The impact of alumina availability on sulfate resistance of slag composite cements

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HIGHLIGHTS

- Al availability is lower in slag cements, with more bound to stable hydrates.
- Ca demand for ettringite formation is lower in slag cements.
- AFt levels plateau after 90 days of attack. Only neat cement damaged.
- Damage in slag blends occur after Ca leaching. Damage mechanism differs from neat cement.
- Insufficient Ca and Al in unreacted slag for future AFt growth (years).

ARTICLE INFO

ABSTRACT

Slag cement pastes prepared with either 40% or 70% of slags by weight were prepared (W/B = 0.5) and subsequently exposed to a $3 \, g \, L^{-1} \, Na_2SO_4$ solution. The slag cements were shown to be more resistant. Initially, ettringite levels rose, then plateaued upon carbonate AFm consumption, although monosulfate was also found to be in equilibrium with ettringite when using an Al-rich slag. Portlandite was initially consumed, to form ettringite, but leached out after prolonged attack until it was fully depleted, or nearly, with subsequently C-A-S-H being decalcified. Any excess aluminium released by the slag was bound to a calcium deficient C-A-S-H phase and hydrotalcite, sheltering the aluminates from ingressing sulfates. Mass balance further revealed that, if the slag in the blends were to fully dissolve to form C-A-S-H and hydrotalcite, there would have been insufficient aluminium and calcium to combine with sulfates to form ettringite. Rather, calcium from C-A-S-H would have continuously leached, leaving behind a silicate skeleton.

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1. Introduction

External sulfate attack encompasses a series of interactions occurring within the cement matrix as sulfates percolate through it [1]. The sulfates react with available aluminium, and calcium, to convert AFm hydrates to ettringite $C_6A\bar{S}_3H_{32}$ and, under extreme circumstances, portlandite to gypsum [2–4].

It is commonly believed that the formation of ettringite and gypsum, from monosulfate and portlandite respectively, are expansive reactions which are the cause the damage [5,6]. Still, ettringite precipitation alone cannot explain the damage caused by sulfate attack, and the link between ettringite formation and expansion is not clear [7,8]. Rather, damage is caused when the expansive ettringite forms in pores small enough to exert a force on the matrix [3,8–11]. Furthermore, Yu proposed that the failure mechanism of mortars bars of slag blends exposed to sodium sulfate solution is dominated by the loss of surface material rather than a generalized expansion, as for plain Portland cement [12].

The replacement of cement with slag has previously been recognized as imparting sulfate resistance, particularly at higher levels of replacement [13–17]. Although the overall aluminium content is higher in a slag cement blend, it does not imply that more aluminium is readily available to react with sulfates. Such systems produce a C-S-H phase with a lower Ca/Si ratio [18–20], thus allowing aluminium incorporation within the phase. A hydrotalcite like phase is also common, binding aluminium. This restricts the amount of free aluminium which would react freely otherwise with sulfates [14,21]. However, it has been seen previously [22] that alumina still promotes AFm formation at early ages, which

may in turn convert to ettringite during attack, worsening resistance. Furthermore, not all of the available alumina goes to form ettringite. Fernandez-Altable has previously observed the formation of monosulfate by the end of their testing period [21].

The role of calcium in sulfate attack cannot be ignored either. Slags are typically calcium deficient compared to cement, therefore lowering the total calcium content of slag cements. A recent study by Kunther et al. [23] found that the crystallisation pressure related to ettringite growth is reduced when the Ca/Si of the C-A-S-H phase is lower.

This study investigates further the impact of alumina content in slag and calcium content in composite cement on sulfate resistance, closely following the changes in hydrate composition and amounts.

2. Materials

A CEM I 42.5 R, conforming to EN 197-1:2011, was chosen for this study along with two ground granulated blast furnace slags differing in composition. The oxide composition of the raw materials is shown in Table 1.

Compared to CEM I, the slags were characterized by being deficient in calcium, and richer in silica, magnesium, and aluminium. The slags were chosen to emphasize the role of aluminium content on sulfate resistance. As such, slag C (12.33%) was richer in aluminium than slag B (7.36%). Similarly, slag C was richer in magnesium and calcium than slag B. However, the Mg/Al molar ratio of the slag was lower than for slag B. The mineralogical composition of the CEM I used is shown in Table 2. The CEM I was compromised of primarily of C_3S and C_2S. The cement was contained moderate amounts of aluminium in the form of C_3A (7.5%) and C_4AF (8.3%). The total calcium sulfate content, as anhydrite and hemihydrate, totaled 4.4%.

