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Physico-chemical and surface characteristics of some granulated slag–fired drinking water sludge composite cement pastes



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Abstract This investigation aims to study the physico-chemical and surface characteristics of some composite cement pastes. Granulated slag (GBFS) was substituted with fired drinking water sludge (FDWTS) with 5, 10 and 15 wt% to prepare composite cements. The hydration characteristics of composite cement pastes were studied by the determination of portlandite and chemically combined water contents at different curing ages of hydration as well as the phase composition of hydration products. The surface properties were studied using the nitrogen adsorption technique. The results showed that the chemically combined water content increased by using FDWTS instead of GBFS. The free portlandite content increased up to 7 days and then decreased up to 90 days. Compressive strength increases with FDWTS up to 5% and then decreases with its increase up to 15% by weight. The specific surface areas (S_{BET} , m²/g) and pore volumes (V_p , ml/g) increased with FDWTS content in composite cement pastes.

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Introduction

Drinking water sludge is a solid waste material produced from the drinking water treatment. Larger quantities of drinking

water sludge are produced during the treatment process. A typical water treatment plant produces about 100,000 ton/year of sludge [1].

The technical and economical problems that arise due to transportation of drinking water sludge out of the plant as well as the severe pollution of the surrounding atmosphere show the utmost necessity of utilizing drinking water sludge as one of the main objectives of our investigations.

Egypt Government management strategy aims to encourage by-product disposal by useful reuse according to environmental concepts. Drinking water total solid (DWTS) depends upon operations and quality involved in the water treatment process. The main constituents of the sludge are SiO₂, Al₂O₃

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and Fe_2O_3 . Therefore, the utilization of drinking water sludge may be widely used in the preparation of pozzolanic and composite cements, soil improvement and lightweight bricks to reduce the cost, energy and environmental pollution [1–5].

Redriguez, et al. [6] studied the sludge addition on physico-chemical and microstructural characterization, water demand, setting and mechanical strength of Portland cement mortars.

Composite cements are hydraulic cements composed of Portland cement and two or more inorganic materials that take part in the hydration reactions and thereby make a substantial contribution to the hydration products. The most important materials were used such as fly ash, ground granulated blast furnace slag, limestone, natural pozzolanas and microsilica [7]. FDWTS and limestone were used for the production of building materials [8].

Pore structure and surface area of hydrated calcium silicates and composite cements containing silica fume were determined by nitrogen adsorption [9–11].

The aim of the present paper is to study the physico-chemical as well as surface characteristics of some composite cement pastes containing granulated blast furnace slag and fired sludge produced from drinking water treatment plants.

Experimental

The materials used in this investigation were granulated blast furnace slag (GBFS) provided from Iron Steel Company, Helwan, Egypt, Ordinary Portland Cement (OPC) from Suez Cement Company and drinking water treatment sludge (FDWTS) from Potable Water Treatment and Sanitation Company, Hehia Station, Sharkia Governorate, Egypt. The drinking water sludge was fired up to 850 °C for 2 h. The chemical analysis of the investigated materials is given in Table 1.

X-ray diffraction (XRD) pattern of FDWTS reveals the presence of quartz as main phase in addition to albite (sodium aluminosilicate), haematite and small amount of anhydrite [12]. On the other side, GBFS is mainly amorphous material [13]. Different cement mixes were made by the partial substitution of OPC with 0, 10, 20 and 30 wt% of GBFS, which are denoted as Mixes I, II, III and IV respectively. Three composite cements were also prepared from OPC, GBFS and FDWTS in which GBFS was substituted with 5, 10 and 15 wt% of FDWTS and denoted as Mixes V, VI and VII respectively. The mix compositions were prepared as shown in Table 2. The surface area of OPC was 3210 cm²/g. The grain size distributions of granulated slag (GBFS) and fired sludge (FDWTS) are given in Table 3. From data represented in Table 3, it can be concluded that the FDWTS is finer than GBFS, which contains 90.35% in comparison with 88.06% up to 50 µm for FDWTS and GBFS respectively.

