



## Effect of hydration kinetics on properties of compositionally similar binders



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### ABSTRACT

Four types of binders, based on the three different clinkers are investigated. These binders are of similar bulk chemical composition but contain different aluminate and silicate phases, which dissolve at different rates. The differences in reaction kinetics result in different phases assemblage at early ages. The phase assemblages tend to converge at later ages. Ettringite, AFm phases, C-S-H and strätlingite are the main hydrates. Their kinetics of formation and quantities depend on the dissolution rate of the anhydrous material. The differences in hydrates assemblage impact on the microstructures. Systems with ettringite or other crystalline hydrates as main hydration products at early ages, result in a coarser porosity. A refinement of the porosity is found in all the investigated samples with the ongoing formation of amorphous hydrates. Two mechanisms responsible for reduced hydration kinetics at later ages are identified: high Al concentration in the pore solution and dense microstructure.

### 1. Introduction

The cement industry is associated with about 5% of human made CO<sub>2</sub> emissions [1]. The CO<sub>2</sub> emissions are caused mainly by the decalcination of the limestone, the fuel and the electricity production [1]. The need to reduce the CO<sub>2</sub> emissions results in changes in the hydraulic binders product portfolio, with the number of materials used as Portland clinker (PC) replacement for the production of composite cement continuously increasing. The replacement of the PC by the supplementary cementitious materials (SCMs) reduces the clinker content in the final composite cement and consequently the CO<sub>2</sub> emissions associated with the cement production [2,3]. In parallel, a lot of effort is focused on the development of the alternative hydraulic binders like belite – ye'elimite – ferrite binder (BYF) [2,4–6] with the aim to produce clinkers with completely different chemistry than PC. BYF cements are receiving increasing attention because they provide a low-CO<sub>2</sub> alternative to Portland cement [7–9]. Calcium sulfoaluminate (BYF) cements contain ye'elimite, belite and calcium ferrite phases as a major constituent [10]. Production of ye'elimite releases significantly less CO<sub>2</sub> compared to alite, which is the main constituent of Portland clinker [9]. Additionally, the clinkering temperature used to produce BYF clinker is lower than that used for Portland cement clinker [9] which further sinks CO<sub>2</sub> emissions.

The motivation for the lowering the PC content in composite cements and development of the BYF-type binders is thus the same. Both approaches are looking for the decrease of the CO<sub>2</sub> emissions using

similar raw materials (limestone, aluminosilicates such as clays and calcium sulfates) when the main difference between the two is the production process [2]. Consequently, despite the differences in the mineralogy of the binders, the cements based on BYF and traditional composite cements may have similar chemical composition and similar final phase assemblage at complete hydration. In the case of the PC based composite cement this can be obtained by blending of the Portland clinker with SCM characterized by a high Al<sub>2</sub>O<sub>3</sub> content, e.g. calcined clay and Ca-rich fly ashes. Another possibility to produce low calcium and high alumina containing binder based on PC is to blend it with calcium alumina cement (CAC). CAC is a special type of hydraulic cement characterized by the lower calcium and higher alumina content than the PC. The main hydraulic phase is monocalcium aluminate, C<sub>12</sub>A<sub>7</sub> and/or CA<sub>2</sub> [9,11]. Despite that production of CAC results in lower CO<sub>2</sub> emissions than Portland cement production, this type of cement is not considered as an alternative to Portland cement systems. Performance evolution of these cements and particularly volume stability (the so called “conversion” process) is challenging for some applications [11]. Additionally, the high costs and limited availability of raw materials needed to produce the CAC cements renders their price high. Due the above mentioned ways of lowering CO<sub>2</sub>, the overall chemistry of the cement produced changes towards less CaO and higher Al<sub>2</sub>O<sub>3</sub>. Depending on the alumina rich sources used, a competition between silicate and aluminate dissolution may occur.

Within this work, we compared the reaction mechanisms of the PC composite cements and BYF systems. We investigated three binders;

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composite cement containing PC and metakaolin as the main cement constituents and a BYF binder. Additionally we have prepared the blends of Portland clinker and calcium alumina cement (CAC). All were characterized by their similar overall chemical composition. We considered the bulk chemical composition of the used materials, independently on the content of the reactive and inert phases. The total chemical compositions of the materials are used during the production process as well as when assessing the environmental footprint of the cements.

The main difference among these systems, apart from different mineralogical composition, is the hydration kinetics of clinker phases. In the case of Portland clinker based systems, C<sub>3</sub>A and C<sub>3</sub>S phases in the presence of sulfate [12,13] react the first. Because of this reaction ettringite, portlandite and C-S-H phases precipitate. Generally, the SCMs react slower than the cement clinker [14–17], though metakaolin is characterized by the high reaction kinetics [18]. The reaction of metakaolin leads to the formation of additional C-S-H and AFm phases [14] and with the increased metakaolin content, strätlingite may precipitate [19,20]. In blends of PC and CAC, the Portland cement clinker and CAC clinker reacts with a similar rate, however, it is believed that in the presence of CA cement, the hydration of PC clinker is delayed [21,22]. The hydration products are similar like in the case of a neat PC system, though with significantly increased amounts of AFm phases [22]. In BYF systems, ye'elimite is the first phase that reacts, followed by belite and C<sub>4</sub>AF [6,23–25]. As a result, mainly ettringite and alumina hydroxide form, and later on strätlingite and C-S-H may precipitate [24].

