



Varying fly ash and slag contents in Portland limestone cement mortars exposed to external sulfates



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HIGHLIGHTS

- Addition of SCMs improved mortar's resistance to external sulfate attack.
- The beneficial effects of SCMs are enhanced at higher temperatures.
- With SCMs moderate and high- C_3A cements were used to create sulfate-resisting mortar.
- Interground limestone content had little to no effect on sulfate resistance.
- Ettringite, gypsum, and thaumasite were found in all mortar bars in 5 °C Na_2SO_4 .

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ABSTRACT

The partial replacement of Portland cement with supplementary cementing materials (SCMs) is known to improve concrete's resistance to external sulfate attack. However, an increase in thaumasite formation has been observed in Portland cements with interground limestone. The effects of varying SCM and limestone replacement levels on the severity of external sulfate attack in moderate- C_3A and high- C_3A Portland cements in 5 °C and 23 °C Na_2SO_4 solution are studied. The partial replacement of Portland cement with SCMs greatly enhances the resistance to external sulfate attack, including thaumasite sulfate attack. The rate of deterioration is strongly correlated to SCM content, C_3A content, and temperature.

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1. Introduction

Concrete specimens exposed to external sulfates can suffer significant loss of strength and structural capacity due to the interaction between external sulfates and the hardened cement paste. This mode of deterioration is known as external sulfate attack (ESA) and is generally categorized into either: (1) classical, ettringite sulfate attack or (2) thaumasite sulfate attack (TSA) [1]. Although extensive research has been carried out to examine the role of limestone in thaumasite formation [2–5], considerable debate exists as to the effect of limestone content on the formation of thaumasite.

It is widely understood that supplementary cementing materials (SCMs), including slag, fly ash, and natural pozzolans improve concrete's resistance to external sulfate attack [6,7]. The amount of SCM required to control expansion due to external sulfate attack varies based on the composition of both the Portland cement and the SCM, as well as the exposure environment [4]. There are several theories as to how and why SCMs improve concrete's resistance to sulfate attack: dilution effect (reduced C_3A content) [8,9]; reduction in calcium hydroxide content (due to dilution of $CaOH_2$ and pozzolanic reaction) [10–12]; decreased permeability [8]; and the formation of more stable hydration products [13].

1.1. Dilution of tri-calcium aluminate (C_3A) content

Tricalcium aluminate [$3CaO \cdot Al_2O_3$] present in Portland cement clinker reacts with water and gypsum to form ettringite [$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$] very early in Portland cement hydration. As hydration continues and the availability of gypsum diminishes

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ettringite is converted to monosulfate [$3\text{CaO}_3\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$], liberating gypsum to react with unreacted C_3A , forming additional monosulfate [14]. If unhydrated C_3A remains after all of the gypsum has been consumed the C_3A can form calcium aluminate hydrates (C_4AH_{13} and C_3AH_6) and, in the presence of calcium carbonate (CaCO_3), calcium carbo-aluminates can be formed ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot x\text{H}_2\text{O}$) [15]. As external sulfates migrate into the already stable concrete, additional sulfate becomes available for reaction in the cement paste. The external sulfates react with monosulfate (and monocarbonate and calcium aluminates if they are present) forming additional ettringite [16].

The aluminate phases discussed above are closely intermixed with the C–S–H gel; the formation of ettringite generates expansive forces in the C–S–H matrix, leading to cracking of the hardened cement paste [3]. Thus low- C_3A sulfate-resisting Portland cements have been developed to lessen the amount of monosulfate and ettringite formed, reducing the expansion and cracking occurring. Alternately, the replacement of Portland cement with SCMs reduces the total amount of C_3A in the cementing materials by diluting the Portland cement. Many researchers have observed considerable improvement in sulfate resistance (measured by expansion) when the C_3A content of the cement is reduced by partial replacement of Portland cement with SCMs or the use of low- C_3A Portland cements [17,9,18]. Types MS (moderate sulfate-resistant Portland cement) and HS (high sulfate-resistant Portland cement) are restricted to maximum C_3A contents of 8% and 5%, respectively [19] to minimize the expansion and cracking developed due to exposure to external sulfates.

1.2. Reduction in calcium hydroxide content

Calcium hydroxide ($\text{Ca}(\text{OH})_2$) in cement paste can react with external sulfates, forming gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) in the hardened cement paste. There is considerable debate as to whether gypsum creates expansive forces leading to cracking of the concrete; however, it is generally believed that gypsum formation participates in the expansion and cracking related to external sulfate attack [20]. The replacement of Portland cement with supplementary cementing materials reduces the amount of calcium hydroxide in the cement paste in two ways: (1) dilution of the Portland cement, and (2) pozzolanic reaction of the SCMs, consuming $\text{Ca}(\text{OH})_2$ [11,12]. Thus, the replacement of Portland cement with SCMs decreases the availability of $\text{Ca}(\text{OH})_2$ to participate in the formation of gypsum with external sulfates.