Each dry mix was homogenized for one hour in a porcelain ball mill using two balls to assure complete homogeneity. The samples were kept in an airtight container until the time of

Table 2 Mix composition of the investigated cements, wt%.

Mix No.	OPC	GBFS	FDWTS	Water of consistency
I	100	–	–	30.0
II	90	10	–	31.0
III	80	20	–	32.0
IV	70	30	–	28.0
V	70	25	5	29.0
VI	70	20	10	30.0
VII	70	15	15	32.0

Table 3 Grain size distribution of GBFS and FDWTS, wt%.

µm	FDWTS	GBFS
0.5–1	0.93	1.48
1–10	46.25	42.93
10–50	44.17	43.65
50–100	6.16	8.29
100–100	0.37	1.28
200–500	2.12	1.72
Total	100	100

paste preparation. The mixing of cement paste was carried out with the water of consistency as shown in Table 2. The amount of mixing water was poured onto the cement and mixed for four minutes. Pellets were made from cement pastes and covered with moistened cotton to reduce the carbonation. The samples were cured in a 100% RH at 23 ± 2 °C for 24 h, and then cured under tap water up to 90 days.

The hydration of cement pastes was stopped by pulverizing 10 g of representative sample in a beaker containing methanol–acetone mixture (1:1), then mechanically stirred for one hour. The mixture was filtered through a gooch crucible, G₄ and washed several times with the stopping solution then with ether. The solid was dried at 70 °C for one-hour until complete evaporation of alcohol then collected in polyethylene bags; sealed and stored in desiccators for analysis [14].

The hydration kinetics was studied by the determination of combined water and portlandite content as a function of curing time up to 90 days.

The combined water content (W_n) was considered as the percent of ignition loss of the dried samples (on the ignited weight basis). Approximately 2 g of the predried sample was gradually ignited up to 800 °C for 1 h soaking time. The results of combined water were corrected from the water of free lime present in each sample [14].

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

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

Oxide (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	MnO	BaO	L.O.I
OPC	21.5	5.07	4.39	64.21	2.0	3.25	0.29	0.23	–	0.15	–	2.4
GBFS	37.48	12.86	0.40	36.7	2.45	0.11	0.71	1.84	0.72	6.24	5.31	–
FDWTS	54.1	28.84	9.92	3.1	0.64	0.54	0.75	0.30	1.28	0.37	0.04	–

calculated [15]. The compressive strength was measured according to ASTM specifications, 109-92.

X-ray diffraction patterns of the hydration products were performed using a Philips diffractometer (PW 1050170). The patterns were run with nickel-filtered copper radiation at 40 kv and 20 mA with a scanning speed 2θ of 2° min^{-1} .

The surface properties, namely, specific surface (S_{BET} , m^2/g), total pore volume (V_p , ml/g) and mean hydraulic radii (r_h , \AA) of various specimens were determined from nitrogen gas adsorption isotherms measured at -196.8°C by using a conventional volumetric apparatus on hydrated cement pastes made of Mixes IV,V,VI and VII. Before carrying out such measurements each solid sample was outgassed under a reduced pressure of 10^{-5} Torr at 50°C for 3 h.

Results and discussion

The hydration characteristics of composite cement pastes were studied by the determination of Portlandite and combined water contents up to 90 days of hydration. The hydration products were identified by using the XRD technique.

Portlandite contents

Fig. 1 illustrates the free portlandite contents of granulated slag cement pastes as a function of curing time. It is clear that the free portlandite content of OPC pastes increases with curing time up to 90 days due to the continuous hydration of alite (C_3S) and belite ($\beta - \text{C}_2\text{S}$) phases liberating portlandite. On the

