



Durability evaluation of cement exposed to combined action of chloride and sulphate ions at elevated temperature: The role of limestone filler



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HIGHLIGHTS

- Limestone filler role on cement durability exposed to SO_4/Cl^- ions, at elevated temperature.
- Limestone presence led to less expansion and higher compressive strengths.
- Non-expansive Friedel's salt was formed in chloride baths reducing DEF.
- Limestone filler reduced DEF and led to refinement of paste pore structure.

ARTICLE INFO

Article history:

Received 12 April 2016

Received in revised form 18 July 2016

Accepted 27 July 2016

Keywords:

Durability

Sulphate attack

Chloride

Blended cements

Limestone filler

ABSTRACT

In the present investigation, the influence of sulphate and chloride ions combined action on cement durability and the role of limestone filler were investigated. Samples of a reference white CEM I42.5 (C_{Ref}) and the corresponding of a white CEM II42.5 (C_{L15}) with a 15 wt% limestone replacement were exposed for a period of 90 days into three different curing baths (saturated $\text{Ca}(\text{OH})_2$ solution, 5 wt% Na_2SO_4 solution and a composite solution of 5 wt% Na_2SO_4 and 5 wt% NaCl), at 50 °C. Their compressive strengths were determined after 28, 56 and 90 days of curing, whereas their expansion was estimated on a weekly basis by the length change measurement. The deterioration products characterization was carried out by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectrometry (FT-IR), Thermal Analysis (TG-DSC) and Mercury Intrusion Porosimetry (MIP). According to the results the addition of limestone filler led to the durability increment, as the corresponding mixtures presented lower expansion and higher compressive strengths, while in all cases the Cl ions presence mitigated the external sulphate attack, a fact that was mainly attributed to the Friedel's salt formation.

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1. Introduction

The deterioration caused by the sulphate ion ingress from the environment, called “external sulphate attack”, plays a major role in the durability of concrete structures. The key issue of sulphate attack's effect on cement paste continues to cause significant concern globally, because the delayed ettringite formation (DEF) due to sulphate interaction could lead to the internal cracking of concrete and to the corresponding loss of strength [1–3].

There is extensive scientific literature on the matter of DEF, suffice herein to point out that ettringite appears in two forms,

which are different not only in size but also in type. Lath-like crystals', ranging from 10 μm to 100 μm , is the main characteristic of Type I, whose formation takes place at relative low concentrations of hydroxyl ion (relatively lower pH values) and its presence during hydration implies higher compressive strengths and lower expansion values. For that reason the ettringite of the above type has been classified as “non-expansive”. On the other hand, rod-like crystals of 1–2 μm in length and 0.1–0.2 μm in thickness (ettringite of Type II), are formed in higher pH values of the pore solution, which could lead in large quantities, through water adsorption, in expansion phenomena. It should be also noticed that the delayed ettringite formation can be accelerated in case of higher temperature treatment, whereas the formation of normal ettringite, which is the result of calcium aluminate hydration in

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the presence of gypsum during setting regulation, is destroyed with the temperature increment [4–6].

The mechanism, through which ettringite is formed, has been well-studied and it has been concluded that the following three conditions must simultaneously apply: a. excess of sulphate ions; b. elevated temperature and c. abundant supply of water [7–11]. In the cement production limestone filler has been extensively used, as a substitute for clinker, as a less energy-demanding material; the percentage of limestone addition, according to European Standards (e.g. EN 197), ranges up to 35 wt%. According to various researchers, a certain amount of 5 wt% limestone addition reacts in order to form calcium-alumina carbonate phases as well as mono-carbonate, such as the more stable AFm phase (opposed to mono-sulphate) [12–14]. The latter results in a greater volume of hydrates and as a result, more aluminates are initially bound in the form of ettringite, thus increasing the sulphate resistance. Furthermore, it has been shown that the higher volume of hydrates products physically lowers porosity [15].

Apart from research being conducted on sulphate-only environments, there has been also an interest regarding the exposure on both sulphate and chloride ions, representing the environment met to marinas or to saline soils. It has been shown that there is an increase in sulphate attack resistance of certain cement types when the solution also contains chloride ions, a fact that has been attributed to the aluminates hydrated phases transformation to the corresponding chloroaluminates phases, having as a consequence the reduction of ettringite formation [16–18]. Furthermore, it has been established that the ettringite solubility in the presence of chlorides ions is three times higher than the corresponding one in an aqueous solution [19,20].

