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Evaluation of the effect of tricalcium aluminate content on the severity of sulfate attack in Portland cement and Portland limestone cement mortars

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A B S T R A C T

It is widely understood that the tricalcium aluminate content of Portland cement is inversely related to the concrete's ability to resist external sulfate attack. Furthermore, recent research has demonstrated a link between elevated levels of interground limestone and accelerated sulfate attack, particularly thaumasite sulfate attack at low-temperatures (below 10 °C). In this paper the relationships between Portland cement C_3A-content, interground limestone content and supplementary cementitious materials (Type F fly ash and silica fume) are explored. The mortar bars cast with high-C_3A cement failed much earlier than the same bars cast with moderate-C_3A cement. External sulfate attack occurred more rapidly at 5 °C than at 23 °C. Limestone content did not affect the rate of external sulfate attack.

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1. Introduction

The durability of a concrete structure is an essential criterion to consider when evaluating the suitability of a concrete mix for its intended environment. If a structure is to be exposed to sulfate-bearing groundwater, seawater, or another potentially sulfate-bearing environment, its ability to resist external sulfate attack is critical. External sulfate ions can enter the matrix of hardened cement paste and interact with hydrated cement compounds, leading to cracking and softening of the hardened paste [1].

The interaction between external sulfates and hydrated cement compounds can lead to the formation of ettringite ($3CaO·Al_2O_3·3CaSO_4·32H_2O$), gypsum ($CaSO_4·2H_2O$) [2] and thaumasite ($CaSiO_3·CaCO_3·CaSO_4·15H_2O$) [3]. This is commonly known as external sulfate attack (ESA). In the presence of limestone (calcium carbonate, $CaCO_3$), monocarbonate may replace some of the monosulfate that would have formed during hydration [4]. Furthermore, increased carbonate content may facilitate the formation of thaumasite rather than ettringite, or ettringite may be transformed to thaumasite [5]. The prior existence of ettringite from external sulfate attack may be necessary for thaumasite to form [6].

Tricalcium aluminate (C_3A) within the matrix of hydrated cement paste will interact with external sulfates, forming ettringite, and in many cases thaumasite [7]. The formation of ettringite causes expansion and cracking of the hardened cement paste, followed by the formation of thaumasite which disintegrates the calcium-silicate hydrates (C–S–H) structure [3,8] thus damaging the concrete and compromising its long-term durability. For this reason, low-C_3A cements are required in sulfate environments in Canada and elsewhere.

Thaumasite formation is more frequently observed at lower temperature (below 15 °C) [9]; however, it has been reported at temperatures in excess of 20 °C [10]. This may be attributed to the kinetics of thaumasite formation; thaumasite formation is a kinetically slow process, particularly at elevated temperatures [11]. Due to the carbonate ion (CO_3^{2-}) required for thaumasite formation, cements produced with higher limestone ($CaCO_3$) replacement levels can be at greater risk for thaumasite sulfate attack (TSA). In several laboratory trials, a correlation has been observed between limestone content and increased deterioration due to TSA [5]. However, limestone content has rarely been linked to thaumasite in field conditions [12].

The current study examines the effect of C_3A, supplementary cementitious material (SCM) and limestone content on the performance of mortar bars stored in sulfate solutions at temperatures of 5 °C and 23 °C. The performance of the mortar bars is compared to

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the current physical performance (expansion) requirements of the Canadian standards.

In Canada, concrete exposed to sulfate environments must meet the requirements of CSA A23.1-09 [13] that imposes maximum limits on the water-to-cementitious-materials ratio (w/cm) and permits only sulfate-resistant Portland cements and/or suitable blends of Portland cement (PC) with supplementary cementitious material. Sulfate-resisting cements are, in turn, defined in CSA A3001-13 [14] that imposes C_3A and expansion limits on Portland cement (which may contain up to 5% limestone), and expansion limits on blended Portland cement (PC + SCM). The requirements are summarized in Table 1. Sulfate-resisting Portland cements must pass a 14-day mortar-bar expansion test, whereas blended Portland cements must pass a 6-month mortar-bar expansion test. Portland limestone cement (PLC), which may contain up to 15% limestone, is not permitted for use in concrete exposed to sulfates unless it is combined with a sufficient level of SCM to meet the pre-scriptive and performance requirements for sulfate-resisting blended Portland limestone cements which are summarized in Table 1. These requirements include testing mortar bars stored in 5% sodium sulfate solution at 5 °C to evaluate the potential for TSA at established minimum SCM replacement levels.

