Utilization of an Industrial Waste Product in the Preparation of Low Cost Cement

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Abstract: Blast-furnace slag is a by-product of the manufacture of pig iron. There are huge amounts of this material produced annually; therefore, the utilization of this solid waste in the production of any industrial product leads to money saving, keeps the area of this factory in a cleaner state and prevents atmospheric pollution. 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 granulated slag 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 addition of granulated slag increases the water of consistency, initial and final setting times, compressive strength as well as total porosity, whereas the free lime and combined water decrease with granulated slag content.

[H. El-Didamony, I.M. Helmy, H. Moselhy and M.A Ali, Utilization of an Industrial Waste Product in the Preparation of Low Cost Cement. Journal of American Science 2011; 7(9):527-533]. (ISSN: 1545-1003). http://www.americanscience.org.

Keywords: Blast-Furnace Slag, Atmospheric Pollution, Pozzolanic Cements.

1. Introduction

The problem of producing pozzolanic cement has been of considerable scientific and technological interest because such addition increases the chemical resistance to sulphate attack, impermeability, lowering heat of hydration and thermal expansion (Hewlett, 1998). The use of pozzolanic cement is increasing world-wide because it needs less energy for production.

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 quenched in excess water and then ground, it acquires cementitious properties. The process of quenching is called "granulation" and the product is known as "granulated blast-furnace slag".

Blast-furnace slag is formed as a liquid at $1350 - 1550^{\circ}$ C in the manufacture of pig iron; limestone reacts with materials rich in SiO₂ and Al₂O₃ associated with the ore or present in ash from the coke. If allowed to cool slowly, it crystallizes to give a material having no cementing properties. If cooled sufficiently rapidly below 800°C, it forms a glass which is a latent hydration cement. 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 ground granulated blast-furnace slag and often consists over 95% glass.

Tunisian blast-furnace slag has been characterized by several physicochemical methods to evaluate its hydraulic reactivity (Samet and Chaabouni, 2004). It has been noted that nearly all the slag 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 slag 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, and
- An improvement of the compressive strength at 28 days, but with a slight decrease at 7 days.

Blast-furnace slag 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 (Daimon, 1980).

Bágel (1998) studied the workability and incorporating 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 slag and silica fume 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 ground granulated blast-furnace slag and OPC. Different blends were prepared from these materials and the physico-mechanical properties were studied.

2. Experimental

The materials used in this investigation were ground granulated blast-furnace slag (WCS), which was provided from iron & steel company, Helwan, Egypt, and ordinary Portland cement (OPC) from Suez cement Company. The chemical analysis of these raw materials is shown in Table (1).

Oxides Materials	SiO_2	Al ₂ O ₃	$\mathrm{Fe}_{2}\mathrm{O}_{3}$	CaO	OgM	MnO	TiO_2	Na_2O	K_2O	BaO	SO_3	S-	L.O.I
WCS	37.48	12.86	0.40	36.70	2.45	6.24	0.72	1.84	0.71	5.31	0.01	0.75	
OPC	21.51	5.07	4.39	65.21	2.00	0.15		0.23	0.29	_	0.25		2.40

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

Different mixes were made by substitution 0, 10, 20, 30 wt. % of cement by slag. These mixes were denoted as M_0 , MS_1 , MS_2 , and MS_3 as shown in Table (2).

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

Mix No.	OPC	Slag
M_0	100	
MS_1	90	10
MS_2	80	20
MS_3	70	30

Each dry mix was homogenized on a roller in a porcelain ball mill with four balls for 1 h to ensure complete homogeneity. The water demand for standard consistency and setting time were measured (ASTM Designation: C87-98, 2002)&(ASTM Designation:, C191-01a, 2002). 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 \pm 1°C for the first 24 hours, then demolded and cured under water until the desired curing time such as 3, 7, 28 and 90 days was reached. After curing, 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 105°C for about 24 hours to remove free water. The resulted dried samples were then stored in desiccators for other physico-chemical measurements. The kinetics of hydration were followed by the determination of free lime (Kondo et al., 1975), as well as combined water content. The combined water content was determined by the ignition loss of the dried paste at 850 °C for 20 minutes based on ignited weight basis minus the loss of the anhydrous blend. The compressive strength was determined up to 90 days. The total porosity, ξ , was calculated by the determination of bulk density, d_p , the total water, W_t , and the evaporable water content, W_e , of hardened cement paste as in the following equation:

 $\xi = (0.99 \times W_e \times d_p)/(1+W_t)$ (Copeland, and Hayes, 1956)

Where:

0.99 is the specific volume of free water in cm^3/g ,

 d_p is the bulk density of the paste, g/cm³,

- W_t is the total water content of saturated hardened paste, % and
- We is the free water of the paste, %

3. Results and Discussion

3.1 Water of Consistency and Setting Time

The results of water of consistency and setting times of slag cement pastes are shown in Fig. (1). Water of consistency of slag cement pastes increases with the slag content. This phenomenon was observed by several authors (Sato, et al., 1986). It seems that the high porosity of the slag is responsible for the increase of water demand (Samet and Chaabouni, 2004).

The slag content generally elongated the setting time which remains in conformity with the European norms (Samet and Chaabouni, 2004) due to the slow rate of hydration of granulated slag in comparison to Portland cement. This behavior can be attributed to the increase of water of consistency which increases the total porosity and elongates the setting time. Also, there is insufficient Ca(OH)₂ to react with the gel coatings around the slag grains which delay further hydration of salg. Accordingly, the initial and final setting times are elongated.