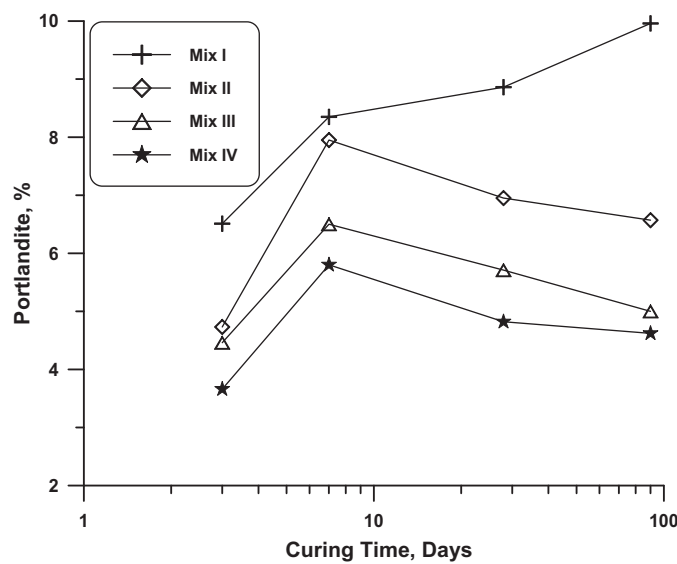


Fig. 1 Portlandite contents for OPC pastes and OPC with different percentages of GBFS up to 90 days.

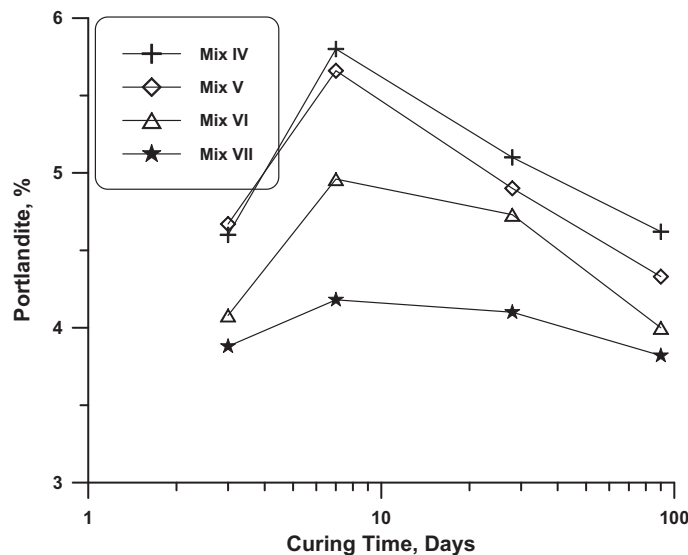


Fig. 2 Portlandite contents for composite cement pastes with different percentages of GBFS and FDWTS up to 90 days.

other side, all pozzolanic cement pastes show an increase of free portlandite content up to 7 days then decreases with curing time up to 90 days. The increase of portlandite up to 7 days indicates that the rate of free portlandite liberation from the hydration of OPC exceeds its consumption by GBFS involving pozzolanic reaction. At later ages, the rate of hydration of GBFS increases and the consumption of free portlandite is higher than its liberation. As GBFS increases the liberated free portlandite decreases accordingly due to the decrease of OPC portion, which liberates lime and the increase of GBFS that activates with higher amount of portlandite [16].

The free portlandite contents of composite cement pastes as a function of curing time are graphically plotted in Fig. 2. The figure illustrates also that the free portlandite contents of all cement pastes increase up to 7 days then decreases up to 90 days of hydration. The substitution of FDWTS on the expense of GBFS tends to decrease the liberated portlandite at

all ages of hydration. All cement pastes contain 70 wt% OPC with various proportions of granulated slag and fired sludge [16]. The decrease of free portlandite with the increase of fired sludge indicates that this sludge has higher pozzolanic activity than granulated slag. This is also due to the presence of free quartz silica which acts as nucleating agent that tends to increase the rate of hydration with fired sludge [17,18].

