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Chloride diffusion and oxygen permeability of mortars with low active blast furnace slag

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HIGHLIGHTS

- The GBFS mortars show the greatest resistance to chloride diffusion and conduction.
- The initial period of wet curing influences the chloride diffusion of GBFS mortars.
- At long term, oxygen permeability of the slag mortars is improved.
- After the diffusiont est, a densification of slag mortars microstructure is observed.

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ABSTRACT

Depending on its hydraulic activity, the use of Granulated Blast Furnace Slag (GBFS) in cementitious materials contributes to improve their durability performances. In this paper, a low reactive Granulated Blast Furnace Slag with is used in modifying mortar composition. Some durability properties of mixes containing 0, 30 and 50% of slag as substitution to OPC are studied. Diffusion and conduction of chlorides at long term are analyzed with different initial wet curing periods. Microstructure of mortars after 360 days of diffusion is observed by means of Mercury Intrusion Porosimetry. The oxygen permeability is analysed at 90 and 360 days of wet curing. The results indicate good performances to chloride diffusion of the mortars with GBFS, especially for a prolonged wet curing. Moreover, the GBFS are inefficient for oxygen permeability at 90 days but they however allow a decreasing over long term.

1. Introduction

The use of granulated blast furnace slag (GBFS) as a cement additive contributes to increase cement production and improve its technical performances while preserving the environment. However, the steel industry produces a very variable quality of slags in terms of chemical composition and glass contents, which directly affects the hydraulic activity of slag [1,2]. When mixed with the clinker, the slag reacts with the calcium hydroxide and forms additional hydrated and this leads to an improvement in the chemical resistance and microstructure [3,4].

Moreover, in literature, several studies report a considerable improvement in transport properties (capillary absorption, permeability and diffusion) of mortars and concretes based on GBFS binder [6–8]. However, this highly depends on the hydration of the slag and consequently on its hydraulic activity.

The durability properties and microstructure of matrices based on cements slag are significantly influenced by the curing conditions (relative humidity and temperature), especially if the slag is slightly reactive. Ortega et al. [9] observed a significant decrease of capillary absorption and chlorides diffusion of CEM III type mortars with prolonged high relative humidity curing. This was attributed to the minimizing drying action and the improvement of water availability for clinker-slag hydration reactions. In another study [10], the same researchers studied the effect of different curing environments (Atlantic and Mediterranean climates) on the chlorides migration in CEM III and OPC mortars. The results showed a good performance regarding chloride ingress resistance in CEM III even in the non-optimal cure environments studied, after an enough maturing time.

Several studies have shown higher performances of cement slag mixtures against chloride attack with regard to OPC based

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mixtures [11–14]. By testing concrete blocks exposed in a natural marine site, Abd El Fattah [15] et al showed a good influence of the slag on chloride penetration and corrosion mitigation. This is often attributed to the improved chlorides binding capacity of hydrates [16]. Florea and Brouwers [17] found that CSH and CAH hydration phases are responsible for about two-thirds of fixing of chloride ions in matrix of cement slag mixtures. However, this binding capacity remains sensitive to the slag composition and to maturity degree.

Natural diffusion test inducing only gradients concentration, even if it is a laborious test, is generally considered to represent the penetration mechanism of chloride ions in concrete with most precision under real conditions of exposure [18]. The ASTM C1202 Conduction Test [19] is commonly used as accelerated test: although it does not yield a diffusion coefficient, it has the advantage of being fast and giving a good indication of chlorides diffusion. However, to see its effectiveness, it is always interesting to quantify the correlation between conduction and natural diffusion of chlorides, in particular in the case of unconventional binder.

In a previous study [20], we examined the microstructure and some durability aspects of mortars containing up to 50% of GBFS with low reactivity index. The results indicated finer porosity and lower water absorption for mortars with GBFS at old ages (90 and 360 days). Moreover, after 90 days of wet curing and 270 days of chloride diffusion, lower diffusion coefficient has been observed for 50% slag substitution level. The present work is a continuity of this previous research and thus, the effect of the wet curing before the diffusion test (90 and 180 days) is presently studied, in comparison to the previous work when only 90-day period was considered. Moreover, the chlorides conduction and the study of the pores distribution of the matrices after diffusion are also studied. And finally, oxygen permeability has been recorded as additional durability index.

