Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement & Concrete Composites 27 (2005) 77–84

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Thaumasite formation in limestone filler cements exposed to sodium sulphate solution at 20 °C

E.F. Irassar *, V.L. Bonavetti, M.A. Trezza, M.A. González

Civil Engineering Department, National University of Buenos Aires Centre, State, B7400JWI Olavarría, Argentina

Received 15 October 2002; accepted 24 October 2003

Abstract

This paper presents a microstructural analysis of mortars made with OPC ($C_3A = 6\%$) and two SRPCs ($C_3A < 2\%$ and $C_3S = 40\%$ and 74%) containing 20% of limestone filler. Specimens analysed were immersed in Na_2SO_4 solution (5% w/w or 0.352 M) with pH control during two years at 20 ± 2 °C. The evolution of attack was determined using XRD semi-quantitative analysis on the material obtained by wearing in layers by millimetre to millimetre of the specimens. Complementary SEM and EDS studies were carried out to confirm the presence of thaumasite. Results show that OPC and high-C_3S SRPC containing 20% limestone filler were found to be more susceptible to sulphate attack than the corresponding plain cement. The attack was characterised by the inward front leading first to the formation of ettringite, later formation of gypsum and finally thaumasite formation, when the decalcification of the mortar lead to the breakdown of C–S–H, providing the required silica. The reaction sequence in Portland limestone cements is essentially the same as in plain Portland cements. The main change is that thaumasite is formed at later stages with decomposition of the ettringite formed during the firsts stage of attack. In SRPC with low C_3S, the attack was limited to the first millimetres and the thaumasite was not detected.

Keywords: Sulphate attack; Limestone filler; Microstructural analysis; SRPC; Thaumasite

1. Introduction

The formation of thaumasite is recognised as a cause of deterioration of Portland cement based products. It has been identified as a deterioration compound in historical buildings [1] and as the last stage of deterioration in marine structures [2]. According to the literature [3], there are two mechanisms of thaumasite formation in mortar and concrete. First, it can be derived from the evolution of ettringite when it incorporates Si^{4+} into its structure, substituting the Al^{3+} ions, and the interstitial replacement of $[(SO_4^{2-})_3\ (H_2O)_2]$ by $[(SO_4^{2-})_2\ (CO_3^{2-})_2]$. Secondly, the thaumasite is the result of the interaction between sulphate and carbonate ions and the C–S–H gel.

Since 1980, the increase of limestone filler addition during the manufacture of cement has contributed to increase the interest studying thaumasite formation in concretes exposed to sulphate environments. In this case, the limestone filler is the internal source that provides the carbonate ions needed for thaumasite formation. The rate of this reaction is greatly increased at cold temperature below 15 °C.

The concrete at risk from this type of sulphate attack includes those made with sulphate resistant Portland cement. Several concretes designed to provide good sulphate resistance have been affected by thaumasite formation according to Crammond and Halliwell [4].

The bibliographic review about sulphate performance of Portland limestone cement (PLC) shows different trends according to the C_3A content in cement, the percentage of limestone filler added and the condition of sulphate environment (temperature, pH control, and concentration and type of sulphate). Some authors [5,6] conclude that the incorporation of filler increases the sulphate resistance of cement, while others [7–10] conclude that limestone filler addition produces a decrease in sulphate resistance of cements.

South-American regions have a mild climate, the mean temperature is in the range of 15–30 °C, and the

---

* Corresponding author. Tel.: +54-228-445-1055; fax: +54-228-445-0628.

E-mail address: firassar@fio.unicen.edu.ar (E.F. Irassar).

0958-9465/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2003.10.003

production of PLC containing up to 20% of limestone filler has growth during the last years. For this reason, it is important to determine the formation of thaumasite in PLC exposed to sulphate solution at temperature above 15 °C. In concrete foundations, the risk of thaumasite formation is increased because it is likely to occur the presence of sulphate ground waters at cold temperature below 15 °C.

This paper reports the results of microstructural analysis of mortar made with different Portland cements stored in sodium sulphate solution for up to two years. A comprehensive analysis of the sequence of attack and the causes of thaumasite formation are presented.

