



Effect of sulfate content on the porosity distribution and resulting performance of composite cements



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HIGHLIGHTS

- Cement pastes porosity measured by dynamic vapor sorption and mercury intrusion.
- Models developed to link the sulfate level, microstructure and strength.
- Sulfate level of cement influences ettringite content and porosity distribution.
- Thermodynamic and micromechanical models reflecting the sulfate impacts.
- Findings explained the effect of sulfate on mechanical performance of cements.

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ABSTRACT

We investigated the effect of sulfate on the porosity distribution and the resulting mechanical performance of Portland-based composite cements. The porosity was investigated by dynamic vapor sorption and mercury intrusion porosimetry technique. Additional experiments were performed and are recalled from the earlier publication (Adu-Amankwah et al., 2018) to assess the phase assemblage. The micromechanical model for strength upscaling was applied to link the sulfate level, resulting microstructure and the mechanical performance.

The results demonstrate that the sulfate content influences the ettringite content and impacts the porosity distribution. The ettringite stabilization by the sulfate added results in a higher solid volume and thus in a lower total pore volume. However, this phenomenon cannot explain the experimental observations of strength loss for high sulfate contents. Dynamic vapor sorption results reveal that there are fewer coarse capillary pores and more fine gel pores as the sulfate content increases. The mechanical model reflecting both aforementioned phenomena enables the reproduction of the strength evolution typical for the sulfate optimization experiments, i.e. the initial increase of the strength with the increasing sulfate content followed by the maximum and strength decrease.

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1. Introduction

Portland cements contain calcium sulfate as one of the components in the range equivalent to 2–5% SO₃. Calcium sulfate is added in order to control the setting time and assure a sufficient workability of the concretes [2]. However, the sulfate also has an impact on the evolution of the compressive strength. In general, there is an optimal content of the sulfate addition regarding the compressive strength, which is often different at early ages and at later ages [2,3].

The origin of the dependency of the compressive strength development on the cement SO₃ content is not yet fully under-

stood. The compressive strength of cementitious materials depends mainly on the porosity volume [2–4]. Thermodynamic modelling suggests that increasing calcium sulfate content in the cement increases the total volume of hydrates by increasing the ettringite content [5,1]. This leads to porosity reduction and hence should result in a higher strength. This phenomenon can well explain the initial increase of the strength up to the optimum sulfate content. However, it cannot explain the strength drop behind the optimum content. Several studies revealed that the sulfate content has only a little impact on the hydration kinetics of the anhydrous cement phases [5,1] at later hydration times, provided that the flash set is avoided. Consequently, the modification of the hydration kinetics cannot explain the aforementioned strength drop.

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Already in the 1960s, Copeland with Kantro and co-workers [6] observed that the sulfate content is influencing the properties of hardened pastes. In alite pastes, the increase of sulfate resulted in a decrease of the water content of the C-S-H accompanied by a decrease of the compressive strength. This influence was further extended to composite cements containing cement clinker, slag and limestone to explain their performance differences [1]. Adu-Amankwah et al. [1] reported that the sulfate dosage modified the microstructure and the properties of the C-S-H phase and particularly its apparent density. Similar findings were presented by Bentur [7] in the case of alite paste. This was further confirmed by the results of Mota et al. [8] who showed that sulfate has a pronounced impact on the C-S-H phase microstructure in alite pastes. In samples with addition of gypsum, a needled like C-S-H morphology was observed instead of a convergent-like morphology in the absence of sulfate ions. However, there is a lack of understanding regarding the exact effect of sulfate on C-S-H morphology and properties and hence on the resulting mortar and concrete performance. It is not clear if the apparent density changes reported in [1] are a result of changes to the properties of the solid C-S-H such as its water content or solid density or if the changes resulted from a different arrangement of the C-S-H and gel porosity.

This contribution follows our previous paper [1] investigating interactions of sulfate within ternary slag-limestone composite cements. Here we focus on the effect of the sulfate on the porosity distribution and the implications to the resulting mechanical performance. The changes to the porosity induced by the different sulfate contents were investigated by dynamic vapor sorption (DVS) technique and mercury intrusion porosimetry (MIP) after 90 days of hydration. At this time, the hydration degree of the samples is high and changes over time are limited allowing for the long in-situ investigations by the DVS. Additional experiments were performed to facilitate the thermodynamic calculations of phase assemblages providing volumes of hydrates, unreacted phases and porosity as functions of the hydration time and the initial cement composition. The micromechanical model for strength upscaling was applied [9] to explain the observed dependence of the mechanical performance on the sulfate level.

