

How sulfates and increased temperature affect delayed ettringite formation (DEF) in white cement mortars

E. Adamopoulou^a, P. Pipilikaki^b, M.S. Katsiotis^a, M. Chaniotakis^b, M. Katsiotti^{a,*}

^a School of Chemical Engineering, Laboratory of Inorganic and Analytical chemistry, National Technical University of Athens, 9 Heron Polytechniou St. Zografou, Athens 15780, Greece
^b TITAN Cement Co. S.A., Group R&D and Quality Department, 18-19200 Eleusina, Greece

ARTICLE INFO

Article history:

Received 20 August 2010

Received in revised form 2 January 2011

Accepted 1 March 2011

Available online 25 March 2011

Keywords:

DEF
 Limestone
 Sulfates
 White cement
 Mortar

ABSTRACT

In this study, white cement CEM I and white limestone cement CEM II-LL A and B with 15%, 25% and 35% limestone substitution were studied. The way delayed ettringite is forming due to exposure to increased temperature (50 °C) and external sulfate attack was examined in mortar samples which were immersed for 90 days in three different solutions: (a) saturated solution Ca(OH)₂ at 50 °C, (b) saturated solution of Ca(OH)₂ at 20 °C and (c) 5% w/w Na₂SO₄ solution at 50 °C. During this period mortar samples were visually observed regularly while their expansion was estimated on a weekly basis by measuring the change of length with a micrometer. At the end of the 90-days period the compressive strength of the mortars was determined and the deterioration products were identified through means of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and thermogravimetric analysis (DTG). The results of this study show that DEF occurred in two forms. Samples cured at increased temperature contained DEF type I, which caused mediocre expansion and damage. Samples cured at increased temperature in the presence of sulfates produced DEF type II, which caused significant damage on the surface and exhibited high expansion.

© 2011 Elsevier Ltd. All rights reserved.

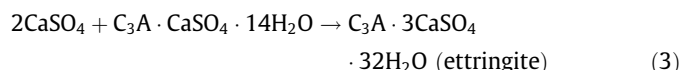
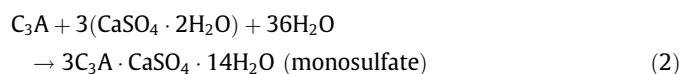
1. Introduction

Delayed ettringite formation (DEF) is the ettringite-related deterioration of concrete regardless of whether or not the concrete member has been subjected to steam curing [1]. It is a phenomenon in which ettringite is generated by accumulating in the concrete after hardening, eventually leading to its expansion and thus, ultimately to the destruction of the concrete or mortar. DEF is promoted by high-temperature steam curing, while normal ettringite is formed as a consequence of the setting regulation during the plastic stage of fresh concrete and is destroyed by steam curing [2–5]. Furthermore, ettringite appears in two crystallizations, different in habit and size. The first one (type I) of long lath-like crystals which range from 10 to 100 μm and several μm thick, formed at low hydroxyl ion concentrations (i.e. with low pH values in the pore solution). In the case of hydrated cements containing significant amounts of type I ettringite crystals, these lead to high strengths and non-expansion, thus the classification of type I ettringite as “not expansive”. The second type (type II) of ettringite is rod-like crystals which range only from 1 to 2 μm long and 0.1 to 0.2 μm thick, which are formed at high hydroxyl ion concentrations. These are present during the hydration of Portland cements and are classified as type II ettringite crystals,

which at large quantities can cause expansion effects through water adsorption [6].

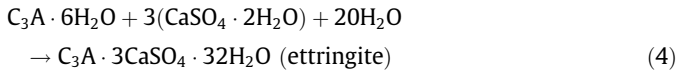
The way ettringite formation and damage mechanism is initiated in the cement matrix has been the point of controversy for the past years. After carrying extensive investigations, different hypotheses were developed by many authors on the matter. It is said that the formation mechanism and ettringite modification play an important role. It has been found that heat treatment at higher temperatures, frost or freeze–thaw, carbonation, moisture effects and with it natural occurring changes in moisture and temperature can cause ettringite formation [6].

Finally, most researchers agree that DEF is created when the following three conditions coincide and apply: excessive sulfates, high-temperature steam curing and sufficient water supply [7–12]. Delayed ettringite is formed into the pores or the cracks of the cement paste due to high sulfate presence. The overall reactions characterizing the delayed ettringite formation process are described by following reactions.



* Corresponding author. Tel.: +30 2107723206; fax: +30 2106397771.

E-mail address: katsiotti@central.ntua.gr (M. Katsiotti).



Pore distribution and shape, the transport of sulfates and external conditions such as temperature and pressure play a major role on delayed ettringite formation. DEF may exist in different sizes (ranging from amorphous colloidal particles to well defined crystals) depending on the conditions of formation. Usually DEF is found in the shape of crystals roughly 1–2 μm long and 0.1–0.2 μm wide. It must be noted that DEF can occur as either types I or II ettringite (as described previously). According to existing literature, DEF created in high pH environment (12.5–12.9) causes expansion and does not contribute in strength development [13–16].

The External Sulfate Attack (ESA) induces damage which is mainly determined by the chemical interaction of a sulfate-rich soil or water, with the cement paste. ESA 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. Soils containing sodium, potassium, magnesium and calcium sulfate are the main sources of sulfate ions in groundwater. Additionally, solid industrial waste, fertilizers, SO_2 found in the atmosphere or in liquid industrial wastes are also regarded high sulfate sources which promote ESA. For ESA to occur the following three conditions must be fulfilled at the same time: high permeability of concrete, sulfate-rich environment and the presence of water [17–20]. As a result of sulfates presence, different hydration products occur. These products appear very rapidly, usually in few hours, and they are involved in the expansion of concrete.

