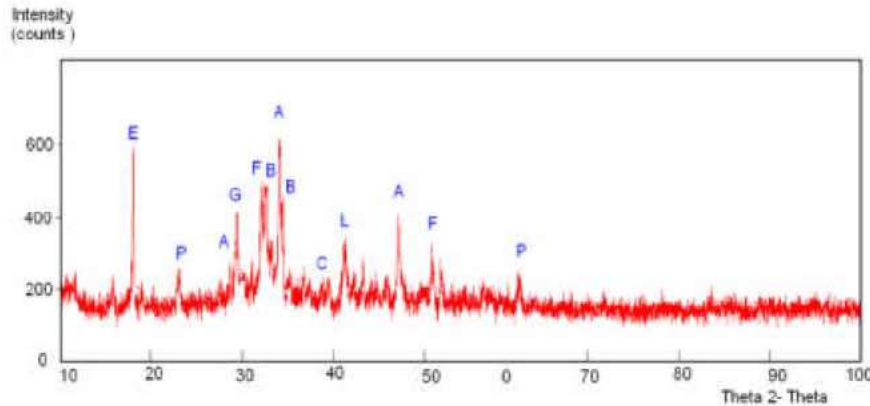


Fig. 5: XRD of sample C₂₅ containing on ordinary portland cement with 25 % GBFS after 8 days of hydration (A=Alite, B=Belite, G=Gypsum, E=Ettringite, F=Ferrite, P=Portlandite, L=Lamite, C=Tri Calcium Aluminate).

The bulk density generally increases gradually with curing time up to 90 days for all cement pastes. This is mainly due to the gradual and continual deposition of the formed hydration products resulting from the hydration of the OPC phases and also from the pozzalonic reactions of ingredient with the librated Ca(OH)_2 which precipitated into the available open pores of the hardened cement pastes [19, 20]. Hence, the total porosity decreases and accordingly the bulk density increases, i.e., the bulk density depends on degree of hydration of the pastes. Generally, as the hydration progresses, the hydration products fill a part of the pore volume, thereby increasing the bulk density. Also the bulk density increases due to the increase of hydration products as calcium hydro silicates and sulpho aluminates. The results of bulk density are in a good agreement with those of total porosity.

The results of compressive strength of the hardened OPC cement pastes made with 0, 5, 10, 15, 20, 25,

30, 35, 40, 45 and 50% of GBFS by weight of cement and hydrated for 1, 3, 8, 28 and 90 days are given in Figure 4. The results show that the compressive strength generally increases with curing time for all cement pastes. This is due to the increase in the amount of hydration products such as calcium hydro silicate and calcium sulpho aluminates. As hydration proceeds, more hydration products and more cementing material are formed and therefore the porosity decreases, which lead to an increase in the compressive strength of all cement pastes with curing time up to 90 days. This is essentially attributed to the gradual decrease of the total porosity and increase of bulk density due to the formation and deposition of the hydration products in the pore structure of the hardened cement pastes. This was reflected positively on the mechanical properties [16, 17]. Figure 5 shows the X-ray diffraction pattern of paste containing on hydrated OPC with 25% GBFS in which, gypsum can be detected by the diffraction peak at