2. Materials

Composite cements, called binders within the following text, were prepared using a commercial CEM I 52.5 R cement according to EN-197, ground industrial granulated blast furnace slag and ground natural limestone. Additionally, ground natural anhydrite was used to fix the overall SO_3 level of the composite cements to 2, 3, 4 and 5%. The detailed composition of each binder is given in Table 1.

Note that the CEM I cement already contained some limestone and calcium sulfate. The binder compositions in Table 1 correspond to a constant clinker:slag:limestone ratio of 50:40:10. The details regarding sample preparation and material properties are given in [1]. When comparing to the cements investigated in our former paper, the sample with 5% SO_3 was added in order to better represent the trends. The same starting materials and procedures as in [1] were used for all samples.

3. Methods

3.1. Experimental techniques

The hydration process was reported earlier [1] for the samples containing 2, 3 and 4% SO_3 . For the sample S-5, that was not investigated within [1], the same hydration kinetics as for sample S-4 was assumed. Within the previous work [1], the impacts of sulfate dosage on hydration kinetics, the hydrated phase assemblages and microstructure were evaluated. The techniques used included isothermal calorimetry, chemical shrinkage, X-ray diffraction supported by the Rietveld-PONKCS method (QXRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM-EDS), mercury intrusion porosimetry (MIP) and thermodynamic modelling.

The paper focuses on assessing the porosity of the samples and to investigate the impact of sulfate content on the porosity distribution and resulting mechanical properties. For this task, an additional set of the samples was prepared and investigated after 90 days of hydration by techniques complementary to those used in [1].

3.1.1. Microstructure

A multi-technique approach was used to study the microstructure of cement pastes at 90 days of hydration. This included thermogravimetry (TGA), mercury intrusion porosimetry (MIP) and dynamic vapor sorption (DVS). These techniques give quantitative as well as qualitative information about the porosity of the investigated samples.

For the TGA and MIP, the hydration was stopped by the solvent exchange method by keeping samples in isopropanol and flushing them with petroleum ether. TGA were performed on about 30 mg of a previously ground material at a heating rate of 20 °C/min under N_2 atmosphere using NETZSCH STA 449F3 device. Crushed and stopped samples were tested by MIP with Pascal 140/440 Porosimeter from Thermo Scientific up to a maximal pressure of 400 MPa. The cumulative pore volume was calculated using the cylindrical and plate model together with the Washburn equation, taking the contact angle and the surface tension of mercury to be 140° and 0.48 N/m, respectively.

DVS was done on freshly ground cement paste (i.e. without stopping) using DVS Adventure from Surface Measurement Systems. The measurements were done on ~20 mg of sample at 20 °C. Sorption isotherms were measured from 98% RH down to 5% in several steps with a convergence equilibrium criterion of 0.005 mg/10 min. DVS sorption isotherms were converted into the pore size distribution using the BJH method [10]. This model assumes cylindrical pores in which there is a coexistence of capillary and adsorbed water on surfaces. The mass change associated with the desorption between 95% RH to 10% RH was assumed to correspond to the so-called 'DVS porosity'. Due to the bottle-ink effect, the DVS porosity also comprises saturated larger pores only accessible via smaller pores.

3.1.2. Mechanical performance

The compressive strength was determined according to EN 196-1, the details are given in [1].

Table 1
Composition of binders investigated (% weight).

| Mix designation | CEM I | Slag | Limestone | Extra anhydrite | Total SO_3 |
|-----------------|-------|-------|-----------|-----------------|---------------------|
| S-2 | 52.13 | 38.74 | 8.71 | 0.43 | 2 |
| S-3 | 51.18 | 38.03 | 8.55 | 2.24 | 3 |
| S-4 | 50.26 | 37.35 | 8.40 | 3.99 | 4 |
| S-5 | 49.34 | 36.67 | 8.25 | 5.88 | 5 |

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