Combined water contents

The combined water contents of hydrated granulated slag cement pastes as a function of curing time are presented in Fig. 3. The figure shows that the combined water contents for all cements pastes increase with curing time. This is also due to the continuous hydration of OPC liberating free Ca(OH)₂ which can activate the hydration of granulated slag cement pastes from two directions. The first liberates

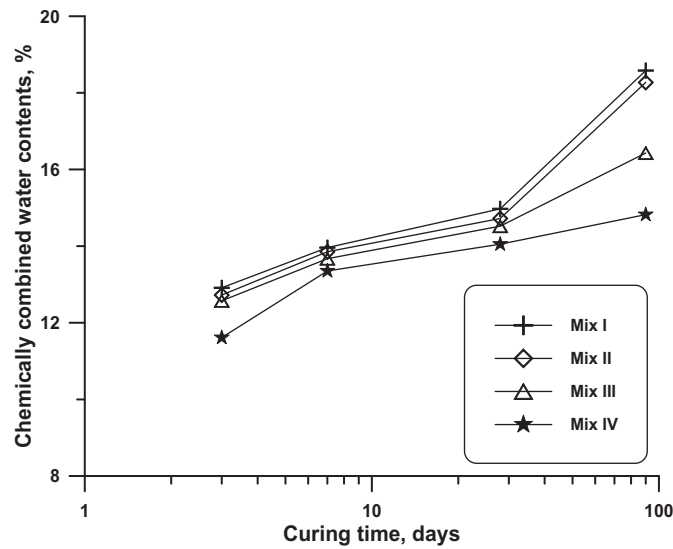


Fig. 3 Combined water contents for OPC pastes and OPC with different percentages of GBFS up to 90 days.

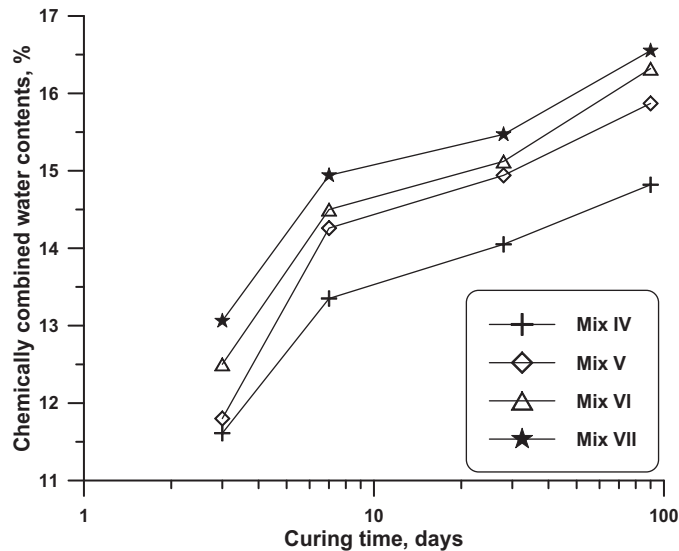


Fig. 4 Combined water contents for composite cement pastes with different percentages of GBFS and FDWTS up to 90 days.

portlandite from OPC and the second is the hydration of GBFS with $\text{Ca}(\text{OH})_2$ forming hydration products such as C-S-H and CASH in addition to the formation of the sulphoaluminate hydrates as well as residual portlandite. Mixes III and IV containing 20% and 30% GBFS show a lower rate of hydration than that with 10 wt% GBFS. This is mainly attributed to the slow rate of hydration of GBFS in comparison with Portland cement. Also, the combined water of any pozzolanic cement pastes is lower than that of OPC paste hydration [19].

The chemically combined water contents of composite cement pastes as a function of curing time are graphically represented in Fig. 4. It is clear also that the combined water content increases with curing time up to 90 days of hydration. The substitution of FDWTS instead of GBFS tends to increase the combined water contents at all curing times. This indicates