On the other hand, the rate of chloride ions diffusion has been found to be higher than the corresponding of the sulphate ones, thus allowing the former to penetrate faster to the interior of cement [21,22]. More specifically it has been reported that the diffusion rate of chlorides in concrete is generally 10–100 times faster than that of sulphate ions, while Rio and Turriziani have shown that the Cl^- diffusion rate in pure and blended cements is twice greater than that of the sulphate ions [23]. This higher diffusion rate of the chloride ions can lead to their faster reaction with hydrated calcium aluminates phases and to the production of the non-expansive Friedel's salt ($\text{Ca}_3\text{Al}_2\text{O}_6\text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) [24], whose stability depends on pH, since it has been shown that as the pore solution's alkalinity decreases, the solubility of the salt increases. On the other hand, the hydrated cement carbonation could lead to the Friedel's salt dissolution [25–28].

The present work is part of a research program [29–31], which aims at the examination of limestone filler addition on the durability evaluation of various cement mixtures exposed to the combined action of sulphate and chloride ions at elevated temperature, focusing on the deterioration products determination and their effects on the produced mortars.

2. Materials & methods

CEM I reference cement, prepared by white cement clinker and gypsum co-grinding, presented a Blaine value of $3400 \text{ cm}^2/\text{g}$, whereas the corresponding value for CEM II/A-L with 15 wt% limestone filler was determined at $4260 \text{ cm}^2/\text{g}$ (Table 1). White cement clinker was chosen to be used for the above mixtures production due to its high C_3A content (about 13 wt%), the phase with which sulphate and chloride ions react in order to produce ettringite and Friedel's salt.

The produced cement mortars, prepared by mechanical mixing and compaction in a mould using a jolting apparatus according to EN196-1 standard, were exposed for a period of 90 days at 50°C to

Table 1
Chemical analysis and physical characteristics of cement used.

Oxides	Chemical analysis (wt%)	
	C_{Ref}	C_{L15}
SiO_2	21.87	19.06
Al_2O_3	5.06	4.65
Fe_2O_3	0.2	0.23
CaO	65.28	68.03
MgO	0.91	0.93
K_2O	0.32	0.28
Na_2O	0.12	0.1
SO_3	3.03	2.98
Cl	0.018	0.017
LOI	1.02	3.98
<i>Physical Characteristics</i>		
Specific Surface (cm^2/g)	3400	4260
Specific gravity (g/cm^3)	3.14	3.13

three different environment conditions: a) saturated $\text{Ca}(\text{OH})_2$ solution; b) 5 wt% Na_2SO_4 solution and c) combined solution of 5 wt% Na_2SO_4 & 5 wt% NaCl. The mortars specimens in the mould were stored in a moist atmosphere (95% RH, $20 \pm 1^\circ\text{C}$) for 24 h and then the demoulded mortars were stored in tanks with the different solutions, until strength testing. Curing at elevated temperature was chosen in order to accelerate the hydration phenomena and the reactions between hydrated phases with the corresponding corrosive anions [2,3]. Inspection of the specimens was carried out regularly, while the determination of the expansion took place by measuring their length. After of 90 days of curing the mortars compressive strengths were determined according to EN196-1 standard.

Additionally, products from the surface of all mortars were collected and were determined by X-ray diffraction was used, using a D8-Focus diffractometer (Bruker) at 40 kV and 40 mA with nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Semi-quantitative phases analysis was carried out by TOPAS software (Bruker-AXS), based on Rietveld algorithm. The characterization of the above products was also carried out by a Spectrum GX (Perkin Elmer) Fourier transform spectrophotometer, in the range of $4000\text{--}400 \text{ cm}^{-1}$, using the KBr pellet technique. The pellets were prepared by pressing a mixture of the sample and dried KBr (ratio, about 1:200) at $8 \text{ tons}/\text{cm}^2$. A Setaram-Labsys thermal analyzer was used for TG/DSC measurements, at a heating rate of $5^\circ\text{C}/\text{min}$ under static condition in the range of $25\text{--}1000^\circ\text{C}$. Scanning electron microscopy was used for the hydration products morphology examination using a Philips XL-30 Environmental Scanning Electron Microscope, equipped with an EDAX DX-4 Analyzer for spot chemical analyses. Finally, A Micromeritics AutoPore III 9410/9420 mercury porosimeter was used for porosimetry measurements, in the range of $1\text{--}4000 \text{ bar}$ mercury intrusion in order to determine pore volume and pore size distribution.

3. Results & discussion

3.1. Physical characteristics

After 90 days of curing at 50°C , all mortar samples' surfaces were examined using a Heine Delta 20 LED Illuminated Loupe (10x) in order to assess their external condition. In all specimens the first deterioration signs were observed at their edges and corners. It was found that C_{Ref} mortars displayed more cracks and expansion in comparison to those with limestone filler. Also, it was evident that mortar samples exposed to the Na_2SO_4 solution displayed significantly greater deterioration in comparison to the mortar samples exposed to the combined solution of sulphate and chloride ions (Fig. 1).

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