

Characteristics of cement pastes containing sulphoaluminate and belite prepared from nano-materials

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HIGHLIGHTS

- ▶ Substitution of OPC with $C_4A_3\bar{S}$ or $C_4A\bar{S}$ + β - C_2S tends to shorten the setting times.
- ▶ The fast setting of cement pastes is due to the formation of Aft and AFm.
- ▶ Substitution of OPC with $C_4A_3\bar{S}$ or $C_4A\bar{S}$ increases the chemically combined water.
- ▶ The addition of $C_4A_3\bar{S}$ or $C_4A\bar{S}$ with belite decreases the free portlandite.
- ▶ Pastes containing $C_4A_3\bar{S}$ or $C_4A\bar{S}$ give higher compressive strength.

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ABSTRACT

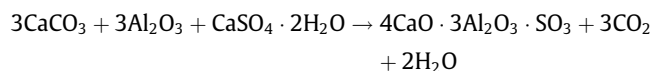
The sulphoaluminate phase $C_4A_3\bar{S}$ as well as β - C_2S represent an important factor for the preparation of rapid hardened sulphoaluminate–belite cement. The hydration of $C_4A_3\bar{S}$ forms ettringite and monosulphate hydrates in addition to the liberation of aluminium hydroxide. The hydration rate of belite is much slower than that of $C_4A_3\bar{S}$, but becomes significant at later ages. Two mixes containing sulphoaluminate ($C_4A_3\bar{S}$) and monosulphate mix ($C_4A_3\bar{S}$, with $8\bar{C}S + 6C$) in addition to belite (β - C_2S) were synthesized from nano-materials after firing at 1250 °C. The hydration characteristics of 10% $C_4A_3\bar{S}$ or 10% $C_4A\bar{S}$ in addition to 10% β - C_2S on the expense of OPC were studied. The results revealed that the substitution of OPC with sulphoaluminate mixes as well as belite shortens the setting times. The rate of hydration of OPC with sulphoaluminate–belite phases is increased from the formation of more sulphoaluminate hydrates and the consumption of portlandite. Also, these mixes give higher chemically combined water contents. The monosulphate hydrate is deposited in some of open pores in the dormant period of hydration that tends to increase the compressive strength of sulphoaluminate–belite cement pastes.

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1. Introduction

Calcium sulphoaluminate, $C_4A_3\bar{S}$, is an important phase for the rapid hardened sulphoaluminate cement. Its formation from molar mixes of the oxides of calcium, aluminium and sulphur derived from synthetic pure chemicals and commercial grade natural minerals, such as limestone, bauxite and gypsum have been studied. The degree of formation of $C_4A_3\bar{S}$ phase in the temperature range of 1100–1325 °C is comparatively higher from pure chemicals. This is due to increased solid state reaction between these oxides [1].

Calcium sulphoaluminate may be also, produced from a starting blend of an appropriate oxide composition by burning at a temperature of about 1250–1300 °C [2,3]:



The sulphoaluminate phase is stable up to about 1350–1400 °C. Its crystalline structure consists of a three-dimensional framework of AlO_4 tetrahedra sharing corners, with Ca^{2+} and SO_4^{2-} ions located in the existing cavities. It belongs to the tetragonal system. Above about 1350 °C this phase becomes unstable and starts to decompose [4]. The Al^{3+} within the structure of the $C_4A_3\bar{S}$ phase may be partially substituted by Fe^{3+} ions. The reactivity of this phase will decline with iron content in the crystalline lattice.

The hydration of $C_4A_3\bar{S}$ depends on whether calcium sulphate and calcium hydroxide are also present, and progresses at temperatures up to 75 °C [2,5,6]. In pure water $C_4A_3\bar{S}$ yields $C_4A\bar{S}H_{12}$ and AH_3 as products of hydration. Two mixes of $C_4A_3\bar{S}$ and $\bar{C}SH_2$ yield ettringite alone, if mixed at a molar ratio of at least 1:2, and a combination of ettringite and monosulfate if the amount of gypsum is

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reduced. Simultaneously aluminium hydroxide is formed as a reaction product. Three mixes of $C_4A_3\bar{S}$ with calcium hydroxide, but without calcium sulfate, yield the hydrogarnet phase C_3AH_6 and an AFm phase of the approximate composition $C_3A \cdot 1/2\bar{C}\bar{S} \cdot 1/2CH.xH$. Four in the presence of sufficient amounts of both gypsum and calcium hydroxide ettringite is formed as the sole reaction product.