Aim of this work is to study the way cement pastes with high limestone content act when exposed to high sulfate environments and increased temperature treatment. The study is mainly focused on determining deterioration products and effects while also verifying the presence of DEF due to the aforementioned conditions. A similar study has been performed by the authors and has been recently published [21]. The previous work is focused more on the time evolution of sulfate induced DEF expansion in white cement mortars. Based on the conclusions drawn from that work, the authors wish to give additional information regarding the expansion of mortar due to sulfate attack, by including an additional mixture (35% limestone substitution) and an additional set of conditions (curing in 20 °C). Accordingly, the effect of temperature on sulfate induced expansion is the main focus in this paper. It must be noted that these papers are complementary and readers are advised to read both works in order to acquire a complete understanding of the sulfate induced expansion mechanism. All in all, the authors believe that the two papers offer a novel insight on sulfate induced DEF expansion, thus assisting in the improvement process of the durability of white cement mortars with high limestone content.

2. Sample preparation and methods

Initially mortars were prepared by mixing white cement CEM I-52,5 with limestone at three different ratios (15%, 25% and 35%), thus creating white cement CEM II. Paste and mortar samples were produced according to EN 196-1. A reference paste and mortar sample was also prepared. Initial and final setting times were determined for paste samples along with normal plasticity water, according to EN 196-1.

Consequently, the cement mixtures were mixed with standardised siliceous sand and water for the creation of mortar specimens. The amount of sand used per specimen was 1350 g of standard siliceous sand whose characteristics are described in EN 196-3. 450 g of cement were added and all samples were formulated with a w/c ratio equal to 0.6. The standard w/c ratio of 0.5 was not applied as the addition of limestone caused the samples to be less workable, while the

0.6 ratio proved to be the optimum regarding the rheology of the fresh mortar samples. The mortars were molded in prismatic moulds with dimensions 4 × 4 × 16 cm. Nine specimens were created from each mixture in order to achieve statistical repeatability and were preserved according to EN 196-1 instructions: for the first 2 days all the samples were preserved in the moulds inside a wet chamber (humidity >95%), then they were unmolded and preserved in a saturated $\text{Ca}(\text{OH})_2$ solution for 12 days (total of 14 days).

After the initial preservation period the mortars were grouped into three separate groups. Three specimens were taken from each mixture for each group which corresponded to a different set of condition, as explained below. First group was cured in a saturated $\text{Ca}(\text{OH})_2$ solution at 20 ± 2 °C for 90 days. The second group was left to hydrate in a saturated $\text{Ca}(\text{OH})_2$ solution at 50 ± 2 °C for 90 days in order to evaluate the effect of increased temperature. Finally, the third group was left to hydrate in a 5% w/w Na_2SO_4 solution at 50 ± 2 °C for 90 days to emulate an environment with high external sulphate presence and increased temperature – both perfect conditions for formation of type II ettringite (which causes expansion).

During this 90-days period the specimens were inspected and their expansion was determined by measuring their length with a micrometer on a weekly basis. It must be noted that soon after the initial exposure to increased temperature and high sulfate presence, deterioration was obvious on the surface of mortars. At the end of the 90-days period, compressive strength of all mortars was measured according to EN 196-1. Additionally, samples were collected from the surface of all mortars and were studied using X-ray diffraction analysis (XRD), TG thermogravimetric analysis and Scanning Electron Microscopy (SEM).

X-ray powder diffraction (XRD) was carried out in a Siemens D-5000 Diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$, 40 kV, 30 mA). The diffraction spectra were collected in the range of 2–60° 2 θ scale, with a step size of 0.03°/s. Powder samples (~1 g) were drilled from a layer of 2 mm thick (where damage from expansion was evident) from the surface and were consequently analyzed. Additional samples were also collected in order to determine the amount of ettringite on the surface of each sample, using the Rietveld quantitative method. In this case the spectra were collected in the range 2–26° 2 θ scale, with a step size of 0.005°/sec. It must be noted that ettringite appears in XRD at 2 θ angles 9.2° (main peak), 15.7° and 22.9°. Quantitative analysis was realized by measuring the integral area at the aforementioned 2 θ angles.

Thermogravimetric analysis (TG/DTG) was carried out in a Mettler Toledo thermal analyzer, using a heating rate of 10 °C/min at the range of 25–1000 °C, in air atmosphere. Specimens (~10 μg) were collected from a layer of 2 mm thick (where damage from expansion was evident) from the surface and were consequently analyzed. The DTG analysis was conducted in order to verify the presence of calcite and determine the remaining portlandite in the surface of each samples.

Finally, the microstructure of the surface as well as the formation and type of ettringite crystals of the treated mortars was studied under a FEI/Quanta 200 scanning electron microscope. Specimens (~1 ml) were collected from a layer of 2 mm thick (where damage from expansion was evident) from the surface and were consequently cast in resin and polished in order to be examined under the microscope.

3. Results and discussion

3.1. Chemical analysis

Mortar specimens were chemically analyzed as shown in Table 1. The amount of C_3A was determined according to Bogue's equations for each cement mixture and is shown in Table 1.

Download English Version:

<https://daneshyari.com/en/article/259840>

Download Persian Version:

<https://daneshyari.com/article/259840>

[Daneshyari.com](https://daneshyari.com)