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Performance of limestone cement mortars in a high sulfates environment

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ABSTRACT

With the aim of studying the influence of cement composition on resistance in high sulfates environment, standard mortars have been produced using ordinary Portland cement (CEM I – 32.5) and limestone cement with 35% limestone (CEM II/B-LL – 32.5). The pore size distribution of the cement pastes was measured. The mortars were immersed in a 5% Na_2SO_4 solution at 20 °C for 1.5 years and the caused deterioration was been visually observed at a regular basis. Furthermore, the mortars expansion was being estimated by measuring the change of length. At the end of the experiment the compressive strength of the mortars was measured. The deterioration products of the mortars have been identified by means of X-ray diffraction, optical microscopy and environmental scanning electron microscopy. The limestone cement based mortar presented cracking that started at the age of 6 months and continued throughout the experiment. It also displayed high expansion after 250 days of immersion in a 5% Na_2SO_4 caused, as proved using the analytical techniques, by the formation of gypsum and ettringite. Concluding, the cement with 35% limestone did not perform as well as ordinary Portland cement under the most aggressive laboratory conditions. Hence, it is obvious that the addition of limestone in the cement leads to a totally different behaviour than Portland cement with respect to the resistance in high sulfates environment.

1. Introduction

Cement production and consumption are considered to be important indicators of economic growth. Considering the amount of produced cement, concrete is clearly the most used construction material. On the other hand cement production is followed by production of large amounts of CO_2, which contribute to the greenhouse effect and the change of the climate of earth. In order to minimize the negative effects of cement production the industry has turned to blended cements in which clinker is substituted for other materials such as granulated blastfurnace slag (ggbs), fly ashes from power plants, natural and industrial pozzolanas or limestone.

Blended cements have to perform as well as ordinary Portland cement and even have improved properties concerning durability of concrete. One of the aspects of durability of concrete is resistance against sulfate attack.

Sulfate attack is a generic name for a set of complex and overlapping chemical and physical processes caused by reactions of numerous cement components with sulfates originating from external or internal sources [1].

External sulfate attack is caused sulfates from ground water, soils, solid industrial waste and fertilizers, from atmospheric SO_2, or from liquid industrial wastes. Ready availability of these sulfates to cause damage to concrete depends on their concentration and solubility, transport of water, and environmental conditions [1].

External sulfate attack on concrete is itself a well-documented phenomenon [2–4], but the influence of the new materials that are being used for the production of blended cement is not yet completely comprehended. Furthermore, results on sulfate performance of cement mortars containing limestone filler show different trends. Some authors [5,6], concluded that limestone filler could increase the sulfate resistance of cement, while other researchers [7,8], found a decrease of sulfate resistance of this cement depending on the replacement level and clinker composition. In these studies the experimental conditions varied widely. The solutions used, Na_2SO_4 and $MgSO_4$ mainly, the concentrations of solutions, the temperature of exposure and the size of the specimens where all different leading to completely different results. In conclusion, the mechanism in which limestone affects the sulfate resistance of cement is far from being well understood.

This study aims at determining the role of limestone on the sulfate attack and therefore mortars were manufactured with cements having 0% and 35% w/w – which is the maximum amount of limestone that can be added to the cement according to the European Standard EN 197-1 – of limestone content which were

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exposed to a 5% Na_2SO_4 solution at 20 °C for 1.5 years. A Na_2SO_4 solution was chosen for this research because as reported in the international literature laboratory test using sodium sulfate can very well represent field conditions (ground water sulfates or soils with gypsum). After this period of time the performance of the two mortars in the high sulfate environment was examined using different techniques.

2. Materials and methods

Ordinary Portland cement (CEM I – 32.5) (0% LL) having Blaine 2550 cm^2/g and limestone cement with 35% w/w limestone (CEM II/B-LL – 32.5) (35% LL) having Blaine 3990 cm^2/g, were produced in a laboratory ball mill. Chemical analysis of the produced blended cements was conducted by X-ray analysis (XRF).

