



Effect of sulfate additions on hydration and performance of ternary slag-limestone composite cements

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HIGHLIGHTS

- The ettringite/AFm balance change the C₃A, slag, and limestone reaction kinetics.
- High sulfate increases AFt but the C-S-H has higher apparent density and water content.
- A finer pore structure is noticed in cements containing lower sulfate content.
- Optimized sulfate content is vital to maximize strength in ternary limestone cements.

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ABSTRACT

The global cement industry is striving to reduce its carbon footprint. Common approaches have included reduced clinker factors by blending cement clinker with supplementary cementitious materials (SCM). However supplies of SCMs are not sufficient to achieve replacement above about 30%. Limestone ternary cements offer the opportunity to reduce the clinker factor of cements while maximizing the efficiency of SCMs. In these cements, calcite from limestone reacts with dissolved aluminates to form carboaluminate and in the process influence hydration of other constituents. However, sulfates which are conventionally added to regulate the early reactions in cement also compete for aluminates. Here we have used complementary techniques to investigate the effects of calcium sulfate additions on hydration, microstructure and performance of composite Portland clinker-slag-limestone cements.

The results show that the presence of sulfate influenced the early-age reaction kinetics of the clinker phases and supplementary cementitious materials. However, even after sulfate depletion, the course of hydration and microstructures formed were significantly influenced. Increasing the sulfate level resulted in a gradual increase of the fraction of ettringite over AFm phases, coarser porosity and lower water content of the C-S-H. These microstructural changes impact the total porosity and hence cement strength in opposing ways, namely porosity is reduced with increasing ettringite fraction while the space filling capacity of the C-S-H is also reduced due to the lower water content of the C-S-H. These findings have important implications for optimizing the mechanical properties and durability of ternary blends.

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1. Introduction

Despite many years of research on cement hydration, many phenomena and interactions are still not sufficiently understood. One example is the effect of sulfate on cement hydration and performance. Sulfate is always a component of Portland cement, present as gypsum, basanite (calcium sulfate hemihydrate) or anhydrite. The main role of sulfate is to regulate early-age cement

properties [1]. However, the addition of sulfate influences not only the setting time but has also a strong impact on the evolution of the compressive strength of cement mortars and concretes.

Primarily, sulfate reacts with aluminate phases and retards the hydration of C₃A, thus controlling early-age properties [1–3]. The products of the reaction between C₃A (and C₄AF to a lesser extent) and sulfate are initially ettringite and later on monosulfoaluminate. The content of the sulfate thus regulates the balance between the AFt and AFm phases in Portland cement [4]. Hence, the sulfate addition modifies the composition of the phase assemblage, the resulting volume of the hydrates, the remaining porosity and

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consequently performance. This is mainly related to the fact that ettringite is characterized by the low density; 1.8 g/cm³ and has a high bound water content compared to the other AFm phases [5]. Thermodynamic calculations show that an increasing sulfate content leads to the formation of more ettringite and less AFm phases, and thus to a larger hydrate volume and lower porosity [6,7]. These theoretical observations agree with experimental observations, where in general the formation of more ettringite is accompanied by an increase in compressive strength [6,8]. However, above 3–4% SO₃ content, a decrease in compressive strength is typically observed [9–11], even though the volume of the hydrates is expected to increase due to greater ettringite formation [1,6,8]. The origin of this phenomenon is not yet understood.

The phenomena described are further complicated in the case of composite cements. In this type of cement, additional alumina is provided by cementitious additions such as fly ash [12,13], slag [7] and calcined clays [14]. This alumina can react with the sulfate. Moreover, modern composite cements contain limestone whose main component is calcite. Ternary limestone blends with aluminosilicate-bearing SCMs and Portland clinker offer the possibility to significantly reduce the clinker fraction of cements [15]. Limestone is a raw material for cement production and it is readily available in most parts of the world. When used without thermal treatment, limestone reduces the clinker factor and hence a lower embodied CO₂ and also maximizes the efficiency of other constituents in composite cements. In this type of composite cements, calcite reacts with the available alumina to form hemi and mono-carboaluminate phases instead of the monosulfoaluminate phase [6,13,14,16–18]. This results in ettringite stabilization, decreased porosity and increased strength. In parallel, gradual reaction of the calcite changes the alumina-sulfate balance during the course of hydration. In addition, the presence of limestone may result in an acceleration of the cement clinker and SCM reaction [6,18]. This means that in systems containing high volumes of supplementary cementitious material, the sulfate content must be carefully adjusted in order to prevent undersulfation and ensure optimal performance [6,14,19]. The optimal sulfate levels is generally higher than expected from the cement clinker only [6].

