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Effect of magnesium sulfate on the durability of limestone mortars based on quaternary blended cements

Z. Makhloufi [a], S. Aggoun [b,*], B. Benabed [c], E.H. Kadri [b], M.Bederina [a]

[a] Laboratory SREML, University of Laghouat, P.O. Box 37G, Laghouat 03000, Algeria
[b] Laboratory L2MGC, University of Cergy Pontoise, F9500 Cergy-Pontoise, France
[c] Laboratory LRGC, University of Laghouat, P.O. Box 37G, Laghouat 03000, Algeria

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ABSTRACT

Currently, the use of blended cements incorporating various supplementary cementing materials, preserved in aggressive environments has become common. This paper describes the investigation results conducted on the evaluation of the resistance to magnesium sulfate solution ($MgSO_4$) of limestone mortars containing simultaneously; limestone filler, blast furnace slag and natural pozzolan. In this study, the deterioration of limestone mortars due to sulfate attack was evaluated by measuring changes in weight, length and compressive strength at the ages of 30, 60, 90, 120 and 180 days of immersion in exposure environments. The X-ray diffraction was also used in order to determine the different mineral phases. It is noteworthy that, the pH variation of the conservation solutions has been monitored during tests. The exposure solution was renewed monthly until the end of tests. The results showed that, the resistance to sulfate attack of mortars made with quaternary binders was better than that of mortars based on ordinary Portland cement.

1. Introduction

The degradation mechanisms, due to the diffusion processes and reactions between the aggressive environment and the cementitious matrix, may be responsible for the damages of concrete structures. The calcium diffusion and the hydroxide ions from external solutions can be coupled with penetration of other aggressive substances such as sulfate ions [1]. These sulfate ions, in an aqueous environment, can be detrimental for hydrated cement, and consequently, for integrity of cementitious material [2]. Indeed, concrete deterioration due to sulfate attacks has elicited much attention compared with other environments [3].

The concrete deterioration by sulfates coming from an outside source constitutes a problem of durability generally observed in concrete structures exposed to sea water, soil and groundwater. This type of attack is characterized by a swelling of material due to the formation of expansive products, which lead at a long term to decohesion of this material and consequently a degradation of its mechanical properties [4].

In spite of several researches, the attack of concretes by aggressive chemical agents is a quite complex process and studies in this context are still in progress. Various parameters, such as the cement composition, the nature of mineral additions, the exposure conditions, etc. were taken into account [5,6]. The use of pozzolans improves the resistance of concrete to sulfates by reacting them chemically with C–H. Moreover, adding pozzolans to cement can refine the pores size of the cementitious materials, reducing thus their permeability, and consequently slows the penetration of aggressive ions in these materials [2].

The use of binary and ternary binders improves the concretes durability. So, the incorporation of fly ash, slag and silica fume decreases the sorptivity of concretes and consequently their permeability [7,8]. The simultaneous use of fly ash and silica fume in concrete enhances the compressive strength at short and long-terms, the same as fly ash with blast furnaces slag and silica fume with blast furnaces slag. However, these additions contribute more to the improvement of the transport properties of concretes such as porosity, accelerated carbonation, capillary absorption and dry–wet cycles [9,10]. Other studies showed that, the quaternary

* Corresponding author. L2MGC, Cergy-Pontoise University, 5, mail Gay-Lussac Neuville sur Oise, Cergy-Pontoise Cedex F95031, France.
E-mail address: salima.aggoun@u-cergy.fr (S. Aggoun).

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blended cements could improve the compressive strength and produce durable mortars and concretes [11–13].

The mineral additions used in cement factories are limestone filler, slag and natural pozzolan. Several works were realized on mortars and concretes in order to study the influence of partial replacement of cement by these various mineral additions on the mechanical performance and durability of these concretes [14,15].

The main objective of this study is to evaluate the resistance to magnesium sulfate solutions of mortars with mineral additions, incorporated simultaneously into cement. The quantification parameters of durability of mortars taken into consideration are the weight and length changes and the variation of compressive strength. The pH monitoring of the cure solutions was carried out every end of the month before renewing the solutions and the mineralogical phases were determined by using X-ray diffraction.

2. Materials

The raw materials of blended cement compositions were obtained from different sources. The used materials are ordinary Portland cement (OPC), limestone filler, blast furnaces slag and natural pouzzolan. Fig. 1 shows the ground materials used in this investigation. The crushed sand and the mineralogical composition of limestone filler of sand determined by SEM presented in Fig. 2. The properties of used cement and mineral additions are given in Table 1. The chemical compositions of all materials used in this study were determined by X-ray's fluorescence (XRF) and the rate of mineralogical compositions was calculated using Bogue equation.

