Influence of curing temperature on the process of hydration of supersulfated cements at early age

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A B S T R A C T

In this paper, the influence of curing temperature was studied for supersulfated cements made with two slags having different chemical compositions. Supersulfated cements (SSC) made with low-alumina slag developed lower porosity, higher compressive strength and degree of hydration at higher temperatures. SSC made with high-alumina slag resulted in higher strengths and presented a more complex mechanism of hydration that was strongly influenced by the solubility of anhydrite.

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1. Introduction

Relative to other building materials, concrete has a low embodied energy and carbon footprint, however, due to the enormous quantity of concrete placed each year, the resulting total embodied energy and carbon footprint is quite large. The concrete industry contributes around 5% to total global CO_2 emissions and approximately 90% of this associated embodied energy and carbon is due to the commonly used Portland cement binder [1,2].

While the concrete industry commonly makes use of some industrial by-products as supplementary cementitious materials to reduce cement content, these replacements are typically in the range of 15–30%. This paper focuses on supersulfated cements (SSC), where Portland cement contents are reduced by 85–90% using ground granulated blast-furnace slag (GBFS) and calcium sulfate.

Supersulfated cements (SSC) were used in the 1950–1960s in Europe, particularly for mass concrete applications. Later changes in the iron manufacturing processes yielded slags that no longer fulfilled the minimum Al_2O_3 content requirement (13%), leading to its use in blends with Portland cement (GBFS-cement) [2].

Recently, the European standard for supersulfated cement was superseded by the norm EN 15743/2009, which no longer requires a minimum Al_2O_3 content for the GBFS. The requirements "consist of at least two-thirds by mass of the sum of calcium oxide (CaO), magnesium oxide (MgO) and silicon dioxide (SiO_2). The remainder contains aluminum oxide (Al_2O_3) together with small amounts of other compounds. The ratio by mass of $(CaO + MgO)/(SiO_2)$ shall exceed 1.0" [3].

SSC are primarily comprised of blast furnace slag, (80–85%), calcium sulfate (10–20%) and an alkaline activator, which is often Portland cement, though in a relative small quantity (around 5%). The small proportion of Portland cement initially hydrates, providing calcium hydroxide (CH), which promotes dissolution of the slag. The dissolved aluminum, calcium and silicon ions from the GBFS react with the added calcium sulfate ($C\overline{S}$) forming ettringite ($C_6 A\overline{S}_3 H_{32}$) and calcium silicate hydrate (C–S–H) phases, as demonstrated in this simplified Eq. 1 [4].

$$C_5S_3A + CH + 3C\overline{S} + 34H \rightarrow C_6 A\overline{S}_3 H_{32} + 3CSH \tag{1}$$
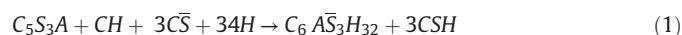
However, the complete series of reactions is complex and not well understood. The hydraulic activity of slag plays a very important role on the process of hydration of SSC and depends on the amorphous phase, lime and alumina contents [5–8]. Gruskovnjak et al. [8] verified that the optimum chemical composition of the slag is more important to its reactivity than the amount of the amorphous phase. They also found that minor hydrate phases, such as AFm phases or hydrotalcite, can also occur as product of hydration.

Besides requiring less energy and producing lower greenhouse gas emissions in its production, supersulfated cement (SSC) can provide resistance to sulfate attack and lower heat of hydration [8–10]. However, the main disadvantage is that the strength development of SSC is slow and strongly dependent on temperature [6], which is also typically observed in Portland cement blends with high slag contents. GBFS blends are not therefore used in applications where the environment temperature is low or where high early age strength is required. The drawback in

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Table 1
Chemical composition of slag (A and B) and cement.

Oxides	Slag A	Slag B	EN 15743	Cement
SiO_2	39.37	32.56	–	20.09
Al_2O3	8.15	13.74	–	5.35
Fe_2O3	0.63	0.41	–	2.30
CaO	38.90	42.27	–	62.49
MgO	11.08	6.04	–	2.50
SO_3	2.63[a]	2.00[a]	–	4.04
Na_2O	0.29	0.19	–	1.05
K_2O	0.35	0.31	–	
P_2O_5	0.01	0.03	–	–
TiO_2	0.35	0.59	–	–
Mn_2O_3	0.57	0.30	–	–
$CaO + MgO + SiO_2$	89.4	80.9	≥66.7	–
Free lime				1.12
$(CaO + MgO)/SiO_2$	1.3	1.5	≥1.0	–

[a] Added SO_3 from gypsum.

the use of GBFS concrete is that its strength development is considerably slower under standard 20 °C curing conditions [11]. Barnett et al. [11] investigated the effect of curing temperature on the development of strength of Portland cement mortars containing GBFS. They observed that the early-age strength was higher at higher temperatures and much more sensitive at higher levels of GBFS, related to its higher activation energy. In relation to supersulfated cement (SSC), no studies have been noted concerning the influence of temperature on its process of hydration. Moreover, unlike slag, the solubility of calcium sulfate, present in SSC up to 20% [3], decreases at high temperatures [12].

