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Retardation effect and corrosion detection of blended cement pastes

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Abstract Different blended cement pastes were prepared from OPC + 10%, 20% and 30% slag (air cooled) by using a water/solid ratio (W/S) of 0.25 (by weight). The hydration was conducted for various time intervals at 1, 3, 7, 28 and 90 days. Each hardened cement paste was tested for its physico-chemical and mechanical characteristics under normal curing conditions. In addition, the phase compositions of the formed hydration products were identified by means of X-ray diffraction (XRD). Moreover, the electrical conductivity and corrosion detection measurements were also carried out for all the previous blended cements under investigation. The results showed that the combined water contents increase gradually with hydration time for all hardened cement pastes and the partial replacement of OPC by slag cause a notable drop in the combined water content for all blend pastes. The compressive strength values obtained for the hardened blended cement pastes is less than that of neat OPC pastes at all ages of hydration up to 90 days but the sample with 30% slag + 70% OPC had the highest compressive strength. The electrical conductivity of the studied blended cement pasts was lower than that of OPC due to less alkali hydroxides when cement is diluted by the added slag. The significance of low potentials of steel bars in these pastes indicates inhibition of corrosion. As a result, it can be concluded that the mineral admixtures retards the hydration and inhibit the corrosion for cement pastes.

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Introduction

The accumulation of some industrial by-products and solid wastes within their industrial areas and their spreading in the surrounding atmosphere represent a severe environmental pollution problem. Also, steel embedded in concrete, corrosion results in the formation of rust. Corrosion also produces pits or holes in the surface of reinforcement steel. When the reinforcement steel corrodes, the formation of rust leads to a loss of bond between the steel and the concrete. Steel in concrete is usually in a passive state against corrosion due to a thin iron

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oxide layer that formed on the steel surface and remains stable in the high alkaline environment of the concrete.

The properties, structure and constitution of slags are reviewed and correlated with reactivity. Later stages of reaction are marked by continued mineralogical and microstructural changes. $\text{Ca}(\text{OH})_2$ is gradually consumed [1]. In the hydration of slag cement, a negligible portion of the heat liberation is that of the hydration reaction of the slag itself. Since the granulated slag acts as a consumer for $\text{Ca}(\text{OH})_2$ which is liberated from Portland cement during the hydration. The hydration of the clinker portion in the slag cement is accelerated by lowering the $\text{Ca}(\text{OH})_2$ concentration in the aqueous phase [2].

Singh et al. [3] proved that the non evaporable water contents are always lower in presence of the waste materials as compared to the Portland cement. Whileas, El-Didamony et al. [4] concluded that the combined water content increases with increasing the amount of silica fume while decreasing with increasing slag content. On other study [5], the reactions of blended cements were slower than Portland cement, and that silica fume reacted earlier than fly ash and slag.

On the other hand, the replacement of a part of clinker by slag has led to an acceptable extension of the setting time, an improvement of the rheological behavior, very good stability to expansion and an improvement of the compressive strength at 28 days, but with a slight decrease at 7 days [6].

Mehta [7] found that the pozzolanic activity was not high enough to affect the strength and other properties of cement during the first 7 days of hydration, but considerable activity was observed during 28–90 days period and beyond. Another study attained that the compressive strength with curing for 28 days was highest when 20% BFS and 5–10% SF were mixed [8]. Jau and Tsay [9] used slag to substitute for up to 50% of cement by weight to make slag-cement concrete. The test results show that the slag concrete with 20–30% substitution has the best corrosion resistance.

Ibrahim et al. [10] used silica fume (SF) and blast furnace slag (BFS) at different ratio instead of Portland cement (PC) to improve the mechanical properties of concrete and to increase the corrosion resistance of steel embedded in concrete. It was observed that the samples with 10% SF + 20% BFS had the highest compressive strength, and that the concrete samples with 10% SF + 40% BFS and 0.35 water-binder ratios had the lowest corrosion current density. As a result, it can be concluded that the mineral admixtures improved the compressive strength, and corrosion current density. The effects of water-quenced (WS) and air cooled (AS) blast furnace slag substitution of Portland cement hydration was studied by Moastafa and Kishar [11]. It was found that at low W/C ratio, the combined substitution of AS (15%) and WS (15%) increased the compressive strength above that of the OPC paste and beyond the strength of pastes substituted by 30% either AS or WS. The corrosion behavior of steel in concrete with Portland cement blended with blast furnace slag and fly ash studied by Dinakar et al. [12] in comparison to the correspond-

ing ordinary Portland cements. The corrosion rates of steel in both fly ash and slag concretes were much lower than the corresponding OPC concretes, with slag concretes showing higher resistance than fly ash concretes. From these studies it is evident that fly ash and slag blended cements is better than their corresponding ordinary cements.