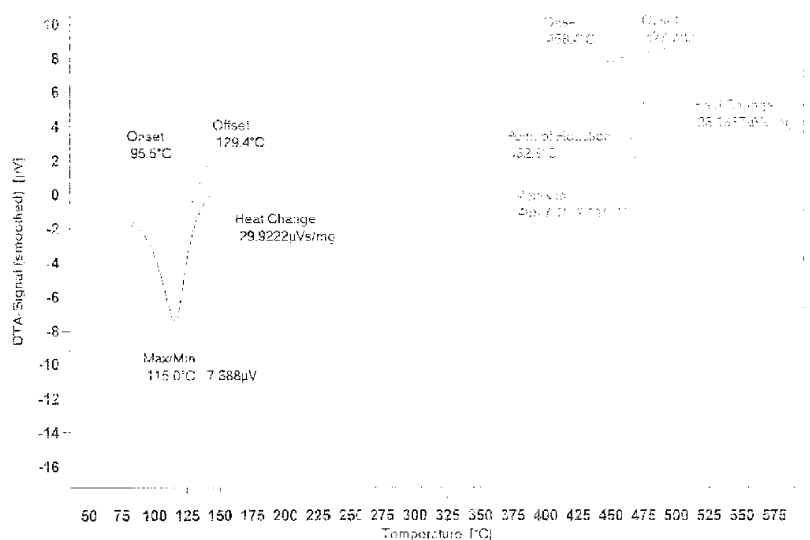


Fig. 6: The DTA thermogram of hydrated OPC past cured at 8 days

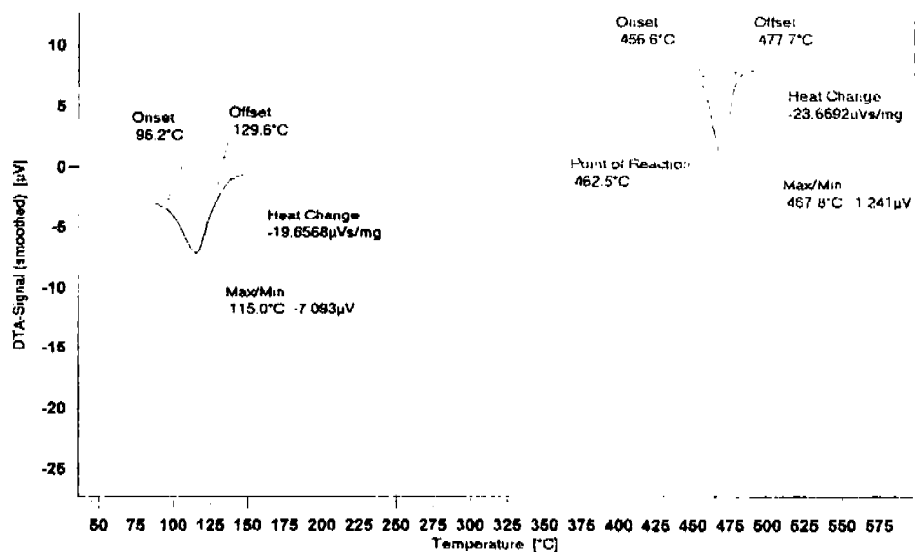


Fig. 7: The DTA Thermogram of hydrated OPC paste containing 40 %GBFS at 8 days

about $2\theta = 29.3696$ ($d = 3.03864 \text{ \AA}$), ettringite can be observed at about $2\theta = 17.9900$ ($d = 4.92682 \text{ \AA}$), alite occur at about $2\theta = 28.6397$ ($d = 3.11440 \text{ \AA}$), $2\theta = 34.0777$ ($d = 2.62883 \text{ \AA}$) and $2\theta = 47.0785$ ($d = 1.92875 \text{ \AA}$), belite can be observed at about $2\theta = 32.5592$ ($d = 2.74788 \text{ \AA}$), $2\theta = 34.3360$ ($d = 2.60964 \text{ \AA}$), the diffraction peak at about $2\theta = 39.3805$ ($d = 2.28620 \text{ \AA}$) corresponds to tri calcium aluminate, ferrite can be detected at about $2\theta = 32.1100$ ($d = 2.78529 \text{ \AA}$) and $2\theta = 50.7775$ ($d = 1.79659 \text{ \AA}$), portlandite corresponds to the diffraction peak at

$2\theta = 22.9915$ ($d = 3.86512 \text{ \AA}$), lamite can be detected by the diffraction at about $2\theta = 41.1955$ ($d = 2.18957 \text{ \AA}$).

Figure 6 shows the DTA thermogram of hydrated OPC pastes cured for 8 days. The thermogram showed endothermic effect in which, the onset of the peak at 95.5°C , the offset at 129.4°C , the mix/min at 115°C is equal to $-7.388 \mu\text{V}$ and heat change is equal to $-29.9222 \mu\text{Vs/mg}$. In addition to endothermic effect in which, the onset at 453.8°C , the offset at 478.7°C , point of reaction at 462.8°C , the mix/min at 467.8°C equal to $2.110 \mu\text{V}$ and heat change

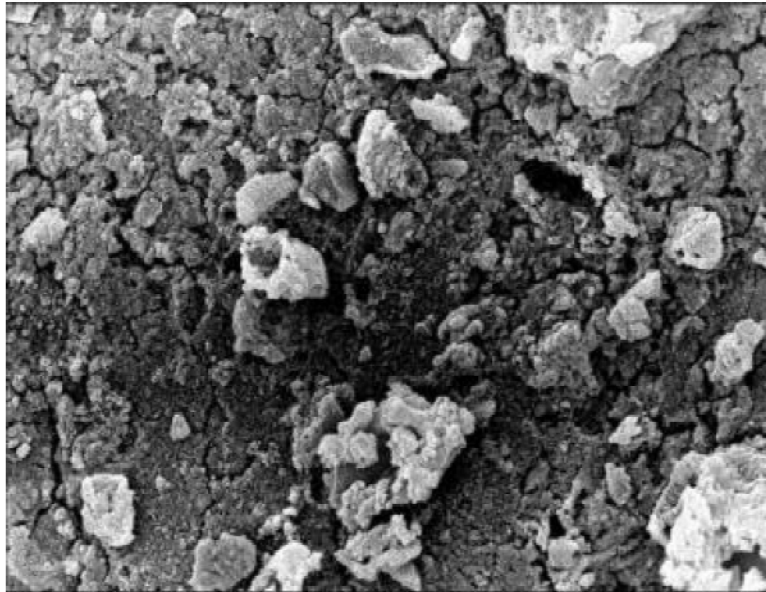


Fig. 8: SEM of sample C20, chemically etching, alite crystals with straight boundaries, belite crystals with curved boundaries, ferrite (white matrix), and aluminates (dark inclusion in white matrix), cracks and pores (black) are also visible. X = 5000.