2. Materials and procedures

2.1. Mortar specimens examined

The specimens analysed were made with ordinary Portland cement (OPC) and two sulphate resistant Portland cements with very different C_3S-content ($SRPC_{low}$ and $SRPC_{high}$). The physical and chemical characteristics of the cements are detailed in Table 1. For all cements, the ASTM C 452 expansion at 14 days was lower than the limit for sulphate resistant Portland cement (0.04%). Portland limestone cements were produced by mixing limestone filler (20% by weight) with each Portland cement. Limestone filler (LF) contains 85% of $CaCO_3$ in calcite form without clay minerals. The main impurity was quartz ($SiO_2 = 11\%$) and it was ground at a Blaine fineness of 710 m^2/kg.

Table 1
Chemical composition and physical properties of Portland cements used

	$SRPC_{low}$	$SRPC_{high}$	OPC
Chemical composition, % in weight			
SiO_2	23.66	21.00	22.19
Al_2O_3	3.00	3.29	4.08
Fe_2O_3	5.41	4.68	3.16
CaO	62.14	66.00	62.74
MgO	0.60	0.67	0.58
SO_3	1.59	2.20	2.48
Alkalis	0.72	0.82	–
Loss by ignition	1.61	1.23	1.86
Composition (Bogue), % in weight			
C_3S	40	74	51
C_2S	38	4	26
C_3A	0	1	6
C_4AF	15	14	10
Fineness blaine, m^2/kg	313	306	285
Compressive strength, MPa			
3 days	11.4	27.3	23.3
7 days	17.6	29.2	35.8
28 days	32.7	32.5	42.8
Expansion (ASTM C 452), %			
14 days	0.015	0.012	0.023
90 days	0.025	0.021	0.048
360 days	0.030	0.045	0.162

Mortar bars (285 × 25 × 25 mm) were cast according to ASTM C 1012 (sand to cementitious material ratio of 2.75 and water to cementitious ratio of 0.485). Specimens were stored in a moist cabinet during 24 h, then they were removed from the mould and cured in saturated lime-water until to achieve 30 ± 3 MPa compressive strength. At this age, mortar bars of Portland and PLC cements were stored in individual plastic tanks (mortar bars volume to sulphate–solution volume 1:4) containing Na_2SO_4 (5% w/w or 0.352 M) at pH-constant (7 ± 1) for a period of 2 years at laboratory temperature (20 ± 2 °C). The pH of test solution was periodically readjusted by titration with a combined solution (0.35 M $Na_2SO_4 + 2$ N H_2SO_4) using a few drops of phenolphthalein as pH-indicator. The volume of titration of solution added was registered. Complete details on sulphate performance, strength development and sulphate demand of PLCs were reported previously [7,8].

2.2. Layer by layer analysis

The compound profile was determined in mortar specimens after 2 years of sulphate immersion. The technique used was as follow: The specimens were tested and the remaining slices were dried at 40 °C over a period of 7 days. Subsequently, using a wearing device, layers of 1-mm depth were obtained from the cast surface to the core of the specimens The powdered material was obtained by cutting perpendicularly to the prism face at 5 mm from both edges of the prism (Fig. 1). The depth of each layer was selected at 1 mm because the sand used in making the mortar passed through a 1.18 mm (No. 16) sieve. For this layer depth, the sample is representative of the compound formed in all structure of mortar including both paste and interfaces. After layer grinding, the material was collected and sieved through a 75 μm (No. 200) sieve to removed the bulk of sand grains. Finally, the material was ground to pass the 45 μm (No. 325) sieve and stored in a desiccator to minimise carbonation before XRD analysis.

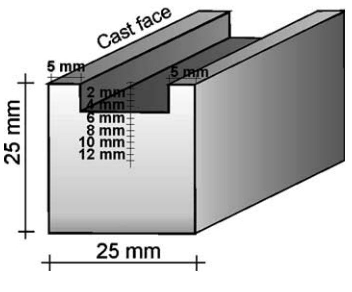

Fig. 1. Diagram of the profile sampling in mortar bars.