Salem and Ragai [13] studied the variations in electrical conductivity of blended cement pastes with hydration time at 30 °C and 50 °C for each paste during setting and hardening processes after gauging with deionized water. The results demonstrate that the electrical response characteristics of setting pastes can be used as an effective means of studying the progress of blended cement hydration, as well as, reflecting the hydraulic reactivity of GS and SF as pozzolanic constituents of the hardening pastes.

The object of this investigation is studying the effect of some industrial solid waste (slag) on physico-chemical, electrical conductivity, mechanical characteristics and corrosion behavior of some blended cements.

Experimental

Ordinary Portland cement (OPC) was provided from Helwan Portland Cement Company, Helwan, Egypt. Finely ground granulated blast-furnace slag of specific surface area 3200 cm^2/g was supplied from National Cement Company, Helwan, Cairo. The chemical composition of starting materials showed in Table 1.

Four mixes were prepared Mo = 100% PC, MI = PC + 10% slag, MII = PC + 20% slag, MIII = PC + 30% slag. The mixing was carried out on a smooth and non-absorbent surface with the aid of an ordinary gauging trowel. After complete mixing the resulted pastes were moulded into cubic specimens by using one-inch cube moulds. The hardened cement pastes were then removed from the moulds after they attained the final setting and cured at about 100% relative humidity for 1 day, the samples were then cured under water for 90 days. The hydration products formed of each sample are identified by means of X-ray diffraction with a nickel filter and $\text{Cu-K}\alpha$ radiation.

Two representative samples of each dried hardened plain and blended cement pastes, exactly about 1 g of each, were weighed in silica crucibles and ignited for one hour at 950 °C in an adjusted muffle furnace, cooled in desiccators then weighed. The chemically combined water (i.e. the amount of water retained after drying) was calculated as $W_n\%$ using the following equation:

$$W_n\% = [(W_2 - W_3)/(W_3 - W_1)] \times 100$$

where, W_1 , the weight of the empty crucible (g); W_2 , the weight of the crucible + sample before ignition (g) and W_3 , the weight of the crucible + sample after ignition.

A set of three cubes, representing the same mix and same age, were used for the determination of the compressive

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

Oxide (%) material	SiO_2	Al_2O_3	F_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl	L.O.I.
OPC	20.34	5.21	3.67	62.28	2.4	2.94	–	–	–	2.4
GBFS	36.9	10.6	1.65	34.3	8.52	0.60	0.83	0.48	0.015	–

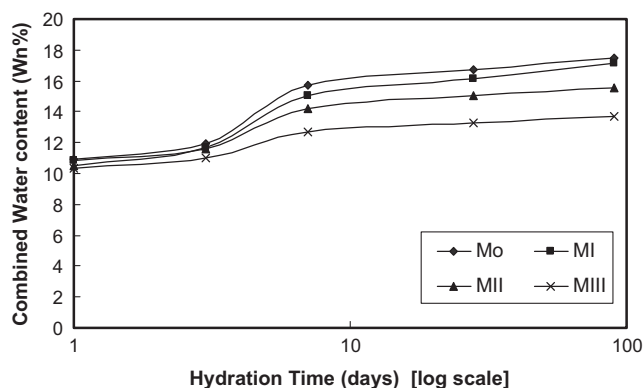


Fig. 1 Combined water content versus hydration age of various mixes.

strength of the hardened cement pastes. The average of the three results expressed was considered, in kg/cm^2 .

The pastes used for conductivity measurements were prepared by mixing the deionized water to exact 10 g samples by using W/S ratio of 0.25. The paste was transferred into a cylindrical plastic sample holder of 15 mm internal diameter, with stainless steel electrodes at both sides with 12 mm distance between them. Electrical conductance of each paste was measured at 30 °C from 5 min up to 24 h of hydration.

