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Thaumasite sulfate attack in Portland and Portland-limestone cement mortars exposed to sulfate solution

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HIGHLIGHTS

- The resistance of a plain Portland cement and a Portland-limestone cement to sulfate attack at 5 °C was evaluated.
- The mortar bars showed deterioration in the form of cracking and spalling, and expansion first.
- Eventually, the samples lost cohesiveness and turned into a white, pulpy mush called thaumasite.
- The expansion due to the formation of ettringite and gypsum preceded the formation of thaumasite.
- Portland-limestone cements are susceptible to the thaumasite form of sulfate attack at 5 °C.

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ABSTRACT

The resistance of a plain Portland cement and a Portland-limestone cement to sulfate attack at 5 °C was evaluated. The expansion of mortar bars exposed to a sodium sulfate solution was measured over time and different phases formed at various stages of the sulfate attack were identified using XRD. Results show that the mortar bars initially formed ettringite and gypsum causing some expansion, but expanded much more and ultimately disintegrated due to thaumasite formation. The opening up of the microstructure, caused by extensive cracking of the samples at the early stages was a prerequisite for the formation of thaumasite.

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1. Introduction

Thaumasite sulfate attack (TSA) is a form of sulfate attack attributed to the formation of thaumasite ($CaSiO_3·CaCO_3·CaSO_4·15H_2O$), a calcium–silicate–sulfate–carbonate mineral. Thaumasite forms in concrete as a result of a reaction between calcium–silicate hydrates (C–S–H) with sulfates in the presence of carbonate ions in wet environments [1]. This reaction can eventually destroy the C–S–H matrix resulting in a soft, white, pulpy mass and disintegration of the concrete. It should be noted that low temperatures below 15 °C, particularly between 0 and 5 °C, are more favorable for the formation of thaumasite [2]. However, a few cases have been reported in which thaumasite sulfate attack is said to have occurred at temperatures around 20 °C or more [3,4]. Thus, although thaumasite formation is accelerated at lower temperatures, it is not necessarily precluded at higher temperatures [5]. It is noteworthy that the formation of thaumasite is not always destructive. In fact, the UK Thaumasite Expert Group [6] termed two varieties of formation of thaumasite as thaumasite formation (TF), and thaumasite sulfate attack (TSA). TF refers to incidences where thaumasite can be found in pre-existing voids and cracks without necessarily causing deterioration of the host concrete or mortar. On the other hand, TSA refers to cases where there is significant damage to the matrix of a concrete or mortar as a result of conversion of calcium silicate hydrates (C–S–H) in the hardened Portland cement to thaumasite.

The mechanism of thaumasite formation in cement mixes is debated. Thaumasite can form as a result or reaction between C–S–H, calcium sulfate, calcium carbonate and water [7]:

$$\begin{aligned} &C\text{—}S\text{—}H + CaCO_3 + CaSO_4 + xH_2O \\ &\quad \rightarrow CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O \quad (\text{thaumasite}) \end{aligned}$$

This is known as the direct route for thaumasite formation. A sequence of stages for direct thaumasite formation has been

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proposed as follows [8]: (1) diffusion of sulfate ions and CH leaching, (2) formation of ettringite, (3) gypsum formation and depletion of CH, (4) decalcification of C–S–H, and (5) thaumasite formation. However, thaumasite can form as a result of reaction between ettringite, C–S–H and carbonate ions in the presence of excess water, commonly known as the woodfordite route [9]. In this path, besides gypsum, the aluminate C_3A and ferrite C_4AF also contribute to thaumasite formation [10]:

$$\begin{aligned}&3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O+3CaO\cdot 2SiO_2\cdot 3H_2O+2CaCO_3\\&\quad+4H_2O\\&\quad\rightarrow 2CaSiO_3\cdot CaSO_4\cdot CaCO_3\cdot 15H_2O+CaSO_4\cdot 2H_2O+2Al(OH)_3\\&\qquad+4Ca(OH)_2\end{aligned}$$

According to this theory, thaumasite and ettringite form as end members from a solid solution, called woodfordite, which can occur through the reaction between ettringite, silicate and carbonate in the presence of excess water. Although this reaction is very slow, the rate rises significantly after an initial period when thaumasite has started to form. It should be noted that the solid solution between ettringite and thaumasite is not continuous [11]. Other mechanisms have been proposed for the formation of thaumasite, including the topochemical replacement of ettringite by thaumasite [12], the through solution mechanism [12], and ettringite as nucleation sites for formation of thaumasite [13]. However, in summary, the formation theories commonly fall into two categories: thaumasite is either formed through decomposition of ettringite or it forms directly from solution.

The risk of destruction of mortar and concrete made with Portland-limestone cement due to the formation of thaumasite during sulfate attack at low temperatures is increased by the presence of fine calcite particles [14]. It has been postulated that the limestone content of Portland-limestone cements can act as the internal source of carbonate ions required for thaumasite sulfate attack [8], although the carbonate must go into solution to react, and both its solubility and the form of the resultant soluble carbonate species are pH dependent. Nevertheless, it is well established that the presence of carbonate, either from limestone and dolomite in concrete aggregates or bicarbonate ions in groundwater, is necessary for thaumasite sulfate attack to occur [15]. As such, since the presence of soluble carbonate is essential for thaumasite sulfate attack to happen, and limestone is basically calcium carbonate, the use of Portland-limestone cements might be of concern with regard to thaumasite sulfate attack.