2. Material and methods

2.1. Cementitious materials

Two different clinker types were used for this study: a moderate-C_3A clinker (8–9% C_3A), and a high-C_3A clinker (11–12% C_3A). The first clinker was interground with two different limestone contents (4% and 15% limestone by mass). Throughout the remainder of the paper, these cements will be referred to as GU-Mod and GUL-15-Mod. The high C_3A clinker was interground with 4% and 10% by mass limestone, referred to as GU-High and GUL-High. Each of the cements studied was blended with varying levels of supplementary cementitious materials. See Table 2 for the chemical compositions of the cementitious materials, and Table 3 for mixture proportions and exposure conditions.

2.2. Mortar testing

Mortar bars were cast with each of the cements (mixed and proportioned according to CSA A3004-C1 and C2 except that the water-to-cementitious-materials ratio (w/cm) was kept constant at 0.485 for all mixes) and exposed to 5% Na_2SO_4 solution at both 23 °C and 5 °C and tested according to CSA A3004-C8. The mortar bars were measured regularly (according to CSA A3004-C8, procedure A and B), and the solution was renewed regularly. When deterioration was observed, mortar samples were studied with X-ray diffraction (XRD) to evaluate which sulfate-bearing phases were present and therefore, what form of sulfate attack was dominating. The XRD samples were finely ground while still in a moist state and immediately scanned from 5° 2Θ to 90° 2Θ at a scan rate of 0.02° per second using a Bruker D8 Advance spectrometer.

3. Results

Only the results from the control bars (100% cement), 25% Type F fly ash bars, and fly ash and silica fume ternary bars in Na_2SO_4 solution are reported here to facilitate comparison of the different C_3A levels. Also, for ease of comparing the limestone contents among different C_3A contents, only GU-Mod, GUL-15-Mod, GU-High, and GUL-High are reported here.

3.1. 23 °C Na_2SO_4 solution

Fig. 1 shows the expansion results for all four cements (both high and moderate-C_3A, GU and GUL cements) in combination with fly ash or ternary blends. The expansion up to 30 months (130 weeks) in 23 °C Na_2SO_4 is reported. Note: GUL-High + 5% SF + 20% F ash was broken after 18 months in solution; therefore further measurements were not possible. As per CSA A3004-C8 procedure A, all control samples failed and all SCM blends passed the sulfate test defined as: ⩽0.10% (Type MSb) or ⩽0.05% (Type HSb) expansion after 6 months or ⩽0.10% (HSb) after 12 months, see Table 1 above. Results were generally unaffected by C_3A content or limestone content within the CSA A3004-C8 time frame.

3.2. 5 °C Na_2SO_4 solution

Fig. 2 shows the expansion data up to 30 months (130 weeks) for all four cements with fly ash and ternary blend mortar bars in 5 °C Na_2SO_4.

The control mortar bars, cast with both moderate- and high-C_3A cements, with both limestone contents exceeded the maximum expansion (⩽0.10% after 18 months) permitted by CSA A3004-C8 procedure B for Portland limestone cements.

Table 1
Requirements for sulfate-resisting cements in Canada (CSA A3001-13).

Cement type	Types permitted	Requirements
Portland cement (PC)	MS or HS	• Limits on C_3A content • 14-Day expansion limit for mortar bars containing gypsum (7% SO_4 by mass of cement)
Blended Portland cement containing SCM[a]	MSb or HSb	• 6-Month[b] expansion limit (0.10% for MSb and 0.05% for HSb) for mortar bars in 5% Na_2SO_4 at 23 °C
Portland limestone cement (PLC)		PLC is not permitted in sulfate exposure classes unless it is used in combination with sufficient levels of SCM to meet the requirements shown below
Blended Portland limestone cement containing SCM[a]	MSLb or HSLb	• 6-Month[b] expansion limit (0.10% for MSLb and 0.05% for HSLb) for mortar bars in 5% Na_2SO_4 at 23 °C • 18-Month expansion limit[c] (0.10% for MSLb and HSLb) for mortar bars in 5% Na_2SO_4 at 5 °C • Minimum SCM replacement levels of 25% Type F fly ash, 40% slag or 15% metakaolin, or of combinations of 5% silica fume with 20% Type F fly ash or 5% silica fume with 25% slag

[a] SCM can be combined with either PC or PLC of the concrete mixture provided it is demonstrated that such combinations meet the requirements for blended PC or blended PLC.

[b] Mortar bars that exceed the 6-month expansion limit of 0.05% for Types HSb and HSLb, cements are still deemed to pass provided that the 12-month expansion does not exceed 0.10%.

[c] If the expansion between 12 months and 18 months exceeds 0.03%, the test must be continued until 24 months, and the 24-month expansion is not permitted to exceed 0.10%.