Calcium sulfoaluminate modified Portland cements may be produced by combining ordinary Portland cement clinker with limited amounts of calcium sulfoaluminate, produced separately, and calcium sulfate. Taczuk et al. [7] studied sulfoaluminate-modified cements with $C_4A_3\bar{S}$ contents between 5% and 20% and with a sulfoaluminate/calcium sulfate molar ratio of 1:8. Calcium sulfate was added as anhydrite or gypsum. The form of calcium sulfate present determined its dissolution rate (the dissolution rate of gypsum is much faster than that of anhydrite) and thus the properties of the produced cement. It was found that the presence of anhydrite tended to favour monosulfate precipitation at the expense of ettringite. As a consequence, such cements exhibited significantly shorter setting times and higher short-term strengths.

Beretka et al. [8] produced a series of cements that contained only the phases $C_4A_3\bar{S}$ (15–50%), $C_5S_2\bar{S}$ (sulfospurrite) (25–77%), and $C\bar{S}$ (anhydrite) (8–25%), but no calcium silicates. Such cements exhibit a very fast initial ettringite formation and strength development, but no additional strength gain at later ages. Mixes with water contents too low for complete conversion of $C_4A_3\bar{S}$ to ettringite exhibit expansion due to delayed ettringite formation, associated with an uptake of water from the environment. While sulfoaluminate-modified Portland cements with limited amounts of $C_4A_3\bar{S}$ and calcium sulfate exhibit no expansion, those with higher amounts of these phases expand and are used as expansive cements.

The hydration of the belite is much slower than that of $C_4A_3\bar{S}$, and becomes significant only after longer hydration times. Very little is hydrated within the first 7 days, and between about 5% and 40% hydrates within 28 days [9–11]. The rate of hydration generally increases with SO_3 content in cement [10]. The C–S–H phase formed in the hydration is mainly responsible for the ultimate strength of the hardened cement paste. Most or all portlandite produced in the hydration of C_2S is consumed in the formation of ettringite, just like the free calcium oxide present in the original clinker. At later ages of hydration limited amounts of this phase may be also formed as larger needle-like crystals, to be precipitated in larger pore spaces still existing in the paste [10]. The gehlenite hydrate, C_2ASH_8 , found in a different system, seems to be a result of the hydration of C_3S or β - C_2S in alumina saturated solution (alumina components), $C_4A_3\bar{S}$ [12].

In mature sulphobelite cement pastes the C–S–H phase and Aft (ettringite) are the two main hydration products. Variable amounts of monosulphate (AFm) and residual gypsum may be also present depending on the amount of calcium sulfate in the original cement. The material contains no, or very little, free calcium hydroxide, as it has been consumed in the formation of ettringite. The alkalinity of the pore liquid is relatively low, at around pH = 9.5–10 [9].

The aim of the present investigation is to study the main physico-mechanical properties of the sulfoaluminate–belite cement pastes containing $C_4A_3\bar{S}$ or monosulphate mix and belite prepared from nano-materials such as $Ca(NO_3)_2$, $Al(OH)_3$, SiO_2 and precipitated $CaSO_4 \cdot 2H_2O$.