This contribution highlights research conducted to investigate the effects of temperature on the process of hydration, compressive strength and porosity of supersulfated cement (SSC). Two slags with different chemical compositions (mainly the Al_2O_3 content) were used to evaluate the performance of SSC under low temperature (lower than 20 °C) and higher temperatures typically experienced at early ages or during thermal curing.

2. Materials and methods

Two slags were used to produce the supersulfated cement (SSC). Slag A had relatively lower amounts of Al_2O_3 and CaO and higher MgO

and SiO_2 contents, but both slags meet the EN 15743 limits (Table 1). X-ray diffraction (XRD) showed that both slags had a glass structure and slag B also contained minor amounts of calcite and anhydrite added during grinding (Fig. 1). Fig. 2 shows that the slags had very similar grain size distribution, both with a d50 of 9 μm. A Canadian type GU (CEM I) [13] Portland cement (Table 1) was used as the alkaline activator.

To obtain anhydrite ($CaSO_4$) for the SSC, gypsum ($CaSO_4 \cdot 2H_2O$) was burned for 1 h at 650 °C [5] and the mineralogical composition was confirmed by XRD (Fig. 3).

The SSC was composed of 85% slag, 10% $CaSO_4$ and 5% GU cement. To study the influence of temperature, two initial curing regimes were investigated:

- Initial Curing Regime 1: cured at 23 °C and 95%RH for 24 h.
- Initial Curing Regime 2: cured immediately after casting at different temperatures of 13, 23, 38, 50 °C and 95%RH for 24 h.
- After the initial curing period, the specimens were demolded and immersed in lime water solution at different temperatures of 13, 23, 38 and 50 °C up to 7 days of age.

Both slags A and B were studied under Initial Curing Regime 1. Initial Curing Regime 2 was conducted only for slag B (high-alumina). For the compressive strength tests, X-ray diffraction (XRD), differential and thermogravimetric analysis (DTA and TGA), and mercury intrusion porosimetry (MIP), mortars and pastes were studied (Table 2).

Compressive strength of 50 mm mortars cubes (1:2.75:0.485—cement:sand:water) was determined at 7 days, as per ASTM C109 [14].

Pastes prepared for MIP, XRD and DTA/TGA analysis at 7 days, were crushed into particles smaller than 9.5 mm, immersed in acetone for 2 h and dried by filtration to remove the pore fluid. These samples were crushed again to obtain particles smaller than 75 μm. These powders were submitted to XRD analysis using CuKα radiation, over a 2θ range of 3–70°, using steps of 0.05° and 1 s counting time, and to DTA/TGA in nitrogen at 10 °C/min. For the MIP, the samples were measured using a Quantachrome Autoscan 60 porosimeter applying pressure from 0 to 414 MPa, assuming a contact angle of 140°. Calorimetry was performed using a TAM Air isothermal calorimeter, on pastes made from 20 g of SSC with w/c 0.4, over a hydration period of 7 days.
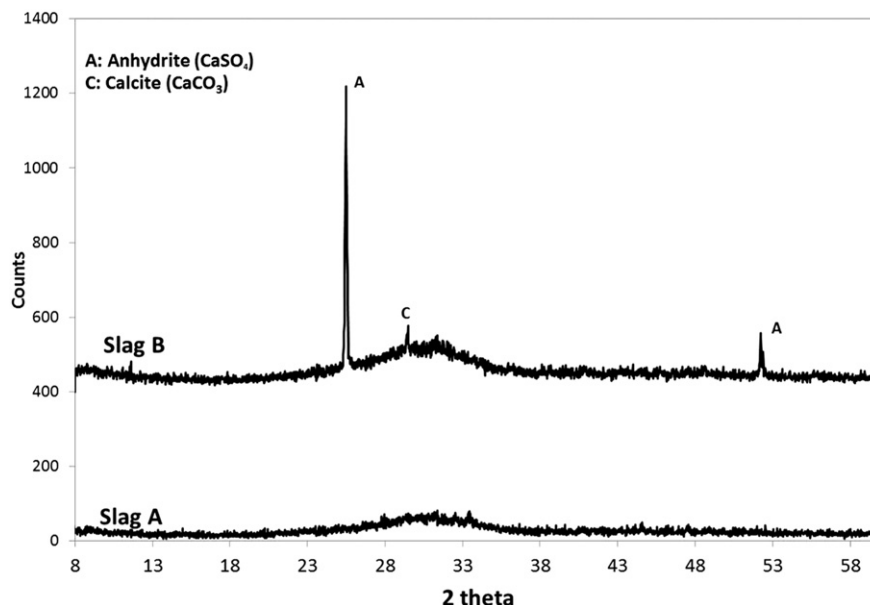

Fig. 1. X-ray diffraction patterns of slags A and B.