1.3. Decreased permeability

It is well known that the incorporation of supplementary cementing materials into Portland cement can reduce the permeability of the cement paste. Although the partial replacement of Portland cement with SCMs can lead to greater overall porosity (particularly at early ages) the permeability is reduced due to a reduction in the pore size and reduced connectivity of the pores [21,22]. The reduced permeability of the SCM blended concrete inhibits sulfates from progressing into the concrete, thus slowing the deterioration due to external sulfate attack.

1.4. Formation of aluminate hydrates, pozzolanic consumption of $\text{Ca}(\text{OH})_2$

The hydration of fly ash, slag and other pozzolans within the Portland cement matrix leads to the formation of additional aluminate hydrate compounds and incorporation of aluminum in the C–S–H forming C–A–S–H [23] and increasing the Al/Si ratio [24] of the hardened cement paste. The hydration of supplementary cementing materials also lowers the Ca/Si ratio in the C–S–H and

the pozzolanic reactions consume Portlandite [$\text{Ca}(\text{OH})_2$], forming additional C–S–H [23]. Bellmann and Stark [13] observed improved resistance to thaumasite sulfate attack in low Ca/Si ratio C–S–H. Schmidt et al. [25] observed improved resistance to thaumasite sulfate attack when greater amounts of aluminum were contained in the cement paste. Furthermore, the consumption of Portlandite during the pozzolanic reactions of the SCMs reduces the amount of calcium available for formation of gypsum during exposure to external sulfates (see Section 1.2 above).

In this study 7 different cements with limestone contents varying from 4% to 22% were used to cast CSA A3004-C8 [26] mortar bars. Varying replacement levels of fly ash, slag, silica fume, and metakaolin were used to evaluate the effectiveness of these SCMs at resisting external sulfate attack at both 23 °C and 5 °C.

This research seeks to explore whether the previously established theories regarding the effects of SCMs on sulfate resistance of Portland cement concrete are valid for Portland limestone cements with varying interground limestone contents. The research explores the relationship between resistance to external sulfate attack and the SCM and limestone contents of the binder at both 23 °C and 5 °C with moderate- and high- C_3A cements. Furthermore, the research explores the relationship between ettringite and thaumasite formation during sulfate attack on SCM-blended Portland limestone cement mortars.

2. Materials and methods

2.1. Mix designs, cementing materials

Two series of mortar bars were cast for this experiment. The first series used a moderate- C_3A (8–9% C_3A) cement interground with 4%, 15%, and 22% limestone (PC, PLC 15, and PLC 22). The second series used a high- C_3A (11–12% C_3A) cement interground with 4%, and 10% limestone (PC and PLC) as well as a Type HS (V) cement (Table 1). The first set of mortar bars includes varying levels of class F fly ash (FA) (<8% CaO), blast-furnace slag, and ternary mixes of both fly ash and slag mixed with silica fume (SF). The second set of mortar bars includes both class CI (8–20% CaO) and class F fly ash, silica fume, metakaolin, and ternary fly ash-silica fume, and fly ash-metakaolin mixes. See Table 1 for the compositions of the cementing materials and Tables 2 and 3 for mixture proportions. The mixture proportions to be examined in this research were developed using the CSA A3001 requirements for blended Portland limestone cements in a sulfate environment [27]. Supplementary cementing materials were used as a replacement for Portland cement, not an addition to Portland cement, for all mixes.

2.2. Method

2.2.1. Sample preparation

All mortar bar mixes were proportioned and mixed according to CSA A3004 with cement to sand ratio of 2.75, and water to cementitious materials (cement + SCMs) ratio of 0.485. After preparing the mortar three mortar cubes ($50 \times 50 \times 50$ mm) and 12 mortar bars ($25 \times 25 \times 250$ mm) were cast and stored over water at 35 °C. [Note: only 6 mortar bars were cast for each of the series 1 mixes.]

After 24 h at 35 °C the cubes and bars were all demoulded, one cube was tested for compressive strength. If 20 MPa was achieved with the mortar cube another cube was tested to confirm the results; if the cube did not reach 20 MPa the other cubes were stored in limewater and tested regularly (every 12–24 h) until 20 MPa was reached as per CSA A3004-C8 [26]. Generally, 1–2 days of limewater curing was required for the mortar cubes to reach 20 MPa. All mortar bars were stored in saturated limewater until 20 MPa was reached.

2.2.2. Sample testing

When the mortar cubes reached 20 MPa half of the mortar bars (3 for series 1, 6 for series 2) were cooled to 5 °C in the saturated limewater and then the initial length measurements were taken. After the initial measurements the bars were moved to 5 °C sodium sulfate solution (5% Na_2SO_4). The remaining mortar bars (either 3 or 6 bars), to be tested at 23 °C, were measured and moved to 5% sodium sulfate solution (33,800 ppm SO_4^{2-}). After the initial measurements were recorded and the mortar bars were immersed in solution they were measured regularly according to the schedule provided in CSA A3004-C8; the solution was replaced after each measurement.

When significant expansion occurred in the mortar bars (3 years in sulfate solution) small samples of the bars were removed and examined with X-ray diffraction (XRD). Cross-sectional slices were taken from the interior of the mortar bars, finely

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