The reinforcement steel bars used in potential measurements were cut out from the same stock. The steel electrode surface was partially coated with a Teflon coating system before embedding them in the mortar. The dimensions were 4 cm long and 1 cm diameter. About 2 cm length of each steel rod was embedded symmetrically across the width of the block, leaving the remaining 2 cm for electrical connection. To measure corrosion potential a two set of cement blocks, free and with different slag concentration, were made. The first set was aged in a humidity chamber that was maintained at an average relative humidity ($\text{RH} \approx 100\%$). Initial potential readings were recorded for each block and subsequent readings taken at an interval of 10 days up to 2 month. The mortar specimens were demoulded 24 h after casting, and were immediately subjected to potential monitoring. The second set is partially immersed in 3.5% NaCl solution. The specimens were then taken out of the humidity chamber NaCl solution for

periodic electrochemical monitoring. To obtain readings, a saturated calomel electrode (SCE) was placed on the mortar surface. The circuit was completed by connecting the cable of the half-cell to a voltmeter and the other cable to the steel specimen. The readings were taken at three different points on each cement block and the average computed as the potential reading for the embedded steel rod.

Results and discussion

Chemically combined water contents (wn %)

The results of chemically-combined water contents ($\text{Wn}\%$) obtained for the various hardened cement pastes in presence and absence of slag are graphically plotted as a function of time in Fig. 1. The combined water contents increase gradually with hydration time for all hardened cement pastes. This is mainly due to the progress of the hydration and precipitation of excessive amounts of the hydration products with increasing age of hydration [3]. The partial replacement of OPC by slag cause a notable drop in the combined water content for all OPC-slag blends. Also, the slag blended cement pastes containing 30% slag Mix (MIII) showed the lowest values of combined water content as compared with those of the other Mixes (MI and MII) at all ages of curing. It seems that addition of slag retards hydration of cement paste especially at higher contents of slag by reducing the sites of nucleation for free lime to react with slag as artificial pozzolana. Consequently, a reduction of the amount of CSH is obtained, these results are in a good agreement with El-Didamony et al. [4].

Compressive strength

Fig. 2 illustrate the results of compressive strength of the various blended cement pastes made of ordinary Portland cement. The compressive strength values of various hardened cement pastes increase with increasing of curing time up to 90 days. This is due to the increase in the amount of hydration products. As the hydration proceeds, more CSH is formed and accumulated in the pore system of the hardened paste. The compressive strength values obtained for the hardened blended Portland cement pastes in which OPC is partially substituted by slag is less than that of neat OPC paste at all ages of

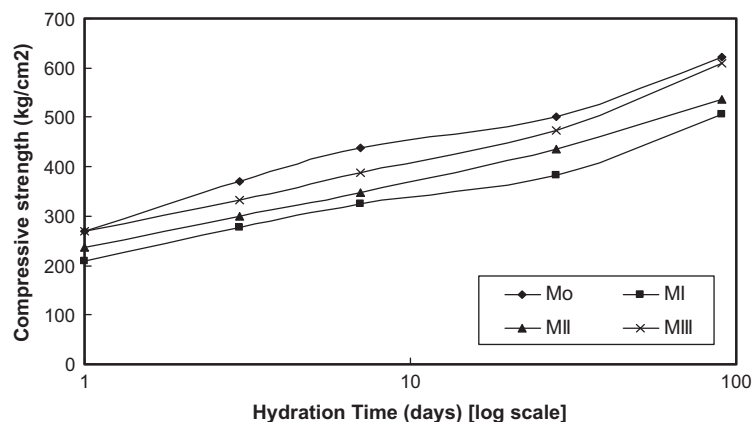


Fig. 2 Compressive strength versus hydration age of various mixes.

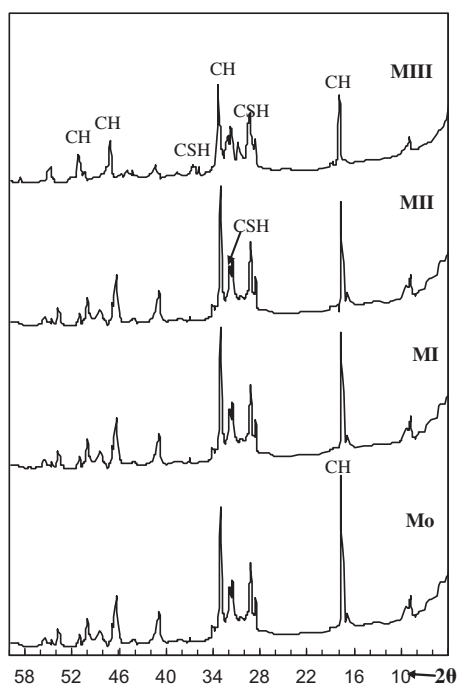


Fig. 3 XRD patterns of different cement pastes after 90 days of hydration.