Consequently, the main objective of this work is to gain experience about the impact of the dissolution kinetics of aluminates and silicate phases on the phase assemblage formed and the resulting microstructure.

## 2. Materials

The chemical and physical characteristics of the materials used, determined by XRF, QXRD and laser granulometry, are given in Table 1, Table 2 and Fig. 1, respectively. Table 2 gives only the main phases presented in the cement clinker, the minor phases are:

- PC clinker contains additionally small quantities of periclase, free lime, arcanite, aphtitalite, and quartz.
- BYF clinker contains additionally small quantities of periclase, free lime, anhydrite, quartz, Ca-langbeinite, merwinite, gehlenite, elles-tadite and enstatite.
- CAC cement consists additionally of gehlenite, perovskite, hibonite and pleochroite.

### 2.1. Cements composition

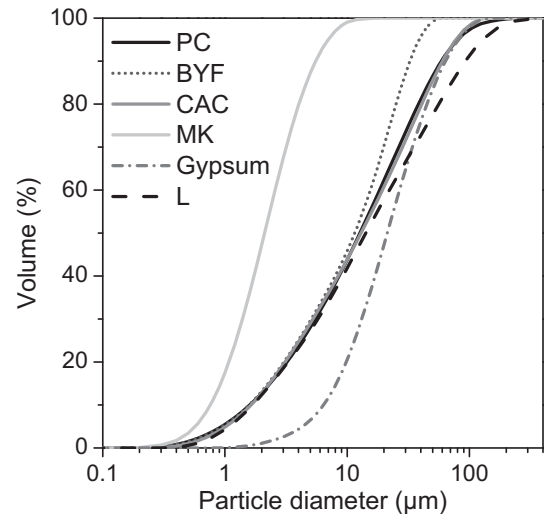
Blends of PC clinker with metakaolin (MK), limestone (L) and

**Table 1**  
Chemical composition of the materials used (% mass).

	PC	CAC	BYF	Gypsum	MK	L
CaO	64.2	37.0	48.4	32.1	0.1	59.9
SiO <sub>2</sub>	21.0	4.8	16.7	1.8	52.2	1.7
Al <sub>2</sub> O <sub>3</sub>	5.3	52.2	18.7	0.6	44.9	0.5
SO <sub>3</sub>	1.5	0.0	7.4	43.6	0.1	0.0
Fe <sub>2</sub> O <sub>3</sub>	3.1	2.3	3.3	0.2	0.6	0.2
MgO	2.6	0.4	2.5	0.3	0.0	0.0
K <sub>2</sub> O	1.2	0.2	0.5	0.1	0.2	0.1
Na <sub>2</sub> O	0.5	0.0	0.3	0.1	0.2	0.0
TiO <sub>2</sub>	0.3	2.5	0.6	0.0	1.1	0.0
MnO	0.1	0.0	0.1	0.0	0.0	0.0
P <sub>2</sub> O <sub>5</sub>	0.2	0.1	0.5	0.0	0.1	0.0
LOI	0.2	1.0	0.3	20.9	0.3	42.6

**Table 2**  
Phase composition of the materials used (% mass).

Phase/material	PC	CAC	BYF	MK	Gypsum	L
C <sub>3</sub> S	56.5	–	–	–	–	–
C <sub>2</sub> S	19.9	4.5	47.0	–	–	–
C <sub>3</sub> A	7.5	–	–	–	–	–
C <sub>4</sub> AF	9.9	–	10.0	–	–	–
Ye'elimite	–	–	24.8	–	–	–
CA	–	66.4	1.1	–	–	–
C <sub>12</sub> A <sub>7</sub>	–	2.5	1.2	–	–	–
Gypsum	–	–	–	–	100.0	–
Calcite	–	–	–	–	–	98.6
Gehlenite	–	17.6	–	–	–	–
Amorphous	–	–	–	> 95	–	–
Other	6.2	9.0	15.9	< 5	–	1.4



**Fig. 1.** Particle size distribution of the materials used.

**Table 3**  
Composition of the cements (% mass).

Material	BYF-G	PC-MK	PC-CA-L	PC-CA-G
PC	–	79	56	50
CAC	–	–	26	26
BYF	96	–	–	–
Gypsum	4	6	6	20
MK	–	13	4	4
L	–	2	8	–

calcium aluminate cement (CA) with similar Al/Si and Si/Ca ratio as the belite calcium sulfo-aluminate ferrite cement used were investigated. The mix proportions are given Table 3.

The blends were prepared to have similar chemical compositions defined by the ratios of Al<sub>2</sub>O<sub>3</sub>/(SO<sub>3</sub> + CO<sub>2</sub>) and (Al<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub>)/CaO. These ratios were selected, because they define the theoretical form of AFm phases and calcium silicate phases formed, respectively. Other oxide ratios are not the same for all the blends (Table 4).

In the case of the BYF and PC-CA systems the very similar chemical composition could be achieved by blending the materials used. However in the case of the PC-MK, it was not possible to increase the alumina content high enough to reach the same level like in BYF, when having the similar calcium content; from this perspective metakaolin is too rich in silica. Consequently, it was decided to keep the same ratio of (Al<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub>)/CaO. Additionally in the cements PC-MK and PC-CA-L the sulfate content was kept close to 3.5% as defined by EN 197-1 standard. Consequently, to keep the similar proportion of the AFt and AFm phases the Al<sub>2</sub>O<sub>3</sub>/(SO<sub>3</sub> + CO<sub>2</sub>) was kept constant.

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