



Properties of a ternary calcium sulfoaluminate–calcium sulfate–fly ash cement[☆]



Socrates Ioannou^{a,*}, Lucía Reig^b, Kevin Paine^a, Keith Quillin^c

^a University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom

^b Universitat Jaume I, Avenida de Vicent Sos Baynat, s/n 12006, Castellón de la Plana, Spain

^c Building Research Establishment, Bucknalls Lane, Watford WD25 9XX, United Kingdom

ARTICLE INFO

Article history:

Received 8 November 2012

Accepted 21 September 2013

Keywords:

Sulfoaluminate (D)

Ettringite (D)

Fly ash (D)

Sulfate (D)

Hydration (A)

ABSTRACT

In this paper, cement combinations based on calcium sulfoaluminate cement (CSAC) were developed and the effect of fly ash and the hemihydrate form of calcium sulfate on the properties of the systems was studied. Fly ash (FA), anhydrite (ANH), flue-gas desulfurization gypsum (FGDG) and plaster gypsum (PL) were used to develop appropriate CSAC/calcium sulfate and CSAC/calcium sulfate/addition systems, the hydration of which was studied. Tested properties of cements were the compressive strength and the setting times. The results suggest that the use of fly ash in the presence of anhydrite accelerates the formation of a strong ettringite-rich matrix that firmly accommodated unreacted fly ash particles, both synergistically contributing to a dense microstructure. At a given sulfate content, the use of anhydrite was shown to be favourable in terms of the setting times, heat patterns and strength development compared to the hemihydrate-based formulations.

© 2013 The Authors. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The blending of by-products and additions with Portland cement (PC) is a well established approach to reducing the CO₂ emissions associated with the energy-intensive manufacture of cement. Currently 3.3 billion tonnes of PC is globally manufactured every year and it is estimated that the embodied CO₂ (eCO₂) for PC production is approximately 930 kg of CO₂ per tonne of PC produced [1,2]. An alternative way to reduce the eCO₂ of concrete is through the use of non-PC based systems as the binding ingredient. Calcium sulfoaluminate cements (CSAC), which have a lower eCO₂ than PC, have been developed and used in China on an industrial scale since the 1970s [3]. The primary raw materials are limestone, bauxite (or an aluminous clay) and gypsum, although by-products such as fly ash may be also used [4]. The preparation of clinker is achieved by burning the raw materials at temperatures in the range 1300–1350 °C in rotary kilns. This is 100–150 °C lower than PC production and thus the energy input requirement is lower. Manufacturing process is similar to that of PC although the resulting clinker has better grindability [5], leading to additional savings of 15–30 kWh with respect to energy consumption [6]. By considering

the eCO₂ emissions of individual cement compounds as given in [7], it can be estimated that the eCO₂ of a typical pure CSAC, consisting of ye'elimite, belite and aluminoferrite, is approximately 600 kg/t. This represents a reduction in eCO₂ of approximately 35% when compared to PC.

The primary hydration product of CSAC is ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) which forms at early ages (less than 48 h) as prismatic needles. Ettringite forms in the presence of sufficient calcium sulfate (gypsum or anhydrite) which can be either blended with the ye'elimite-rich clinker or added in the raw meal intergrinding process. The optimum amount of calcium sulfate for dominant formation of ettringite depends on several parameters i.e. the ye'elimite content, the calcium sulfate content and their respective molar ratios [8]. If there is deficiency in calcium sulfate, then there is a tendency for monosulfoaluminate to form; whereas an excess of calcium sulfate may lead to unstable expanding systems. Other products of the hydration of CSAC are mainly aluminate hydrates and calcium silicate hydrates. Unreacted ye'elimite is also typically present. Strengths of CSAC-based cements may reach over 40 MPa at 24 h [9] and they have been reported to exhibit very good resistance to aggressive environments, particularly to sulfate environments [10,11]. This is because aluminate-based phases are bound as sulfoaluminates at early stages of hydration and these are not available for reaction with external sulfate agents to form expansive ettringite.

The work reported in this paper aims to investigate the influence of two main aspects revolving around the optimization of hydration and performance of CSAC-based cement systems. The first is the form of calcium sulfate incorporated in the system recognising that the hemihydrate form is more readily available than anhydrite. The second aspect covered the development of a ternary system through the use of a low

Abbreviations: E, Ettringite; A, Anhydrite; Y, Ye'elimite; L, Gehlenite; Q, Quartz; S, Stratlingite; G, Gypsum; M, Mullite.

[☆] This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

* Corresponding author at: Wolfson Centre for Materials Processing, Brunel University, Kingston Lane, Uxbridge, UB8 3PH London, United Kingdom. Tel.: +44 7939983468.

E-mail address: Socrates.ioannou@brunel.ac.uk (S. Ioannou).

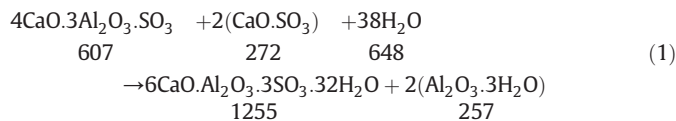
eCO₂ addition, particularly fly ash, which could provide a better balance between performance and eCO₂.