The cement composed of clinker was mixed with 5% of gypsum in laboratory during grinding. The natural pozzolan of volcanic origin presents an apparent density of 1200 kg/m^3 and a specific density of 2600 kg/m^3. The apparent density of limestone is 1500 kg/m^3 and its Specific density is 2700 kg/m^3. Before grinding, the slag appears in form of sand. For the raw granulated slag (unmilled), the shape of grains is spherical of a particle size 0/5 mm; its color is light yellow with a porous structure. Its apparent density is 1000 kg/m^3 and its specific density is 2800 kg/m^3. The Blaine fineness of cement is 350 m^2/g and that of all mineral additions is 380 m^2/g. The sand used for the formulation of mortars is manufactured sand from crushed limestone, its particle size distribution ranges from 0 to 2.5 mm. The mixing water is a tap water.

3. Experimental procedure

For each blended cement, five samples of mortars based on fine limestone aggregates were prepared. A summary of mortar mixtures used is shown in Table 2. For all mixtures, the composition of mortars was kept constant as the following: water/sand/binder = 0.5/3/1. In order to obtain comparable workability, a plasticizer was added to the mixture.

In this study, a comparable workability it was opted for different mixtures. In preliminary tests before making mortars with quaternary binders and before using superplasticizers, several mixtures with binary and ternary binders have been developed using various mineral additions.

From these preliminary tests we have concluded that for a given workability, the water demand for mixtures with cement + PN, is very high compared to mixtures with C + LF and C + BFS because workabilities of the latter two mixtures are close to each other.

In this study, a constant W/B ratio was adapted. So, for this constant ratio, workability of mixtures will be different or variable according to the nature of the used addition and that is why the superplasticizer was used to reduce the W/B ratio, which explains that the amount of the mixing water on both parts so that the workability of mixtures may be close to each other, that is almost equal in our study because it is the W/B ratio which remains constant = 0.5.

The mixing procedure was made according to EN 197-1 standard [16]. The fresh mixes were placed in molds of 40 mm × 40 mm × 160 mm and 25 mm × 25 mm × 285 mm, then compacted using a vibration table. The prepared mortar samples were covered with a plastic film and kept in temperature of 23 ± 1 °C and relative humidity (RH) of 50% in laboratory environment for 24 h. After demolding, all specimens were cured in lime saturated water (23 ± 1 °C) during 28 days. After this period of cure, part of the samples (half of the series of samples) was stored in lime water as control specimens. The specimens remaining were immersed in 5% magnesium sulfate solution (5%$MgSO_4$) at 23 ± 1 °C, up to 180 days. Samples of each composition were immersed separately in a solution tank. The different compositions of mortars with their cure conditions are summarized in Table 3. At the end of every term of curing in various environments and before conducting mechanical tests, samples were stored in a dry room at 23 ± 1 °C and 50% relative humidity. The compressive strengths were determined on dry specimens.

The curing solutions were renewed every 30 days. Measurements of weight changes of mortar specimens were carried out on specimens of 40 × 40 × 160 mm, and that of compressive strength were carried out according to European EN196-1 Standard [17] on half specimens of 40 mm × 40 mm × 160 mm, at an age of 28 days of immersion in lime water and for 30, 60, 90, 120 and 180 days in exposure solutions (lime water and sulfate solutions) after 28 days of exposure in lime water. The values of the relative compressive strength (RCS) were calculated by the following relationship:

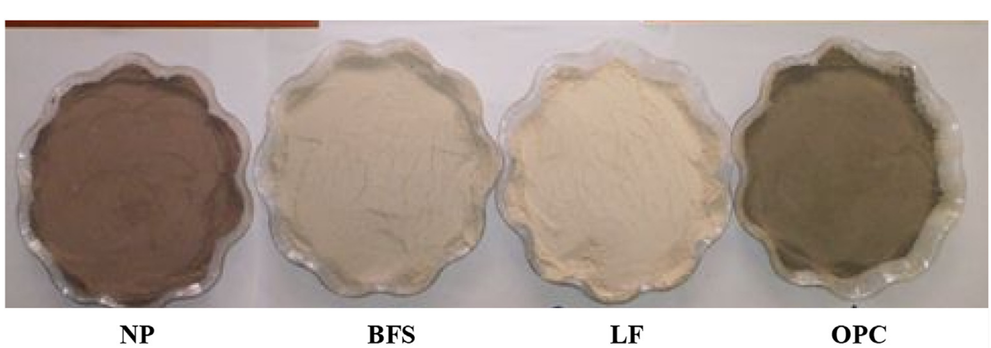

Fig. 1. Grinded materials.