3. Methods

Pastes were used to assess sulfate resistance, according to the mix designs shown in Table 3. The specimens were prepared by replacing either 40% or 70% of the cement by weight with slag. A further blend, containing 3% additional anhydrite by weight, was prepared using slag C at 40% replacement. Note, the overall SO_3 content accounts only for that supplied by the clinker and the added anhydrite.

50 mm long 25 mm diameter paste cylinders were prepared to assess any changes in microstructure during attack (Fig. 1). All samples were cured for a period of 14 days in water baths prior

Table 1
Compositions of the raw materials, determined by XRF (% weight).

		CEM I	Slag B	Slag C
LOI 950 °C	%	2.62	(+0.85)[a]	(+1.57)[a]
SiO₂	%	19.2(1)	39.7(5)	34.3(5)
Al₂O₃	%	5.5(0)	7.3(6)	12.3(3)
TiO2	%	0.2(7)	0.2(5)	0.9(3)
MnO	%	0.0(4)	2.5(4)	0.4(0)
Fe₂O₃	%	2.7(7)	1.3(3)	0.5(2)
CaO	%	62.2(8)	38.1(8)	38.4(9)
MgO	%	2.1(9)	7.6(5)	9.5(8)
K₂O	%	0.9(3)	0.6(5)	0.4(8)
Na₂O	%	0.0(8)	0.1(3)	0.2(4)
SO₃	%	3.1(0)	1.8(3)	2.6(1)
P₂O₅	%	0.1(7)	0.0(1)	0.0(1)
Total	%	99.15	99.69	99.93
Amorphous	%	–	99.0	98.3
Mg/Al		–	4.74	3.52

[a] The sample was oxidized with HNO_3 before determination of LOI.

Table 2
Mineralogical composition of CEM I.

Phases		CEM I
C₃S	%	61.0
β-C₂S	%	11.9
C₃A	%	7.5
C₄AF	%	8.3
Calcite	%	3.7
Anhydrite	%	2.9
Hemihydrate	%	1.5
Other	%	3.2

Table 3
Mix design of all blends.

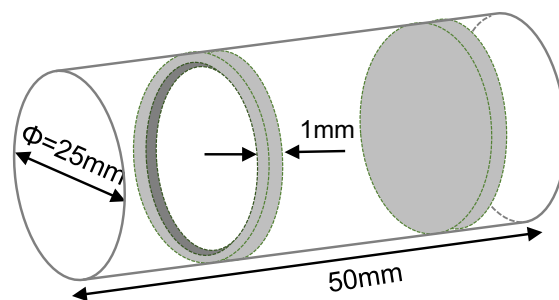|	C₁	C₁40S_b	C₁40S_c	C₁40S_c$	C₁70S_c
CEM I	1.00	0.60	0.60	0.58	0.30
Slag	–	0.40	0.40	0.39	0.70
Anhydrite	–	–	–	0.03	–
w/binder	0.50	0.50	0.50	0.50	0.50
w/cement	0.50	0.83	0.83	0.86	1.67
Final SO₃ in cement (%)	3.1	1.86	1.86	4.96	0.93

Fig. 1. Schematic drawing of the paste samples prepared for sulfate attack.

to exposure to a 3 g L^{-1} Na$_2$SO$_4$ solution, which was renewed fortnightly. The volume of the solution was four times that of the samples. The experimental setup was carried out in closed containers under ambient conditions (20 °C) and no precautions were taken to prevent carbonation. The pastes were characterized by scanning electron microscopy (SEM) in backscattered electron mode, X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and mercury intrusion porosimetry (MIP).

The samples in this study are referred to by their total curing time, and not by the time exposed to sulfates, e.g. a sample a 28 day sample has, in fact, only been in a sulfate bath for 14 days.

SEM analyses were conducted on pastes, from which transverse cuts were taken using a Struers Accutom-50 (Struers diamond cut-off wheel MOD 13). 2 mm thick cuts were taken near the middle of the sample, where the ingress of sulfates was radially unidirectional. The disks were freeze dried to constant weight and subsequently resin impregnated. The samples were polished using silicon carbide paper and any remaining scratches removed with diamond paste (down to 0.25 µm). Energy dispersive X-ray (EDX) point analyses were conducted on micrographs with a 130 × 97 µm field of view; a 12 × 12 grid point was set up and measurements were taken from the edge of the sample to a depth of 5 mm, at 0.5 mm intervals. Any measurement associated with CH, anhydrous phases, and porosity was removed from the data. As such, the sulfate profile was measured and any changes in hydrate assemblage and composition were assessed. Further EDX point analysis was also performed on the slag hydration rims near the surface and at a depth of 5 mm.