This paper reports on investigations of the interactions of sulfate within ternary slag-limestone composite cements. The impacts of sulfate dosage on hydration kinetics, the hydrated phase assemblages and microstructure are studied. The changes induced by the different sulfate content were correlated with the changes in the compressive strength development. Techniques used include 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.

2. Materials and methods

2.1. Materials

Ternary slag-limestone composite cements with a total sulfate content of 2%, 3% or 4% of SO₃ (designated as S-2, S-3 and S-4, respectively) were investigated. In order to prepare the composite cements, industrial CEM I 52.5 R cement, ground granulated blast furnace slag and natural limestone were used. Natural anhydrite additions were used to meet the targeted SO₃ levels.

The chemical composition and specific surface area of the materials, determined by XRF and Blaine measurements respectively, are shown in Table 1. The mineralogical compositions of the cement and the supplementary materials are shown in Table 2 and Table 3 respectively. The particle size distribution of all the

Table 1

Chemical composition (% weight) and Blaine fineness of the investigated materials.

Material	CEM I	Slag	Limestone	Anhydrite
SiO ₂	20.4	34.9	2.0	2.0
Al ₂ O ₃	5.6	11.6	0.8	0.6
TiO ₂	0.3	1.1	0.0	0.0
MnO	0.0	0.3	0.0	0.0
Fe ₂ O ₃	2.5	0.5	0.3	0.2
CaO	62.1	41.8	53.1	38.3
MgO	1.7	5.8	0.6	1.5
K ₂ O	0.7	0.5	0.1	0.2
Na ₂ O	0.0	0.0	0.0	0.0
SO ₃	3.5	3.1	0.0	52.2
P ₂ O ₅	0.1	0.0	0.0	0.0
LOI	2.0	(+1.45)	42.3	3.7
Blaine Fineness, m ² /kg	593	454	328	472

constituent materials, measured by laser granulometry, is shown in Fig. 1.

The mix proportions used are detailed in Table 4. The clinker to SCM ratio was maintained at 50:50, with limestone considered as an SCM where incorporated. The total sulfate contents were attained by adding the required amounts of ground anhydrite. The 1.9% calcite and the sulfates in the CEM I 52.5 R were accounted for in calculating the total limestone and sulfate contents for the ternary blends. The formulated cements were homogenized in a laboratory ball mill for at least 3 h, using polymer balls to prevent further grinding of the materials.

2.2. Methods

Compressive strength was measured in accordance with EN 196-1. Mortar prisms, 40 × 40 × 160 mm were made from 1 part of cement to 3 parts of sand at 0.5 w/b ratio using a 5-litre capacity digital mixer. The prisms were demolded after 24 h and immediately stored in water at 20 °C until testing. Six test specimens, obtained from splitting the prisms into halves were tested at selected ages up to 90 days.

To clarify the compressive strength evolution as a function of the sulfate content in the cements, hydration was followed, and microstructures were characterized, using paste samples. These were prepared according to the procedure for mortar preparation, as described in EN 196-1 but without aggregates using a vortex mixer. The mortar samples were prepared on a 5-litre capacity digital mixer. Care was taken to ensure homogeneous mixing by additional hand mixing during the mixing breaks.

Isothermal calorimetry was conducted on 9.0 g of paste prepared with 0.5 w/b ratio. The heat of reaction was measured continuously for 28 days at 20 °C using an 8-channel TAM Air calorimeter. Reference channels were filled with ampoules containing 6 g of quartz mixed with 3 g of deionized water.

Chemical shrinkage was measured by dilatometry, with 15 g of paste prepared with a 0.5 w/b ratio. The paste was mixed by hand for 2 min before being poured into a plastic beaker, 34 mm in diameter and 68 mm high. The beakers were tapped to level the paste and remove any entrapped air. The rest of the beaker was filled with deionized water, using a plastic syringe to minimize disturbance. The beaker was then sealed shut with a rubber stopper through which a 1 ml pipette was passed; with water filling the pipette in the process. A few drops of paraffin oil dyed with 1-(methylamino) anthraquinone, was added on top of the water, acting as a tracer, to follow the total shrinkage. Chemical shrinkage was continuously measured with a 10 MP camera, automatically capturing an image every 5 min for 28 days, monitoring the height of the tracer in the pipette. The images were analyzed using Zeiss Axiovision analyzer.

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