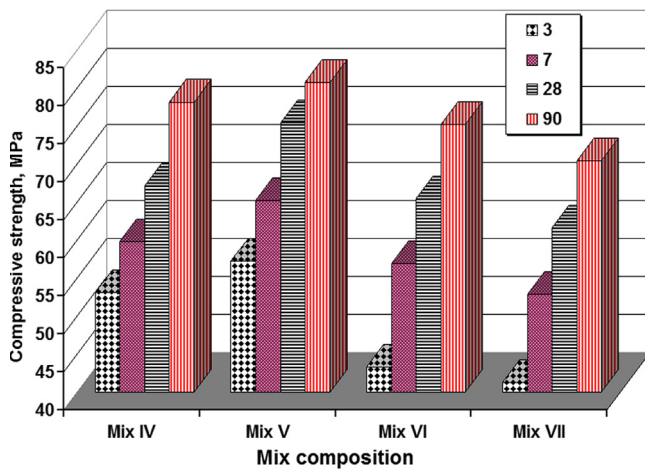


Fig. 5 Compressive strength of composite cement pastes with different percentages of GBFS and FDWTS up to 90 days.

also that the FDWTS is more pozzolanic than GBFS because FDWTS contains free quartz, which acts as a nucleating agent that increases the rate of hydration. The free portlandite content of composite cement pastes decreases with FDWTS content on the expense of GBFS due to the presence of quartz, which acts as a nucleating agent that accelerates the hydration [16–18]. In addition, the presence of two pozzolanic materials with free quartz which acts as a nucleating agent and the decrease of grain size of FDWTS as compared with GBFS increase the rate of hydration.

Compressive strength

Compressive strength of composite cement pastes hydrates up to 90 days as shown in Fig. 5. It is clear that, the compressive strength increases with an increase of FDWTS replacement up to 5% and then decreases with its increase up to 15% by weight. Obviously, the replacement of GBFS by FDWTS enhances the strength. Mix V increases the compressive strength values by 7.53, 9.23, 12.23 and 3.48-folds in comparison with Mix IV at 3, 7, 28 and 90 days respectively.

Effect of FDWTS as pozzolanic material depends on its content, surface area and characteristics of composite cement. The increase of compressive strength attributed to the formation of more hydrated products with curing ages, the accumulation of these hydrated products within the available pore spaces giving higher strength values. The compressive strength decreases with content of FDWTS up to 10–15%. 5% FDWTS can act as a nucleating agent, which gives higher compressive strength at different curing ages, this is due to the formation of additional hydrated products such as C-S-H and CASH formed from the reaction between liberated free portlandite and active silica and alumina containing FDWTS. These hydrates enhance the compressive strength values, so

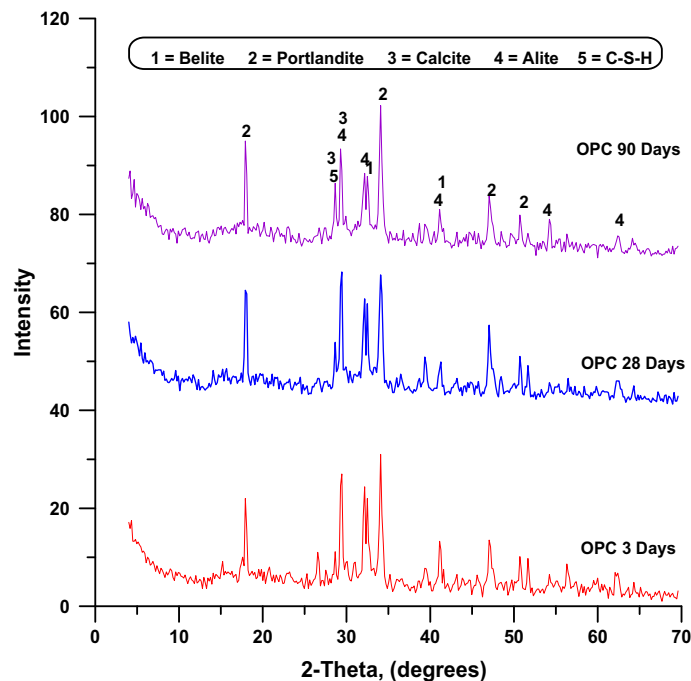


Fig. 6 XRD patterns of OPC pastes at various ages of hydration.

we can conclude that FDWTS is a more pozzolanic material than the GBFS.