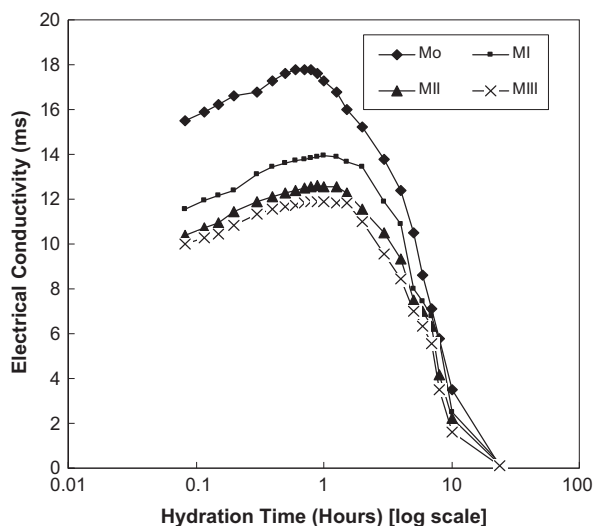


Fig. 4 Electrical conductivity–hydration time curves obtained of various mixes.

hydration up to 90 days. From Fig. 2 we can noticed that by increase amount of slag added to cement paste, the value of compressive strength increase as a result to the pozzolanic reaction between slag and free lime released during OPC hydration and formation of additional amounts of CSH which leads to increase in the compressive strength values. This result is in a good agreement with other studies made by Ibrahim et al. [10] and Moastafa and Kishar [11].

Phase composition

The XRD patterns (Fig. 3) of all the studied mixes showed that the hydration products formed were CH and CSH. The inten-

Table 2 Potential readings of reinforced steel concrete with different furnace slag/cement ratio in different test media (a) under relative humidity (100%) and (b) immersed in 3.5% NaCl.

Time (days)	Potential reading (mV)							
	100% R.H. BFS%				3.5% NaCl BFS%			
	0	10	20	30	0	10	20	30
0	98	95	63	47	198	168	154	123
10	103	98	73	68	205	177	178	125
20	115	106	96	68	220	198	205	145
30	115	105	106	87	215	198	210	163
40	135	116	103	95	247	223	215	168
50	139	123	111	98	263	230	226	189
60	158	137	129	110	289	279	263	206

sity of calcium hydroxide in the blank was increase with time up to 90 days. The presence of slag decreases the intensity of the CH due to the pozzolanic reaction forming more CSH phase. By increasing the amount of slag the CH contents decrease.

Electrical conductance

The relation between conductivity and hydration time for all the pastes are shown in Fig. 4. The initial hydration of the OPC constituents is responsible for the increased conductivity values at the initial stages of hydration. The gradual decrease in the conductivity values after the peak maximum reflects the alkali stay in pore water, the decrease of conductivity is more due to the decrease of the mobility of the ions once the porous network starts to depercolate. Increasing the percentage of slag in the OPC-slag blends is associated with a reduction in the initial conductivity values at the earlier ages of hydration. The lower intensity of the conductivity maxima are observed for the blended pastes compared with that of the neat OPC paste is mainly due to partial replacement of OPC by 10, 20 and 30 wt% of slag.

Potential measurement

The corrosion potentials as a function of exposure time for reinforced steel electrodes in OPC mortar specimens contained (0%, 10%, 20% and 30% slag by weight of cement), in different media are shown in Table 2. The results show that the values obtained fall within the range of accepted passive condition [14]. The significance of these low potentials is that corrosion may be delayed. Comparing these results, it is observed that, in 3.5% NaCl solution the protective film formed on the steel rod inhibited only for a short period, whereas under humidity condition, the film provided a more effective barrier against further corrosion of steel rod. This could be attributed to the continuous diffusion of chlorine ions through the cement pastes and depassivating the protective layer on the reinforcement steel. Better resistance to corrosion is achieved on addition of slag to OPC.

Conclusions

The main conclusions derived from this investigation are summarized as follows:

- (1) Combined water contents decrease with increasing the percentage of slag.
- (2) Increasing the amount of slag decrease the compressive strength values.
- (3) The corrosion rates of steel in OPC-slag blends were much lower than the corresponding neat OPC.
- (4) The electrical conductivity values for all the investigated specimens exhibit an initial increase during the first few minutes of hydration and then decrease continuously with increasing age of hydration up to the final stages.

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