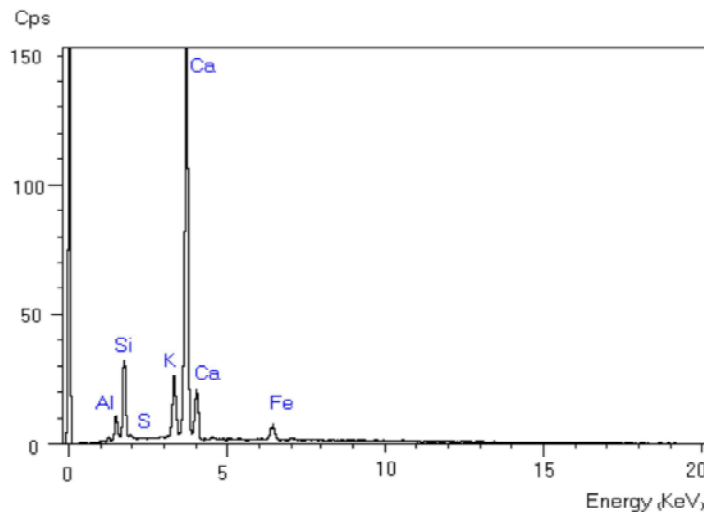


Fig. 9: EDAX microscope of sample C20 showing, the distribution of different elements (Mg, Al, S, Si, K, Ca, Fe) with different ratios

equal to $-23.1837 \mu\text{Vs}/\text{mg}$ were observed. Figure 7 showed the DTA thermogram of hydrated OPC pastes containing 40% GBFS cured for 8 days. The thermogram showed endothermic effect in which, the onset of the peak at 96.2°C , the offset at 129.6°C , the mix/min at 115°C equal to $-7.093 \mu\text{v}$ and heat change equal to $-19.6568 \mu\text{Vs}/\text{mg}$. In addition to endothermic effect in which, the onset at 456.6°C , the offset at 477.7°C , point of reaction at 462.5°C , the mix/min at 467.8°C equal to $1.241 \mu\text{v}$ and heat change equal to $-23.6692 \mu\text{Vs}/\text{mg}$ were observed.

Microstructure of the different samples was examined in polished, chemically etched surface. The main constituting elements of the formation phases were determined by EDAX SEM of mix (C₂₀) which contain 20% GBFS. Fig. 8 shows the well identified alite (light grey), belite (dark grey), curved boundaries, ferrite (white matrix), aluminates (dark inclusion in white matrix) and with different crystal sizes (1.36, 1.82, 2.50 μm) and cracks and pores (black). EDAX of grain present in Fig. 9 showed main constituting elements (Mg, Al, K, Ca and Fe).

CONCLUSION

Ordinary portland cement (Derna) and GBFS (Musrata) were used in this investigation. Blast furnace slag is a by-product formed in the process of iron manufacture from the fusion of limestone with coke and siliceous as well as aluminous residues remaining from the ore after the reduction and separation of iron. The proportion of slag rises to the surface and trapped off from time to time. The proportion to iron produced by the blast furnace varies with the richness in iron of the ore. The essential components of slag are the same oxide as those present in portland cement, namely lime, silica and alumina but with different proportions. The by-product, blast furnace slag is used for the preparation of blended cements which helped in reducing the costs; thereby conserve the energy sources as well as the environment.

In this investigation, the optimum composition of blends made with OPC and blast furnace slag was investigated. The blended cement pastes were prepared by mixing with water of consistency, moulded into 5×5×5 cubic inch steel moulds. After moulding, the cubes were cured in a humidity chamber at 100% relative humidity at 23 ± 2 for 24 hours, then demoulded and cured under tap water until time of testing. The physicochemical properties such as compressive strength and bulk density; and hydration characteristics such as combined water were studied. Water of consistency increase the GBFS content in portland and blended cement pastes. The chemically combined water content increases with the amount of GBFS in all blended cement pastes. Bulk density generally increases gradually with curing time up to 90 days for all cement pastes. This is mainly due to the gradual and continual deposition of the formed hydration products resulting from the hydration of the OPC phases and also from the puzzalonic reactions of ingredient with the librated $\text{Ca}(\text{OH})_2$ which precipitated into the available open pores of the hardened cement pastes. Total porosity generally decreases with curing time for all hardened cement pastes due to the filling up of the available pore volume with the hydration products, as the hydration proceeds. Also, it is seen that with increasing GBFS, the total porosity decreases due to the increase of the rate of hydration of cement paste at early ages. The OPC pastes show the higher of total porosity. Compressive strength generally increases with curing time for all cement pastes. This is due to the increase in the amount of hydration products such as calcium hydro silicate and calcium sulpho aluminates. As hydration proceeds, more

hydration products and more cementing material are formed and therefore the porosity decreases which lead to an increase in the compressive strength of all cement pastes with curing time up to 90 days.

XRD for different samples show presence of gypsum, ettringite, alite, belite, tri calcium aluminate, portlandite, ferrite, lamite and magnesium iron oxide. XRF for different samples show increase of the percentage of GBFS in the different samples leading to increase the percentage of FeO and decrease the content of CaO due the formation of alite, belite, aluminate, ferrite, gypsum and ettringite. Microstructure of the different samples was examined in polished, chemically etched surface. The main constituting elements of the formation phases were determined by EDAX.

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