XRD results

XRD patterns of the hardened OPC pastes hydrated at 3, 28 and 90 days as seen in Fig. 6. The figure shows the presence of portlandite, CSH, CaCO_3 with residual belite and alite

phases. It is clear that the peaks of belite and alite decrease with curing time up to 90 days, due to the continuous hydration. On the other side, it is clear that the peak intensity of portlandite increases with curing time from the continuous liberation of portlandite from the hydration of belite and alite phases.

Fig. 7 illustrates the XRD patterns of hydrated composite cement pastes cured up to 90 days. The patterns show the same hydration products of cement pastes. The increase of GBFS

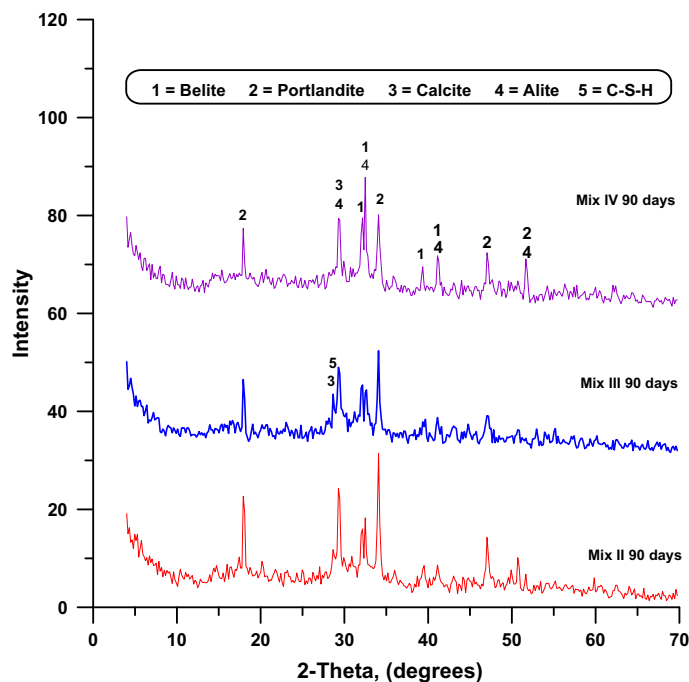


Fig. 7 XRD patterns of OPC pastes with GBFS and FDWTS at 90 days.

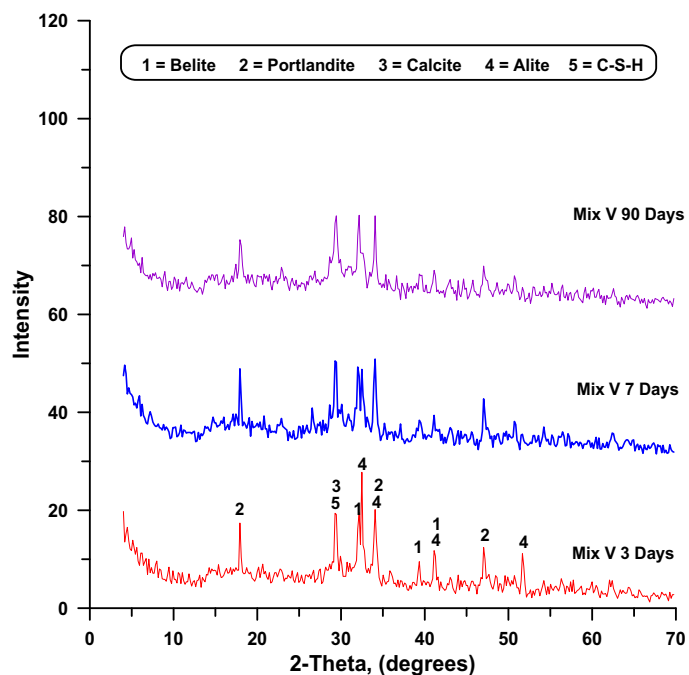


Fig. 8 XRD patterns of composite cement pastes (Mix V) at various ages of hydration.

from 10 up to 30 wt% tends to decrease the amount of liberated lime due to the activation of GBFS with some of lime in addition to the decrease of the OPC portion which is the source of portlandite liberation.