2. Experimental technique

The materials used in this work were nano- $Ca(NO_3)_2$, nano- $Al(OH)_3$, nano-silica and $CaSO_4 \cdot 2H_2O$ as obtained from Prolabo company. Nano- $Al(OH)_3$ was prepared from Al-dross after leaching with commercial HCl then precipitated by ammonia solution at pH = 8 [13]. Nano-silica was also synthesized by acid hydrolysis of sodium silicate Na_2SiO_3 using 0.5 N HCl and stirred slowly at 60 °C at pH between 1

and 2 [14]. Nano- $Ca(NO_3)_2$ was freshly prepared by the addition of nitric acid (1:1) to $CaCO_3$ to complete reaction then evaporated at 60 °C until solidification. The powder of $Ca(NO_3)_2$ was dried at 50 °C for 24 h. The materials were investigated for their chemical composition by using XRF, XRD and TEM. Table 1 summarizes the chemical composition of nano- SiO_2 and nano- $Al(OH)_3$. Fig. 1 shows XRD patterns of nano-silica and $Al(OH)_3$. Fig. 2 shows TEM micrograph of nano- SiO_2 and nano- $Al(OH)_3$ with crystal sizes of 13 and 38 nm [14].

OPC cement was provided from Almasria Cement Company. The chemical analyses of investigated cements are given in Table 2. The mix composition of investigated mixes is given in Table 3.

The calcium sulfoaluminate phase ($C_4A_3\bar{S}$), anhydrous monosulphate mix ($C_4A\bar{S}$) and active belite (β - C_2S) were prepared from the stoichiometric amounts of above materials. Each mix was separately mixed in a ball mill for one hour to attain complete homogeneity; this was followed by firing at 1250 °C for 2 h, then cooled suddenly in air [14]. Table 3 shows the mix composition of investigated sulfoaluminate–belite cements.

The water of consistency and setting times were measured according to ASTM Designation C191 [15], then pressed in $0.5 \times 0.5 \times 0.5$ in.³ moulds. The moulds were cured in a humidity chamber at 100% RH at room temperature 23 ± 2 °C for 24 h, then demoulded and cured in the humidity chamber till the times of testing (3, 7, 28 and 90 days) were reached. At the end of each curing time, the hydration of the paste was stopped and the combined water and free portlandite contents were estimated on the ignited weight bases as described elsewhere [16,17]. The phase composition of hydration products was also followed by using XRD and DSC techniques.

3. Results and discussion

3.1. Sulfoaluminate–belite cement pastes

This section deals with the characteristics of OPC (M0) and OPC-sulfoaluminate (MS) as well as OPC-sulfoaluminate–belite (MSB) cement pastes. The hydration characteristics of these cement pastes were investigated by the determination of combined water and free lime contents as well as compressive strength at the different curing ages. The hydration products were identified by the aid of XRD and DSC techniques for some selected samples.

3.1.1. Water of consistency and setting time

The water of consistency, initial and final setting times of M0, MS and MSB cement pastes are graphically represented as a function of sulfoaluminate and belite contents in Fig. 3. The results show that the water of consistency of sulfoaluminate cement pastes is higher than that of Portland cement. This is basically due to the formation of ettringite which has water content [18]. Moreover, the higher surface area of sulfoaluminate gives high surface area of blended cement compared with that of Portland cement due to the water demand increases. It is clear that the water of consistency of the sulfoaluminate–belite cement pastes (MSB) is nearly the same of the plain OPC, due to the low rate of hydration of belite at early ages. The results of Fig. 3 indicate also that the initial and final setting times are shortened with the addition of sulfoaluminate and belite phases. This is attributed to the very rapid hydration of $C_4A_3\bar{S}$ forming needle-like ettringite, which is responsible for the quick setting of sulfoaluminate cements [19]. Furthermore, with the addition of the nano-particles of these phases, the average particle size is getting smaller and the setting time is shortened.

3.1.2. Chemically combined water contents

The chemically combined water contents of M0, MS and MSB cement pastes are graphically plotted as a function of curing time in Fig. 4. The combined water content generally increases with curing time due to the progress of hydration and formation of hydration products such as CSH, sulfoaluminate hydrates and C_2ASH_8 [12].

The chemically combined water contents of sulfoaluminate and sulfoaluminate–belite cement pastes are higher than those of OPC. This is related to the very fast hydration reaction rate of calcium sulfoaluminate phase which results in a rapid consumption of mixing water with the formation of ettringite which has a

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