Fig. 1: Water of consistency and setting time of slag cement pastes

3.2 Combined Water Content:

The combined water content of hydrated slag cement pastes is graphically represented as a function of curing time in Fig. (2). It can be generally observed that the combined water contents increase gradually with curing time for all hardened cement pastes. This is attributed to the progress of hydration. With 30 % slag, the combined water content is higher than OPC at 90 days. This is attributed to the reaction of slag with liberated $Ca(OH)_2$ at later ages (28–90 days) forming additional hydration products having high water content such as gehlenite hydrate (C_2ASH_8) and calcium aluminosilicate hydrates which increase the combined water content.



Fig. 2: Combined water contents of OPC and slag cement pastes up to 90 days

3.3 Free Lime Content:

The free lime content of hydrated slag cement pastes is graphically represented as a function of curing time in Fig. (3). It was generally found that free lime content increases gradually with curing time for all hardened cement pastes. This is attributed to the continuous hydration of C_3S and β -C₂S liberating hydrated lime. The increase of slag content tends to decrease the free lime contents (Salem, et al., 1995). The continuous increase of free lime of slag cement pastes with curing time up to 90 days is mainly due to the higher content of liberated lime during the hydration of Portland cement fraction which exceeds the amount of free lime consumed by slag hydration. This is sufficient to activate the hydration of granulated slag without any decrease after 28 days.



Fig. 3: Free lime contents of OPC and salg cement pastes up to 90 days

Figure (4) Shows the XRD diffractograms of the hardened slag cement paste made of mixture MS₃ (70% OPC + 30% WCS) cured at 3, 28 and 90 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), increases with curing time. This is due to the continuous hydration of β -C₂S and C₃S. Also, the peaks of unhydrated phases of β -C₂S and C₃S decrease with curing time due to the continuous hydration of β -C₂S and C₃S. The CaCO₃ (CC) is also detected and overlapped by CSH at 3.03 Å.

Figure (5) Shows the FTIR patterns of hydration products of different Portland slag cement pastes (M_0 , MS_1 , MS_2 and MS_3) after 90 days of

curing. It is clear that, the band at 3640 cm⁻¹ which is due to the stretch vibration of OH⁻ group of protlandite (CH) (Saika et al., 2002) decreases with the amount of slag. This is attributed to increase the amount of OPC replacement, which decreases the amount of OPC reactive phases. The peak at 3443 cm⁻¹ is due to free water (Alons and Palomo, 2001). The band at 1436 cm⁻¹ is attributed to presence of calcite, possibly formed due to carbonation of the pastes (Bensted, 1974). The intensity of the band at 986 cm⁻¹ which is due to Si – O stretching vibration of C S H (Saika et al., 2002) increases in MS₂ and MS₃ (indicating increasing of formation of CSH), i.e. has higher hydraulic properties.



Fig. 4: X-ray diffraction patterns of hardened cement pastes containing mixture of (70% OPC + 30% WCS) immersed in tap water up to 90 days



Fig. 5: Infrared spectra of OPC and slag cement pastes after 90 days

3.4 Bulk Density and Total Porosity:

The bulk density and total porosity of cement pastes cured up to 90 days are shown in Figs. (6) and (7) respectively. The bulk density of the hardened cement pastes increases and the total porosity decreases with curing time due to the filling of the pores of the hardened pastes. The bulk density decreases and the total porosity increases with slag content. This is attributed to the increase of water of consistency, which plays an important role in the values of bulk density and total porosity. The water of consistency of the slag cement pastes was higher than that of OPC paste. Generally, the bulk density of the slag cement pastes is lower than the Portland cement. The calcium silicate hydrate formed during the hydration of granulated slag cement paste has low C/S as well as water content. This tends to decrease the bulk density, and increase the total porosity of the cement paste.



Fig. 6: Bulk density of slag cement pastes up to 90 days



Fig. 7: Total porosity of slag cement pastes up to 90 days

3.5 Compressive Strength:

The results of compressive strength of cement pastes cured up to 90 days are graphically plotted as a function of curing time in Fig. (8). It is clear that the compressive strength increases with curing time for all cement pastes. As the hydration proceeds, more hydration products and cementing materials are formed. This leads to an increase in 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. This leads to decrease the total porosity and increase the compressive strength of the cement paste. The increase of slag content decreases the compressive strength especially at the early ages of hydration, due to the increase of water of consistency as well as low hydration characteristics in comparison to OPC. Slag contributes to hydrate after seven days thus improving the strength at medium and later ages (Menéndez, et al., 2003). 30 % slag gives the highest compressive strength value at 90 days. This is also due to the high amount of consumed lime that tends to increase the compressive strength of the cement paste; this result is in a good agreement with that of combined water content.

It is to be noted that the numerical results of compressive strength are only comparative. This is since the size of specimens tested is much lower than that specified by standards.



Fig. (8): Compressive strength of salg cement pastes up to 90 days

Conclusions

From the above findings it can be concluded that:

- Slag increases the water of consistency and elongates the setting time,
- 30% slag increases the combined water content at 90 days as well as the compressive strength, and
- The bulk density and the free lime decrease and the total porosity increases with increased slag content.

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7/7/2011