Fig. 8 shows the XRD patterns of composite cement paste mix V containing 70 wt% OPC + 25 wt% GBFS with 5 wt% FDWTS hydrated up to 90 days. It is clear that as the hydration precedes from 3 up to 7 days the intensity of portlandite increases which is confirmed from the chemical analysis. The rate of liberation of portlandite exceeds the rate of consumption with GBFS. On prolonged hydration up to 90 days the peak of portlandite decreases due to the activation of GBFS and FDWTS with portlandite.

Surface characteristics

Fig. 9 shows the nitrogen adsorption–desorption isotherms for hydrated composite cement made of Mix V (70 wt%

OPC + 25 wt% GBFS + 5 wt% FDWTS) as representative sample. Adsorption–desorption isotherms of all investigated cement pastes belong to type II of Brunauer classification. These isotherms are characterized by being irreversible in all cases investigated exhibiting narrow hysteresis loops which close at ≈ 0.7 P/P. From the adsorption isotherms the specific surface area could be calculated by the application of the BET equation using the cross-sectional area of nitrogen of 16.2 Å [20]. The values of (S_{BET} m²/g) obtained for the cement paste were calculated on the ignited weight basis. The results of Fig. 10 showed that for all cement pastes the specific surface areas (S_{BET} m²/g) decrease with hydration time (degree of hydration). The decrease of specific surface area with curing time for all cement pastes is mainly due to the partial filling of the pore system with increasing age of hydration, this leads to a sort of hindrance of nitrogen molecules towards major parts of the total pore system. Therefore, nitrogen molecules become inaccessible towards a larger fraction of the total pore

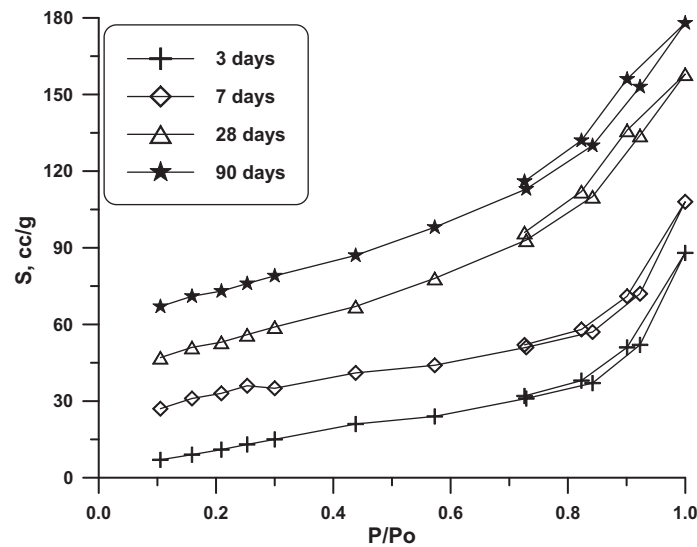


Fig. 9 Adsorption–desorption isotherms for nitrogen gas on composite cement pastes made of Mix V at various ages of hydration.

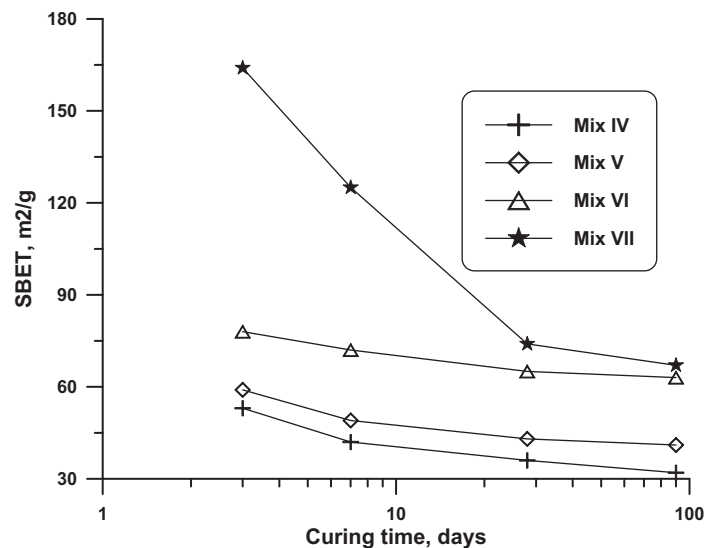


Fig. 10 Variation of surface areas for composite cement pastes with different percentages of GBFS and FDWTS up to 90 days.