Several studies have confirmed the susceptibility of concrete made with Portland-limestone cements or carbonate aggregates to the thaumasite form of sulfate attack [16–25]. Other studies found that sulfate-resistant Portland cements showed no better resistance than ordinary Portland cements against thaumasite sulfate attack [15,26,27]. As such, due to this uncertainty about the performance of Portland-limestone cements in sulfate environments, their use is not allowed by the Canadian Standard CSA A3000 cement standard in sulfate exposures unless combined with the specified minimum percentages of supplementary cementing materials and after passing tests for sulfate resistance at both 5 °C and 23 °C [28]. The newly revised ASTM C595-12 blended cement specification also allows up to 15% interground limestone but it is not allowed for use in sulfate exposures [29].

In this study, the resistance of a plain Portland and a Portland-limestone cement with 21.8% limestone against sulfate attack at a low temperature were evaluated. The expansion of mortar bars exposed to a sodium sulfate solution was measured over time to assess the sulfate resistance. Also, different phases formed at various stages of the sulfate attack on the samples were identified using X-Ray Diffraction (XRD), to monitor the progression of the sulfate attack.

2. Experiments

The sulfate resistance of one high-C_3A cement clinker interground to make two cements with and without limestone was examined. The cements used were CSA Type GU (ASTM Type I) (without any limestone) and a non-standard GUL22 with limestone content of 21.8% (CSA limits Portland-limestone cements to 15% limestone). The cements were obtained by intergrinding limestone with a 12% C3A cement clinker. The chemical compositions and physical characteristics of the cements are presented in Table 1.

The CSA 3004-C8 (Procedure B) test, an adapted version of the ASTM C1012 sulfate resistance test, where mortar bars are stored at 5 °C, was used to determine resistance to the potential for the thaumasite form of sulfate attack. This low temperature favors the formation of thaumasite in sulfate attack. Also, the limestone content of the Portland-limestone cement would act as an internal source of carbonate ions contributing to the formation of thaumasite. As per the standard, mortar mixtures, proportioned as 1 part of cement, 2.75 parts of graded sand, and water-to-cement ratio of 0.485 by mass, were cast. Each mix consisted of 9–50 mm mortar cubes and 6 25 × 25 × 285 mm mortar bars. Immediately after molding, the molds were covered, placed over water in a closed container, and stored in a 38 °C oven for 24 h. At 24 h, the specimens were demolded and all of the bars and cubes, except two of the cubes, were stored in saturated limewater at 23 °C. The 24 h compressive strength of the two cubes were determined and if the mean strength of the two samples was at least 20 MPa, the mortar bars were then transferred to a refrigerator and kept there for 24 h to cool to 5 °C. If the strength was less than 20 MPa, the mortar specimens were kept at 23 °C until 20 MPa was attained. Next, the initial lengths of the mortar bars were recorded and they were immersed in a 5 °C 50 g/L (5%) sodium sulfate solution prepared in advance and stored in a refrigerator for 24 h. The containers were then stored at 5 °C and the volume proportion of the solution to volume of mortar bars was kept within the specified ratio of 4 to 1. Also, the temperature of the refrigerator was checked periodically using a thermometer to make sure that it was within the range of 3–7 °C, as required by the standard. Subsequent measurements of the length and mass of the mortar bars were performed at 1, 2, 3, 4, 8, 13, and 15 weeks after immersion in solution. The sulfate solution was changed after each reading and the samples were stored in 5 °C solutions prepared at least 24 h prior to the measurement. After 15 weeks, the measurements were done in intervals of about 28 days (4 weeks). Specific measurements at 6, 12, 15, 18, and 24 months were carried out, where applicable, to obtain values that could be compared with CSA and ASTM specifications for sulfate-resistant cement combinations. According to the CSA standard, for a Portland-limestone cement or its blends with SCMs to be classified as resistant to TSA, the average expansion of mortar bars shall be less than 0.10% at 18 months at 5 °C (CSA A3004-C8, Procedure B).

Upon completion of the test or when the samples were observed to have exhibited deterioration, XRD was performed on the samples to identify the phases formed after exposure to sulfate solution. The samples used for XRD were about 25 × 25 × 25 mm, and were either cut from a mortar bar or collected from the remainders of the deteriorated mortar bars. The small pieces were first dried in a vacuum oven at 38 °C for a minimum of 24 h. Then, the sand part of the samples was selectively removed as much as possible by crushing the samples and sieving

Table 1
Chemical compositions and physical characteristics of the used cements and slag.

	Type I	GUL22
Chemical composition (%)		
SiO_2	20.61	17.44
Al_2O_3	5.52	4.64
Fe_2O_3	2.19	1.86
CaO	63.36	59.79
MgO	2.41	2.29
SO_3	4.17	4.07
K_2O	1.22	1.07
Na_2O	0.23	0.20
TiO_2	0.26	0.22
SrO	0.09	0.08
P_2O_5	0.13	0.12
Cl	0.03	0.02
Free CaO	0.88	0.86
LOI	0.58	8.90
Limestone	0	21.8
Physical characteristics		
Blaine (m^2/kg)	402	562
Retained on 45 μm (%)	8.6	16.7
Specific gravity	3.15	3.03

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