2. Experimental program

2.1. Materials

In this study, Ordinary Portland Cement (OPC) type CEM I 52.5N with a fineness of 4200 cm^2/g was used for mortar mixes. Algerian Granulated Blast Furnace Slag (GBFS) was used in this work. It was ground in a laboratory mill to a Blaine fineness of 4150 cm^2/g. A broad characterization of this slag was carried out in previous studies [3,20] which showed its low rate of alumina and magnesia contents as well as its low hydraulic reactivity. The chemical composition of cement and slag are given in Table 1. Standardized sand with maximum particle size of 2 mm was used for mortars mixes.

2.2. Mixtures properties and curing procedures

The mortar mixes (M0, M30 and M50) have a Sand to Binder ratio of 3:1 and Water/Binder (W/B) ratio of 0.5. The binder for mortar M0, M30 and M50, was obtained by partial substitution of cement with 0, 30 and 50% of slag, respectively. Substitution was made by mass of cement. Mortars specimens were cast according to European Standard EN 196-1 [21]. They were demoulded after 24 h and cured in moist room at 20 ± 2 °C and more than 95% relative humidity until the age of testing. Properties (compressive strength and water water absorption by immersion P_W) of hardened mortars with and without GBFS are shown in Table 2 [20].

Table 2
Compressive strength, water absorption by immersion P_W of mortar with and without GBFS.

		Compressive strength (MPa)		Water absorption by immersion P_W (%)	
Mortars	Slag (%)	90 days	360 Days	90 Days	360 Days
M0	0	68.6	76.0	15.99	15.72
M30	30	67.2	74.5	17.10	16.76
M50	50	55.7	67.5	18.31	17.90

2.3. Test procedures

2.3.1. Chloride permeability tests

2.3.1.1. Steady state diffusion test. Rates of diffusion of Cl^- ions into mortars are monitored using two compartment diffusion cells. 8 mm thick mortar blocks are sawed from 80 mm diameter specimens and stored in $Ca(OH)_2$ saturated solution. Prior to the test, each specimen is polished with 600-grade emery paper, rinsed with deionised water and surface dried with a tissue before being fitted into the diffusion cell (Fig. 1). After fitting with epoxy resin and sealing with silicon paste, the cells are filled at one side with $Ca(OH)_2$ solution and at the other side with 1 Mole NaCl in a saturated $Ca(OH)_2$ solution [20]. At periodic intervals, chloride concentration is determined by potentiometric titration from a 10 ml sample of the solution in cell 2. The occurrence time (breakthrough time) was calculated from the intercept of the concentration versus time date (minimum rate of 30 mg/l of Cl^-ions is reached in the cell 2). The effective diffusion coefficient is calculated, when the steady state is reached, according equation (1) (in m^2/s).

$$D_e = \frac{V_1}{A}\frac{\Delta C_1}{\Delta t}\frac{e}{(C_2 - C_1)} \quad (1)$$

with $\Delta C/\Delta t$: an increase of chloride concentration in cell 1, C_1 and C_2: chloride concentrations of cells 1 and 2, A: section of mortar slices, e: thickness of mortar slices and V_1: volume of cell 1.

The diffusion test was carried out on two sets of mortars preserved before the test during 90 and 180 days of wet curing. At 360 days of diffusion, samples of mortar were taken and Mercury Intrusion Porosimetry tests were carried out.

2.3.1.2. Conduction test. The specimens of 96 mm diameter and 50 mm thick are conditioned by achieving vacuum pressure on the dry specimen and maintaining for 3 h, vacuum saturation for a period of 1 h after adding de-aerated water, and further soaking under water for a period of 18 h. The specimens were kept in a moist curing (95% RH, 20 °C) environment during 90 and 180 days before performing the chloride conduction test (the rapid chloride permeability test), according to ASTM C 1202–94 standard [19].

2.3.2. Mercury Intrusion Porosimetry

In order to analyze pore size distribution, the different mortars have been examined by Mercury Intrusion Porosimetry (MIP). This test was carried out on two series of samples:

Table 1
Chemical composition of cement and slag.

	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	Free CaO	SO_3	Loss of ignition	Na_2O	K_2O	Insoluble residue
OPC	18.4	61.3	5.6	0.9	3.8	0.20	3.3	2.2	0.42	0.78	0.50
GBFS	41.2	42.84	9.19	2.12	3.44	–	0.15	0.2	0.10	0.70	–