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Hydration of C_4AF in the presence of other phases: A synchrotron X-ray powder diffraction study

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HIGHLIGHTS

- Hydration behaviour at early ages of C_4AF was studied in this work.
- The gypsum effect, amount of water and presence of ye'elimite were investigated.
- Synchrotron X-ray powder diffraction has been mainly used.
- A structural study for the $C_3A_{0.845}F_{0.155}H_6$ phase was performed.
- The hydration of C_4AF is inhibited by the presence of pseudocubic ye'elimite.

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ABSTRACT

Hydration behaviour of C_4AF in selected experimental conditions has been determined. C_4AF has been hydrated in the absence and presence of gypsum, two polymorphs of ye'elimite and different water/solid ratios. C_4AF in the presence of water hydrates to form mainly a hydrogarnet-type phase. The crystal structure of $C_3A_{0.845}F_{0.155}H_6$ is reported from the Rietveld analysis of its synchrotron X-ray powder diffraction pattern. The hydration of C_4AF in the presence of gypsum gives AFt. However, the mixture tetracalcium aluminoferrite/gypsum/ye'elimite gives both AFt and AFm phases. C_4AF hydrated with ye'elimite in the absence of gypsum gives only AFm. Ye'elimite has inhibited tetracalcium aluminoferrite hydration.

1. Introduction

X-ray powder diffraction (XRPD) is very well suited for *in-situ* studies of chemical processes involving crystalline materials [1,2]. During the last years, it has been reported quantitative phase analysis of cements, clinkers and supplementary cementitious materials by combining XRPD and Rietveld methodology [3–6]. More recently, this procedure has been expanded to hydrated cementitious systems [1,7] and in some of these studies, the non diffracting fraction was also determined [8–10], although a more precise term was coined: Amorphous and Crystalline not-quantified content (ACn) [11]. Furthermore, the use of intense monochromatic X-rays, such as synchrotron X-rays, coupled with a fast X-ray detection system permits high-resolution time-resolved diffraction experiments allowing *in-situ* measurements during the hydration process of cements [1,12,13].

The tetracalcium aluminoferrite phase, C_4AF in cement nomenclature, also known as brownmillerite, is the major iron-containing phase in Ordinary Portland Cement (OPC) and is also present in iron rich belite calcium sulfoaluminate cements [14,15]. This phase has been deeply studied [16–19] and for this reason, their crystal structures and chemical compositions are currently known, including the structural variations which have placed in the $Ca_2(Fe_{2-y}Al_y)O_5$ series [20], where y can oscillate from 0 to about 1.33 [19] in high iron content cements. In Portland cements this phase is supposed to have an ideal composition with $y = 1$. However, it has been reported that other elements could be also present in the composition of the C_4AF phase and for this reason the A/F ratio is not exactly unity [21].

In the absence of any other phases, the hydration of C_4AF is similar to the hydration of C_3A, in which a C–A–H gel first coats the C_3A grains. This gel presents metastable hexagonal C–A–H plates that

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finally convert to the stable cubic hydrate C_3AH_6 [22–24]. However, the hydration products are (quite often) assumed to incorporate some iron in the case of the tetracalcium aluminoferrite phase [25–29]. Firstly, in the hydration of tetracalcium aluminoferrite with water a metastable type-gel C-(A,F)-H [28] is formed and with the time this gel converts to a hydrogarnet phase, also known as katoite, $C_3(A,F)H_6$ [28], with an Al/(Al + Fe) ratio of about 0.4. However, other authors [25,30,31] stated that solid solution between C_3AH_6 and C_3FH_6 is not formed.

The exact Al/Fe ratios of the hydrogarnets are as yet under debate but it is generally accepted that the Al/Fe ratio of the crystalline products is greater than in C_4AF itself [32].

The hydration of C_4AF [28] could be written as:

$$C_4AF + 10H \rightarrow C_3AH_6 + FH_3 + CH \qquad (1)$$

where FH_3 indicates a hydrated amorphous Fe-containing gel. If the case that Fe is incorporated into the hydrogarnet product, then the reaction could be expressed as:

$$C_4AF + 10H \rightarrow \frac{4}{3}C_3(A_{0.75}F_{0.25})H_6 + \frac{2}{3}FH_3 \qquad (2)$$

When calcium sulfates are added, the direct hydration of C_4AF to $C_3(A,F)H_6$ is inhibited. Consequently, ettringite is the common hydration product observed in this case. There are some theories about the mechanism governing the retardation process. However, the formation of hydroxy-AFm gel surrounding C_4AF particles which yields to ettringite crystallization centers is the most likely mechanism [29].

In the presence of a source of sulfate the reaction could be formulated as [28]:

$$C_4AF + 3C\bar{S}H_2 + 30H \rightarrow C_6A\bar{S}_3H_{32} + CH + FH_3 \qquad (3)$$

where $C_6A\bar{S}_3H_{32}$ denotes ettringite (also known as AFt). Again, iron may be incorporated in the ettringite structure as detailed by [26] according to reaction (3.1):

$$C_4AF + 4C\bar{S}H_2 + \frac{106}{3}H \rightarrow \frac{4}{3}C_6(A_{0.75}F_{0.25})\bar{S}_3H_{31} + \frac{2}{3}FH_3 \qquad (3.1)$$

where $C_6(A_{0.75}F_{0.25})\bar{S}_3H_{32}$ stands for iron-bearing AFt.

