



Phase assemblage in ettringite-forming cement pastes: A X-ray diffraction and thermal analysis characterization



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ABSTRACT

The study attempts to describe the evolution of the solid phase composition with ongoing hydration in three different calcium aluminate rich cement paste mixtures by means of XRD and thermal analysis. The phase assemblage was followed quantitatively at discrete ages of 1, 7, 28, 56 and 90 days. Ettringite was the main crystalline hydration product. Quantification of amorphous fractions using the external standard method was performed and relatively high amounts of amorphous fractions were reported in all the cases.

Thermal analysis revealed that the X-ray amorphous hydrate fraction was mainly composed of monosulphate, AH_3 and C-S-H. The presence of strätlingite, was not clearly manifested in any of the DTG curves. A mass balance calculation based on stoichiometric reactions was performed in order to estimate the amounts of monosulphate, AH_3 , and C-S-H. The quantities of the amorphous portions obtained from QXRD were observed to be higher as those estimated from mass balance calculations. Additional calculations from oxide balance suggested that besides AH_3 monosulphate and C-S-H, an X-ray amorphous AFm or/and C-S-H type like phase might form in the early age of hydration.

During Rietveld refinement, the impact of the number of Chebyshev background polynomials in the determination of amorphous content was investigated.

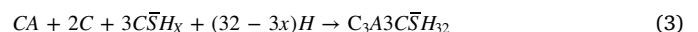
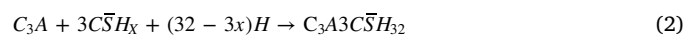
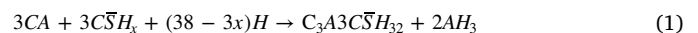
1. Introduction

1.1. Background

Fast setting binders are often composed of three mineral components which are Portland cement (PC), calcium aluminate cement (CAC) and calcium sulphate ($C\bar{S}H_x$). In PC/CAC/ $C\bar{S}H_x$ ternary systems, two mixes can be distinguished, a CAC richer mix and a PC richer mix. As reported by several researchers [1–3] these compositions are mainly used as technical mortars for concrete fast repair and protection, or flooring installation with selfleveling compounds. Ettringite is one of the main phases formed in such systems. Although not really proven, several studies suggest that fast setting is related with ettringite formation [4–7]. The formation of ettringite occurs through solution [8]. Besides ettringite, other hydrates such as, C-S-H, AH_3 and AFm constituents are formed (cement notation will be used throughout the text with A: Al_2O_3 , C: CaO, F: Fe_2O_3 , H: H_2O , M: MgO, S: SiO_2 , \bar{S} : SO_3 , T: TiO_2).

The hydration steps of ternary systems composed of OPC, CAC and $C\bar{S}$ are complex. Some of the main reactions occurring during the hydration process are described below. When a ternary binder system

(PC / CAC / $C\bar{S}H_x$) encounters water, the phases dissolve and the following reactions take place:



where $x=0$ for anhydrite, $x=0.5$ for hemihydrate and $x=2$ for gypsum.

When the calcium sulphate is depleted, ettringite reacts with remaining anhydrous CA to form calcium monosulphate (AFm phase).



Other coupled reactions between hydrates and anhydrous phases coming from the different cements, are also relevant and most of them can be found in the literature [6]. The complexities of the mechanisms involved in these systems have been reported by various studies [9–11].

1.2. Scope of the present study

Despite the available data on the hydration mechanisms of ternary

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binders, there is still a debate what the formation of considerable amounts of X-ray amorphous hydrates and their composition as the hydration proceeds concerns. AH_3 and C-S-H are assumed part of it, while there are indications that besides C-S-H and AH_3 , other hydrates not detectable by X-ray and thermal analysis could form [12–16]. Nevertheless the above mentioned studies were focused on calcium sulfo-aluminate (CSA) based systems and few work has been done in the characterization and quantification of amorphous phases in mixtures of Portland cement, calcium aluminate cement and calcium sulphate [17]. Therefore, a series of experiments was set-up and the amorphous fractions of three different ettringite-forming pastes (CAC rich mixtures) were investigated by means of X-ray diffraction and thermal analysis.

X-ray diffraction in combination with the Rietveld method was carried out to identify the formed hydrates and their changes over time. Since the Rietveld quantitative phase analysis only considers the crystalline phases [18] and normalizes their sum to 100%, successful strategies that account for the potential amorphous or minor non-identified crystalline phase have been adopted [19]. In the present work, the external standard methodology [20–22] was applied to quantify absolute phase contents and to calculate from there an overall amorphous content. Thermogravimetric analysis (TGA) has been adopted as complementary technique to X-ray diffraction as the method is able to identify X-ray amorphous hydrates. The results obtained by both methods were compared. Stoichiometric or mass balance calculations were additionally applied to estimate the content of X-ray amorphous phases such as, AH_3 C-S-H and monosulphate. Furthermore, the role of the number of background coefficients in the accurate determination of the amorphous phase content was investigated.