Using these cements, mortars were prepared according to the European Standard EN 196-1. A standard siliceous sand with continuous grading up to 2 mm according to the European Standard EN 196-1 was used. The sand/cement ratio was equal to 3 and the water/cement ratio 0.5. The $4 \times 4 \times 16$ cm specimens were cast and kept 2 days inside the mould and 12 days in a saturated $Ca(OH)_2$ solution. After that, three mortar prisms of each cement were exposed to a 5% Na_2SO_4 solution and another three remained in the saturated $Ca(OH)_2$ solution at 20 °C for 1.5 years. During this period of time the specimens were visually inspected at regular intervals and their expansion was measured with a micrometer. At the end of the experiment compressive strength of all the mortars was determined using the European Standard EN 196-1. Furthermore, the deterioration products of the mortars immersed in a 5% Na_2SO_4 solution were identified using X-rays diffraction analysis (XRD) in the surface layer and the core and also optical microscopy in thin sections and environmental scanning electron microscopy (ESEM) were carried out.

Furthermore, cement pastes with water/cement ratio of 0.5, were produced and maintained inside a wet chamber at 20 °C and 95% RH for 6 months so that they hydrate and gain full strength after that the samples were oven dried at 40 °C and crushed so that their pore size distribution could be measured using a Mercury Intrusion Porosimetry (MIP).

3. Results and discussion

3.1. Chemical analysis

The chemical analysis of the cements is presented in Table 1. Using the Bogue equation the percentage of the components of the used in the production of the two cements clinker was calculated and the results are presented in Table 2. Since the clinker used was the same in both cements and the limestone that is introduced in the CEM II/B cement contains calcite at a percentage above 99%, it is obvious that the percentage of C_3A that takes place in the ettringite formation is lower in the case of the limestone cement.

3.2. Mercury intrusion porosimetry

In this study, the cumulative intruded volume curve (Fig. 1) and the incremental intrusion volume vs radius curve (Fig. 2) are presented in order to estimate and evaluate the pore structure of the hardened and dried cement pastes. From these measures it is obvious that the two hardened cement pastes present significantly different pore size distributions.

Table 2
Bogue Composition of the clicker used to make the cement

	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Clinker	68.40	8.87	6.63	10.16

The two most important parameters that can be derived by the cumulative intruded volume curve is the total porosity of the cement and its pores critical diameter. These parameters values are presented in Table 3.

It is obvious that the total porosity of the ordinary Portland cement is lower that that of the limestone cement. And this is an indication that the limestone cement might have higher permeability.

The critical diameter (d_{cr}) that corresponds to the steepest slope of the cumulative porosity curve is marked in Fig. 1. The critical pore size controls the transmissivity of the material [9]. The critical pore diameter is the most frequently occurring diameter in the interconnected pores that allows maximum percolation [10]. Limestone cement paste has a greater critical diameter than Portland cement paste.

Therefore, since limestone has higher total porosity and larger interconnected pores it also has a higher permeability.

Fig. 2 shows that there is a lack of distribution of pores sized from 50 to 10,000 nm in the limestone cement paste curve. These pores are called large capillaries [11] and have a great effect transport processes. On the other hand limestone cement paste has a great amount of pores in sizes from 10 to 50 nm which are called medium capillaries [11] that do not exist in the Portland cement paste. It is also noticeable that limestone cement has a narrow distribution of pores of only few nanometers in the area of medium capillaries and that indicates geometrical homogeneity. These results support the idea that limestone cement paste has more uniform pores in the area of medium capillaries that contribute to the transmissivity of the materials.

3.3. Optical inspection

Optical inspection of the specimens at regular intervals showed that the mortar with 35% limestone presented cracking initiated at the age of 6 months starting from the edges of the mortar and gradually evolved towards the central portion of the sample. At later stages of degradation cracking was accompanied by delamination and exfoliation. On the other hand the mortar without limestone did not present any macrocracking. Photographs of the two mortars at the age of 1.5 years are presented in Fig. 3a and b. Nevertheless, sole visual inspection can be misleading, more rigorous methods were used to evaluate the performance of this mortars subjected to sulfate attack.

3.4. Expansion

The plot of expansion of the mortars, immersed in a 5% Na_2SO_4 solution as well as in a saturated $Ca(OH)_2$ solution, versus time is presented in Fig. 4. Until the age of 250 days the mortar without

Table 1
Chemical analysis of the cements

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	Na_2O (%)	SO_3 (%)	LOI	Blaine (cm^2/g)
CEM I	19.53	4.29	3.09	63.55	3.04	0.62	0.14	3.20	2.6	2550
CEM II/B	14.34	2.91	2.58	67.00	2.02	0.41	0.11	1.50	12.7	3990