Successively, ettringite can decompose to form an AFm monosulfoaluminate hydrate in the presence of C_4AF as stated next:

$$C_6A\bar{S}_3H_{32} + C_4AF \rightarrow 2C_4A\bar{S}H_n + C\bar{S}H_2 + (26-2n)H + FH_3 + CH \qquad (4)$$

If there is any amount of C_4AF, this could react with gypsum to form AFm ($C_4A\bar{S}H_n$), then the reaction could be expressed as:

$$C_4AF + C\bar{S}H_2 + (n+2)H \rightarrow C_4A\bar{S}H_n + FH_3 + CH \qquad (5)$$

Moreover, it has been reported [28] that a partial series of solid solutions can be formed between C_3AH_6 and C_3FH_6; accordingly the previous equations could be also expressed in terms of $C_x(A,F)_yH_z$ or $C_x(A,F)_y\bar{S}_wH_z$.

The main purpose of the present work has been to study the hydration of C_4AF phase in different environments: in the presence and absence of gypsum and in the presence of both polymorphs of ye'elimite, stoichiometric (orthorhombic) and solid solution (pseudo-cubic). The interest of studying these systems as simple mixtures is to better understand the hydration mechanisms of new eco-cements based on calcium sulfoaluminate, which contains different polymorphs of ye'elimite with C_4AF [12,14]. In order to do so, synchrotron XRPD (SXRPD) and Rietveld methodology are employed. The advantage of using high energy radiation is mainly the minimization of microabsorption effects. Kinetics of hydration have been established and correlated to calorimetric data. Scanning electron microscopy (SEM) has been also done to corroborate the results. Moreover, high-resolution SXRPD and transmission electron microscopy (TEM) were used to refine the crystal structure of one of the hydrated crystalline phases, $C_3(A,F)H_6$.

2. Experimental section

2.1. Sample preparation

Tetracalcium aluminoferrite (C_4AF) was prepared by mixing suitable amounts of $CaCO_3$ (99.95%, Alfa Aesar), Al_2O_3 (99.997%, Alfa Aesar) and Fe_2O_3 (99.945%, Alfa Aesar), to obtain approximately 50 g of sample with targeted chemical formula of Ca_2AlFeO_5, i.e. $x = 1$. The raw mixture was ground for 5 min and heated at 1000 °C for 4 h (heating rate of 10 °C/min). After that, the powder was ground for 45 min in a Micro-deval machine with a cylinder container and steel balls and was pelletized (600 mm diameter and 1000 MPa). Finally, the pellets were heated at 1350 °C for 4 h (heating rate of 10 °C/min) followed by quenching from high temperature with an air flow.

Moreover, stoichiometric (st-) $Ca_4[Al_6O_{12}]SO_4$ and solid solution (ss-) $Ca_{3.8}Na_{0.2}Al_{5.6}Fe_{0.2}Si_{0.2}O_{12}SO_4$ ye'elimites has been used for this study. Ye'elimite polymorphs were prepared as previously reported [33,34].

C_4AF was mixed, in some cases, with gypsum (g), stoichiometric (st-) or solid solution (ss-) ye'elimite. Table 1 reports paste mix proportions, including water/solid (w/s) ratios. The gypsum used for the hydration studies was that marketed by BELITH S.P.R.L. (Belgium).

For this study, *in-situ* SXRPD experimental set up was employed. All the anhydrous mixtures were mixed with 15 wt% of SiO_2 (99.56%, ABCR) as an internal standard [13,35] and SXRPD data were collected to obtain the initial phase assemblage (t_0). This standard presents an amorphous content of 12.7(1) wt% which was determined by the external standard method [36]. Moreover, it is important to bear in mind that in the reported water/solid ratio, the amount of internal standard is not taken into account. Pastes were *ex-situ* prepared and immediately loaded into glass capillaries of 0.5 mm of diameter with a syringe. The capillaries were sealed with grease to avoid any water loss.

2.2. Synchrotron X-ray powder diffraction (SXRPD)

SXRPD patterns were collected at room temperature in Debye–Scherrer (transmission) mode using the high-resolution X-ray powder diffraction beamline of ALBA synchrotron (Barcelona, Spain) [37]. The wavelength, 0.61975(1) Å, was selected with a double-crystal Si (111) monochromator and determined from Si640d NIST standard ($a = 5.43123$ Å). The diffractometer is equipped with a MYTHEN detector especially suited for time-resolved experiments. The capillaries were rotated during data collection to improve diffracting particle statistics and the synchrotron beam was focused in the detector to improve the powder diffraction peak shapes. The data acquisition time was ~15 min per pattern to attain very good signal-to-noise ratio over the angular range 1–35° (2θ).

The diffractometer is also equipped with a detector system based on crystal analyzers in the diffracted beam especially suited for extremely high-resolution experiments giving also a very flat background. One of the samples was measured

Table 1
Paste mix proportions in weight percentages (wt%). The total heat evolved at 2 days of hydration is also given.

Mixture	C_4AF wt%	$st\text{-}C_4A_3\bar{S}$ wt%	$ss\text{-}C_4A_3\bar{S}$ wt%	Gypsum wt%	Water/solid	Total heat (J/g)
$C_4AF\_0.8$	100	–	–	–	0.8	–
$C_4AF\_g\_1.0$	65.3	–	–	34.7	1.0	382.4
$C_4AF\_st\text{-}C_4A_3\bar{S}\_g\_1.0$	32.7	49.1	–	18.2	1.0	382.2
$C_4AF\_ss\text{-}C_4A_3\bar{S}\_g\_1.0$	32.7	–	49.1	18.2	1.0	409.1
$C_4AF\_st\text{-}C_4A_3\bar{S}\_g\_0.7$	32.7	49.1	–	18.2	0.7	–
$C_4AF\_st\text{-}C_4A_3\bar{S}\_g\_1.3$	32.7	49.1	–	18.2	1.3	–
$C_4AF\_st\text{-}C_4A_3\bar{S}\_1.0$	66.6	33.4	–	–	1.0	–