The results obtained from this combined study gave useful insights concerning the formation of amorphous fractions in ettringite-rich pastes. The study highlights the fact that besides C-S-H and AH_3 the formation of an additional X-ray amorphous AFm or/and C-S-H type like phase is very likely to occur.

2. Materials and methods

2.1. Materials, compositions and sample preparation

During the experiments we made use of Ordinary Portland cement, calcium aluminate cement and calcium sulphate (α -Hemihydrate). In these so-called ettringite systems [23], there are several situations depending on the proportions of each material. The used formulations that were studied here are shown in Table 1. In System A the amount of CAC and $C\bar{S}$ is high and very low amount of OPC were used. The amount of OPC was increased in system B and system C contains only CAC and $C\bar{S}$.

Chemical and mineralogical compositions of the materials are shown in Table 2. The chemical composition was measured by X-ray fluorescence (XRF) and the mineralogical composition was determined by XRD. It was found that OPC does not contain significant quantities of amorphous material and all in all, we were able to observe an amorphous content of 2.8 wt%. Meanwhile, an amorphous content of 7.4 wt% was detected in calcium aluminate cement. In Table 3 the composition of the mineral phases present in each system is provided.

All the experiments were performed at 21 °C and at a water to

Table 1
Formulations of the investigated cement pastes.

Systems	OPC (wt%)	CAC (wt%)	α -HH (wt%)
A	13	64.5	22.5
B	31	49	20
C	–	70	30

Table 2
Chemical and mineralogical composition of the materials used.

	OPC (wt%)	CAC (wt%)	α -HH (wt%)	OPC (wt%)	CAC (wt%)	α -HH (wt%)
C_3S	55.2			CaO	62.2	37.7
C_2S	16.4	2.6		SiO_2	20.0	4.2
C_4AF	14.8	14.7		Fe_2O_3	3.8	17.1
C_3A_{cubic}	5.3			MgO	1.4	0.73
C_3A_{orth}	1.3			Al_2O_3	4.8	39.2
CA		61.3		K_2O	0.95	< 0.1
$C_{12}A_7$		2.3		P_2O_5		0.1
C_2AS		4.4		Na_2O	0.1	0.1
$C\bar{S}$	0.5			TiO_2	0.18	1.8
$C\bar{S}H_{0.5}$	1.6		96.5	SO_3	2.7	0.09
$C\bar{S}H_2$			0.9			
$CaCO_3$	1.4		2.6			
Arcanite	0.6					
Perovskite		5.9				
Magnetite		1.5				
Amorphous	2.8	7.4	0			

Table 3
Mineralogical composition present in the mixes A, B and C.

	System A	System B	System C
C_3S	7.2	17.1	–
C_2S	3.8	6.4	1.8
C_4AF	11.4	11.8	10.3
C_3A_{cubic}	0.7	1.6	–
C_3A_{orth}	0.2	0.4	–
CA	39.5	30.0	42.9
$C_{12}A_7$	1.5	1.1	1.6
C_2AS	2.8	2.2	3.1
$C\bar{S}$	0.1	0.2	–
$C\bar{S}H_{0.5}$	21.8	19.8	29
$C\bar{S}H_2$	0.2	0.2	0.3
$CaCO_3$	0.8	1	0.7
Arcanite	0.1	0.1	–
Perovskite	3.8	2.9	4.1
Magnetite	1	0.7	1.0
Amorphous	5.1	4.5	5.2

binder ratio (here the term binder includes OPC, CAC, and $C\bar{S}$) of 0.4. This is equivalent to a water cement ratio (w/c) equal to 0.52, 0.5, and 0.57 for system A, system B and system C respectively.

Water was added to the premixed powder and the resulting paste was mixed with a paddle at a rotation speed of 500 rpm for 90 s, then a manual mixing was performed for 30 s and finally mixed again for 90 s at 500 rpm. Moulds of the prepared samples were put in a climatic chamber with 100% RH for the first 24 h, and after 24 h all the pastes were demoulded and cured under water at 21 °C. Samples were tested in time intervals of 1, 7, 28, 56 and 90 days. At the designated time, slices about 3 mm thick were cut using a water lubricated saw. The first layer (1 mm thick) of the paste exposed to water was discarded in order to remove the possible leaching of Ca^{2+} induced by the curing.

Hydration was stopped by applying the solvent exchange method using isopropanol as a solvent. The 3 mm thick samples were immersed in isopropanol for 7 days and stored in a desiccator for 3 days as described in [24,25]. After stopping the hydration, samples were ground to a grain size smaller than 63 μm and delivered for XRD and TGA analysis. All the specimens were stored in small air-tight plastic bags in a desiccator containing silica gel and soda lime to create a dry and CO_2 free environment in order to protect them against possible carbonation and further hydration due to humidity.

2.2. Analytical methods

2.2.1. Laboratory X-ray powder diffraction

X-ray diffraction (XRD) analyses were done with a PANalytical

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