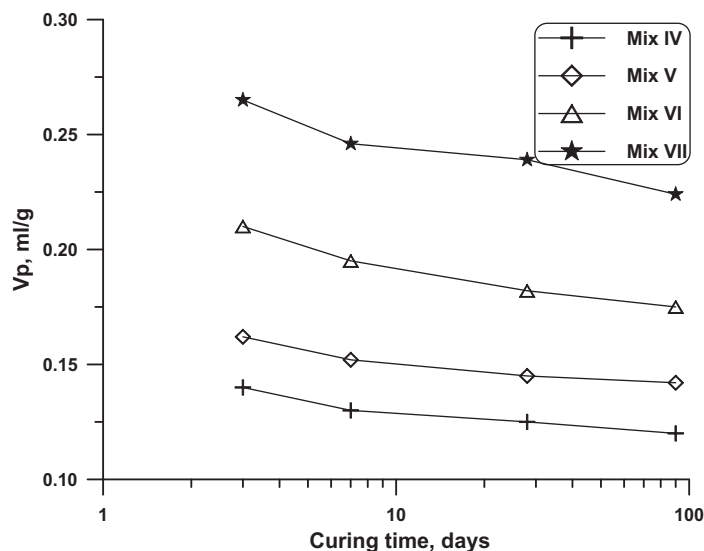


Fig. 11 Variation of pore volumes for composite cement pastes containing different percentages of GBFS and FDWTS cured up to 90 days.

system with time of hydration as a result of the accumulation of larger quantities of hydration products within the pore system of the hardened pastes.

Evidently, the results of Fig. 10 indicated also that the partial substitution of GBFS by FDWTS leads to a consequent increase in the specific surface areas (S_{BET} m^2/g) of the resulting composite cement pastes made of V, VI and VII as compared with the granulated slag cement paste made of Mix IV without FDWTS replacement cement. This result is mainly associated with the increase of the initial porosities of the hardened pastes made of composite cements containing FDWTS (Mixes V, VI and VII) as controlled by the initial water/solid ratios of the fresh pastes. Therefore, the increase in the standard water of consistency of the fresh cement pastes containing fired sludge leads to an increase in the initial porosity of the fresh pastes made of Mixes V, VI and VII as compared with the paste made of Mix IV. Evidently, the increase in the porosity of these composite cement pastes (Mixes V, VI and VII) leads to an increase in the accessibility of nitrogen towards larger fractions of the total pore system leading to relatively higher surface areas when compared with the surface area of OPC-GBFS pastes of Mix IV.

Total pore volume V_p (ml/g) was taken as the saturation value of the isotherm, pore volume for hydrated pastes is graphically represented in Fig. 11. It is clear that pore volume V_p (ml/g) decreases continuously with hydration time for all cement pastes, on increasing amount of FDWTS, the pore volumes increases, this shows the corrected dependence of pore volume on the amount of FDWTS present and the low hydraulic properties of GBFS. Evidently, the increase of total pore volume depends on the amount of water/solid ratios and accumulation of hydration products.

Conclusion

From the above finding it can be concluded that:

1. FDWTS is a more pozzolanic material than the GBFS.

2. The free portlandite content of pozzolanic and composite cement pastes increases up to 7 days and then decreases up to 90 days.
3. Replacement of FDWTS instead of GBFS leads to an increase in the chemically combined water and hydration products.
4. Compressive strength increases with FDWTS up to 5% and then decreases with its increase up to 15% by weight. 5% FDWTS can act as a nucleating agent, which gives higher compressive strength at different curing ages.
5. The specific surface areas and pore volumes decrease with hydration time, whereas increase with FDWTS content.

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