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Behavior of ternary blended cements containing limestone filler and fly ash in magnesium sulfate solution at low temperature

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HIGHLIGHTS

- Studied the behavior of some ternary blended cements into 5% $MgSO_4$ solution, at 5 °C.
- The presence of both limestone and fly ash does not decrease the vulnerability of cements.
- After 90 days of exposure, compressive strengths decrease for all samples.
- The deterioration products were gypsum, ettringite and thaumasite–ettringite solid solution.

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ABSTRACT

The behavior of ternary blended cements with limestone filler and fly ash additions into 5% magnesium sulfate solution was evaluated. The presence of both limestone and fly ash in cement does not seem to decrease the vulnerability of cements to magnesium sulfate attack at 5 °C in comparison with limestone filler or fly ash cements. After 90 days, the compressive strengths decrease for all specimens (from 33.5 MPa to 16.4 MPa for Portland cement mortar and from 35 MPa to 13.8 MPa for 10% fly ash cement mortar) as a consequence of higher amount of deterioration products which exerts pressure in the capillare pores.

1. Introduction

Cement production is responsible for about 5% of the global man made CO_2 emission. For each tone of cement being produced, an average of 0.87 tons of CO_2 is being emitted [1,2]. A reduction of the CO_2 emission during cement production can be possible by using alternative fuels, by optimizing the heat transfer and using supplementary cementitious materials (fly ash, granulated blast furnance, silica fume etc.) and fillers, without compromising the quality of the cement and concrete properties. The use of limestone fillers has physical, chemical and environmental effects on cements. Limestone filler can accelerate early age hydration of Portland cement by interacting with calcium aluminate hydrate provided by Portland cement hydration. This leads to calcium carboaluminate hydrate formation instead of calcium monosulfate aluminate hydrate [3–6]. In these conditions, higher quantity of ettringite can slightly improve mechanical strengths. Fly ash can provide additional calcium aluminate hydrate which increases the effect of limestone filler.

During this research, investigations of ternary blended cements containing limestone filler and fly ash were performed in order to obtain supplementary information regarding the influence of cement replacement ratio by fly ash and/or limestone powder [1,7–11]. According to [1], after 120 days of hardening, the compressive strengths of cements with 5–10% limestone filler and 25–30% fly ash were close to those of Portland cement.

The carboaluminate formation, the ettringite stabilization and the supplementary CSH (formed by pozzolanic reaction) increase the solid volume of hydrates and decrease the permeability of the ternary blended cements [9,12,13]. As a result of this a higher resistance of blended cements against sulfate attack is expected.

The behavior of blended cements in sulfate solution is an actual research topic.

The sulfate attack of limestone Portland cement mortars/concretes involves the thaumasite formation, particularly at low temperatures (<5 °C). Thaumasite formation requires a calcium silicate source, carbonate and sulfate anions, excess humidity and

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low temperature [14–21]. Carbonate ions source can be limestone powder or calcium carbonate formation as a result of atmospheric carbonation [22]. The thaumasite formation mechanism is still controversial.

According to Bensted [23,24], the following routes could form thaumasite:

- Direct route (reaction (1)) between CSH phases with SO_4^{2-} and CO_3^{2-} ions or atmospheric CO_2, Ca^{2+} ions and excess of water;
- Woodfordite route (reaction (2)), take place below 15 °C, from ettringite by substitution in its structure of Al^{3+} ions with Si^{4+} ions in the presence of CO_3^{2-} ions [23–26].

$$C-S-H + CaCO_3 + CaSO_4 + xH_2O \rightarrow CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O \quad (1)$$

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CaO \cdot 2SiO_2 \cdot 3H_2O + 2CaCO_3 + 4H_2O \rightarrow CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O + CaSO_4 \cdot 2H_2O + 2Al(OH)_3 + 4Ca(OH)_2 \quad (2)$$

According to Crammond [27], SO_4^{2-} ions react with Ca^{2+} ions, Al^{3+} ions, CO_3^{2-} or HCO_3^- ions and Si^{4+} ions to form ettringite, gypsum or thaumasite depending on ions concentration, stability of precipitates and relative solubility of competing species.

Kohler et al. [28] proposes a heterogeneous nucleation mechanism of thaumasite on the surface of ettringite including the disintegration of CSH takes place in cement paste.

The aim of this study is to investigate the behavior of ternary composite cements (Portland cement-limestone filler-fly ash system) as pastes and mortars immersed into magnesium sulfate solution at 5 °C. The time evolution of compressive strengths of samples cured in water/immersed in 5% sulfate solution were determined. In addition to analyzing the visual appearance of samples, SEM and EDX analysis were used in order to asses the deterioration of the samples and to identify the deterioration products. Thermal analysis (DTA) was also applied.