1.1. The calcium sulfate source

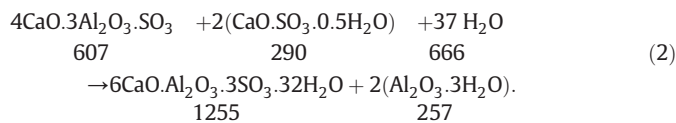
There is a considerable experimental activity on CSAC that has been focusing on the use of anhydrite as the calcium sulfate source in the CSAC system. Extensive work throughout the last decades is encapsulated in review articles [12,13]. Indeed, consensus indicates that anhydrous calcium sulfate is the predominant and preferable calcium sulfate source within the system. The use of other forms of calcium sulfate, particularly hemihydrate, however, is not fully documented so as to offer justifications of any cost-based, environmental-based or performance-based advantages associated with anhydrite preference in CSAC. Moreover, such lack of available data does not provide a clear indication of the influence of the hemihydrate of calcium sulfate on the hydration of CSAC. A more detailed look is therefore required at this type of calcium sulfate.

The intrinsic properties of both hemihydrate calcium sulfate and anhydrite are compared and established [14,15]. Setting times of the hemihydrate are known to be considerably short due to its high solubility (typically in the range of 7–9 g/l) and its reactivity, as opposed to that of anhydrite (approximately 2.5–3.0 g/l) [16]. Eqs. 1 and 2 suggest that during the reaction of both calcium sulfate forms with ye'elimite, the quantities of ettringite and Al(OH)₃ formed are comparable. The only parameter that varies is the amount of water needed for complete phase formation.

Ye'elimite + anhydrite:



Ye'elimite + hemihydrate:



Based on the available literature and data, it is therefore necessary to distinguish the beneficial characteristics offered by each form of calcium sulfate when incorporated in a CSAC system.

1.2. The use of fly ash in CSAC/calcium sulfate system

Although the eCO₂ associated with the use of an optimized CSAC/calcium sulfate system may be lower than that of PC, potentially greater savings may be achieved based on the development of ternary CSAC-based systems with maintained performance properties.

By-products from coal combustion plants are associated with almost zero eCO₂, whilst they may provide microstructural and mechanical advantages to cementitious systems when incorporated at optimum percentages. One advantage is the pozzolanic reaction. The use of low

eCO₂ pozzolanic by-products – particularly fly ash – in the CSAC system, may instigate reaction with Ca(OH)₂ yielding from belite hydration in CSAC thus providing additional C–S–H gel. Previous studies on compressive strengths of CSAC/fly ash blends suggest a slight decrease in strengths when fly ash contents are higher than 10% [17]. However, there is still limited understanding and lack of data on the hydration mechanisms of such systems. Given this, and by considering the advantageous effect of particle packing that fly ash may potentially provide when acting as a low-eCO₂ filler, then it is possible that a more sustainable system may be developed whilst maintaining its mechanical and microstructural properties.

2. Materials and methods

The materials used in this study are shown in Table 1. Particle size distribution was determined using a Malvern Mastersizer 2000 laser diffraction equipment. Anhydrite (ANH), plaster (PL) and flue gas desulphurization gypsum (FGDG) were used as the calcium sulfate sources in the CSAC system.

The ye'elimite content in the CSAC clinker was found to be 71% and the belite content was 15%, although no calcium sulfate was detected. To confirm the sulfate type in FGDG, PL and ANH, TG analysis (20 °C to 300 °C at a rate of 10 °C/min) was conducted and mass losses of 5.43% and 5.16% respectively were obtained in the range of 135–137 °C. No mass loss was observed in ANH.

In order to assess the hydration processes of the systems, cement pastes were prepared at a w/c ratio of 0.5 and cured in a 20 °C water-curing tank until age of testing. TG and XRD analyses were performed after 1, 3, 7 and 28 curing days and SEM images of the pastes cured for 28 days were obtained, assuming that this period was adequate for allowing full formation of all hydration products. Acetone was used to arrest the hydration of the cements.

Setting times of the pastes were determined in accordance to BS EN 196-3:1995 [19]. Heat of hydration was determined using a Wexham development JAF conduction calorimeter. Mortar samples were prepared to assess the mechanical properties and dimensional changes of the combinations. The compressive strength was conducted in accordance to BS EN 196-1:1995 [20] and the dimensional changes were monitored on air-cured mortar samples stored in conditioning chamber (maintained 20 °C, 65% RH) at 1, 7, 28 and 90 days of age.

For the development of appropriate CSAC/calcium sulfate combinations, the following criteria were taken into consideration:

- Achievement of a cement strength class equivalent (or higher) to that of a 42,5N (or R) conventional cement as defined in BS EN 197-1:2000 [21]
- A calcium sulfate content lower than the value which creates dimensional instability. This was achieved experimentally by monitoring the dimensional change of CSAC/calcium sulfate cement pastes at increasing calcium sulfate contents.
- A minimum content of calcium sulfate in the system to ensure ettringite formation and avoid monosulfoaluminate formation by using stoichiometric approach.

Table 1
Materials used in the experimental.

Material	Abbreviation	Particle density (kg/m ³)	Mean diameter size (µm)	Particle size distribution (µm)	
				d ₁₀	d ₉₀
Calcium sulfoaluminate cement	CSAC	2790	25.3	2.2	64.8
Fly ash, category N to BS EN 450-1:2012 [18]	FA	2290	34.5	2.4	81.6
Calcium sulfate: flue gas desulfurization gypsum	FGDG	2520	47.4	8.7	119.2
Calcium sulfate: gypsum plaster	PL	2600	27.5	3.2	86.2
Calcium sulfate: anhydrite	ANH	2950	24.5	2.3	42.1

Download English Version:

<https://daneshyari.com/en/article/7885668>

Download Persian Version:

<https://daneshyari.com/article/7885668>

[Daneshyari.com](https://daneshyari.com)