2. Materials and methods

The materials used in this research work are: Portland cement – CEM I 52.5 (CEM I) according to SR EN 197-1 [29], limestone filler (L), and fly ash (FA) (see Table 1).

Mineralogical composition of Portland cement was: 72.63% C_3S, 1.02% C_2S, 9.76% C_3A and 10.34% C_4AF. Its specific surface area (Blaine) was 4190 cm^2/g.

The limestone powder contained 85% $CaCO_3$ and had a Blaine specific surface area of 5200 cm^2/g.

The type *F* fly ash [30] had a Blaine specific surface area of 2108 cm^2/g and the pozzolanic activity index was 87%. Pozzolanic activity index was determined according to Romanian standard SR 13298 [31]. It was calculated as a ratio between compressive strength of blended cement (75% Portland cement + 25%FA) mortar and Portland cement mortar. The mortars had been left in the mold for 24 h, then cured for 4 days in water at 20 °C, for 46 h in water at 50 °C, for 2 h in water at 20 °C and then tested.

Table 1
Chemical composition of CEM I and FA.

Chemical composition (%w)	CEM I	FA[a]
SiO_2	18.46	53.10–53.40
Al_2O_3	5.85	26.50–27.87
Fe_2O_3	3.40	8.34–8.84
CaO	63.16	2.82–3.50
MgO	0.41	1.51–1.60
SO_3	1.65	0.25–0.38
PC	6.48	1.46–2.29

[a] $\%Na_2O = 0.72–0.75$; $\%K_2O = 2.22–2.78$.

Blended cements were prepared by homogenization of Portland cement with fly ash and limestone into a rolling ball mill. For comparison, only fly ash and limestone were considered as addition in blended cements (10–30% FA and 10–20% L, respectively –Table 2).

The mortars prepared with such binders had a water/cement ratio of 0.5 and binder/siliceous sand ratio of 1:3. The prepared samples for compressive strengths determinations having sizes of 20 mm × 20 mm × 20 mm had been preserved for one day in the mold and up to 28 days in water at 20 °C. At this age, some samples were immersed in 5% $MgSO_4$ solution at 5 °C and the others had been continuously cured in water at 20 °C until testing time (from 2 to 360 days).

The compressive strength was determined using a WPM machine. The compressive strengths were considered as relative strengths, (CSrel (%)), according to relation:

$$CS_{rel} = \frac{CS_1}{CS_2} \cdot 100$$

where: CS_1 is compressive strength of blended cements immersed in sulfate solution or cured in water for t days;

CS_2 – compressive strength of blended cements or CEM I cured in water for the same period of time.

All values presented in the paper are the average value of three determinations.

Paste prisms with sizes 20 mm × 20 mm × 120 mm of some selected binders (water/binder ratio = 0.5) were prepared in order to study the processes and products of their interaction with magnesium sulfate solution at low temperature. After 28 days of curing in water, the specimens were immersed in 5% $MgSO_4$ solution at 5 °C. The magnesium sulfate solution was replaced every three months.

The visul examinations on selected mortars imersed into sulfate solution at regular intervals were performed in order to record surface deteriorations.

DTA and SEM analysis using a Shimadzu DTG-TA-50H apparatus and a HITACHI S2600N Scanning Electron Microscope equipped with Energy Dispersive X-ray spectrometer, were used in order to obtain information regarding the interaction processes between specimens and sulfate solution and the morphology of reaction products. The electron microscopy analyses were performed on samples taken from either hard-core or surface zone (corroded zone). A thin conductive coating (gold) was added on the samples prior to imaging.

3. Results and discussion

3.1. Visual examination

The visual examination of samples cured in sulfate solution was carried out after 60, 90 and 196 days of exposure into sulfate solution.

After 60 days, the samples presented some deteriorations of corners and edges; samples with blended cements containing 10% and 20% limestone (C-L10 and C-L20) were more affected than reference sample (C) and samples with blended cements containing fly ash-single or associated with limestone filler.

After 90 days of exposure in sulfate solution, samples C-L10 and C-L20 were characterized by some white efflorescence (substance) and surface spalls. These are present on the surface of reference sample (C) too.

Increasing the time exposure to 196 days results in serious damages of specimens C, C-L10 and C-L20 and small pieces falling off the edges and surfaces of the samples (Fig. 1). The presence of fly ash only does not seems to retard the sulfate attack considering the appearance of C-FA10 sample in comparison with C sample. The presence of both limestone and fly ash seem to decrease the vulner-

Table 2
Codes and compositions of studied binders.

Code	CEM I (%w)	L (%w)	FA (%w)
C	100	–	–
C-L10	90	10	–
C-L20	80	20	–
C-FA10	90	–	10
C-FA20	80	–	20
C-FA30	70	–	30
C-FA10-L10	90	10	10
C-FA20-L10	70	10	20
C-FA10-L20	70	20	10