Contribution of limestone to the hydration of calcium sulfoaluminate cement

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ABSTRACT

Calcium sulfoaluminate (CSA) cements can be blended with mineral additions such as limestone for properties and cost optimization. This study investigates the contribution of limestone to the hydration of a commercial CSA clinker regarding the hydration kinetics, hydrate assemblage and compressive strength. Nine formulations were defined at M-values of 0, 1.1 and 2.1 (M = molar ratio of anhydrite to ye'elimite) without and with medium and high limestone contents.

Calorimetric results indicate that limestone accelerates the hydration reaction especially at M = 1.1, probably due to the filler effect. The phase assemblages were calculated by thermodynamic modeling using Gibbs Energy Minimization Software (GEMS). With increasing limestone content the formation of ettringite and calcium monocarboaluminate is predicted at the expense of calcium monosulfoaluminate. With increasing M-value more ettringite is predicted at the expense of the monocarbonate and less calcite takes part in the hydration reactions.

The modeled results compare well with the experimental data after 90 d of hydration, except that calcium hemicarboaluminate was found instead of monocarbonate, which is assumed to be due to kinetics considerations.

The lowest compressive strength occurs in ternary formulations, whereas in the absence of calcium sulfate, strength is significantly higher.

The results presented here indicate that in CSA cements, limestone accelerates early hydration kinetics, takes part in the hydration reactions at $M < 2$, and has a positive effect on strength development in systems without anhydrite.

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1. Introduction

Concrete made of Portland cements (OPC) is the most used construction material worldwide, and its production accounts for about 5% of the man-made CO_2-emissions [1–3]. A low CO_2 potential alternative to OPC are calcium sulfoaluminate cements (CSA) [1], which contain about 30–70 wt% ye'elimite ($C_4A_3\overline{S}$) as a clinker constituent. Typically, various amounts and types of calcium sulfate are blended with the CSA clinker in order to optimize the formulation for the aimed application. The general hydration reactions in CSA-based systems are as follows [4,5]. Without calcium sulfate, ye'elimite hydrates to calcium monosulfoaluminate

(monosulfate) and aluminum hydroxide (1; cement notation: C = CaO, A = Al_2O_3, $\overline{S}$ = SO_3, H = H_2O, $\overline{C}$ = CO_2):

$$C_4A_3\overline{S} + 18H \rightarrow C_3A \cdot C\overline{S} \cdot H_{12} + 2AH_3 \qquad (1)$$
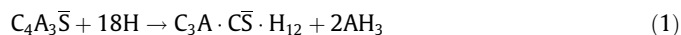
In the presence of anhydrite or gypsum, ettringite is formed together with aluminum hydroxide (2):

$$C_4A_3\overline{S} + 2C\overline{S} + 38H \rightarrow C_3A \cdot 3C\overline{S} \cdot H_{32} + 2AH_3 \qquad (2)$$
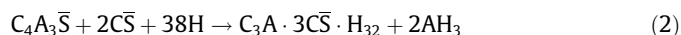
The molar ratio of the calcium sulfate per ye'elimite is known as the "M-value" [6] and determines the ratio of ettringite to monosulfate in the hydration products.

With regard to the hydration kinetics, previous studies have indicated that the hydration of CSA cements and the resulting properties of CSA-based construction materials mainly depend on the amount and the reactivity of the added calcium sulfate [7–15]. The effect of calcium sulfate (anhydrite and gypsum) on the hydration of ye'elimite was investigated at M-values of 0, 1, 2, 3 and 4 [15]. The authors have concluded that both gypsum

and anhydrite accelerate the hydration of ye'elimite by shortening the dormant period from 6 h without calcium sulfate to 4 h for $M = 1$, respectively 2 h for $M \geqslant 2$ in the presence of anhydrite. Similar results were obtained using a commercial CSA clinker [14].

However, as CSA cements are still significantly more expensive than OPC, cost reduction is an important issue. An option is to blend them with mineral additions such as limestone. In the case of OPC, calcite is allowed as an addition up to $\leqslant 5$ wt% in CEM I and $\leqslant 35$ wt% in CEM II according to the European Standard EN 197-1. Such an addition of limestone to OPC not only lowers the cement cost, it accelerates early hydration by providing additional nucleation sites for C–S–H and enhances strength development at low addition levels [16–23]. Furthermore, in the presence of calcite, calcium monocarboaluminate (monocarbonate) is present in the hydration assemblage instead of monosulfate, which indirectly stabilizes ettringite. Thus, the volume of hydrate phases formed is increased if small amounts of limestone are added, which results in a higher compressive strength [24,25].

Only a few studies have investigated the effect of calcium carbonate on the hydration of CSA cement with respect to the hydration reactions [26–28]. A comparison of the effect of quartz and limestone fillers on hydration kinetics and hydrate assemblage of CSA cements indicates that the setting time is accelerated in the presence of limestone filler compared to quartz filler due to an enhanced early hydration [26,29]. In addition, limestone powder also improves the long-term compressive strength compared to quartz filler. With limestone less monosulfate is formed, while monocarbonate and hemicarboaluminate (hemicarbonate) and more ettringite are present. This indirect stabilization of ettringite leads to a higher total volume of solids [24,26].

The hydration of pure ye'elimite with or without gypsum ($M = 0.63$ or 0) and with or without 10 wt% added calcite or vaterite was examined by Ref. [28]. Regarding the reaction kinetics, the authors showed that calcium carbonate caused the maximal rate of the hydration heat evolution to occur earlier than for the mixes without calcium carbonate, which corresponds to the results of Ref. [27]. In particular, vaterite had a stronger effect than calcite and the acceleratory effect is even more pronounced if gypsum is in the formulation. Regarding the formation of hydrates, their results indicated that both calcite and vaterite react with monosulfate to form ettringite and monocarbonate but that gypsum was lowering the reactivity of both carbonates. Furthermore, they could show that calcium carbonate, especially vaterite in the absence of gypsum, also contributes to the compressive strength.

The goal of this study is to investigate the contribution of limestone to the hydration of a commercial CSA cement regarding (a) the effect of limestone on the hydration kinetics, (b) the contribution of limestone to the hydration reactions depending on the added amount of anhydrite, (c) the formed hydrate assemblages and (d) the effect of the limestone on compressive strength. For those reasons, nine formulations were defined with M-values of 0, 1.1 and 2.1. Formulations without limestone serve as reference systems, and six systems with limestone were investigated at $M = 0$, 1.1 and 2.1 with medium (9–14 wt%) and high limestone contents (16–25 wt%). Hydration kinetics was assessed by isothermal calorimetry. The equilibrium phase assemblages were predicted by thermodynamic modeling using the geochemical speciation code GEMS-PSI and then compared with experimental data obtained by X-ray diffraction analyses.

2. Materials and methods

2.1. Materials and binder formulations

The raw materials used are a commercial CSA clinker, anhydrite and a finely milled limestone filler. The chemical compositions are

presented in Table 1. The density and specific surface of the materials were measured according to EN 196-6, and the free lime according to the method of Franke [30]. The clinker mineralogy was determined by X-ray diffraction using Rietveld refinement. The particle size distribution was analyzed by laser diffraction using a Malvern Mastersizer X. Prior to analysis, the components were dispersed in isopropanol by ultrasound. The particle size distributions are illustrated in Fig. 1. The CSA clinker and the anhydrite show a bimodal grain size distribution with mostly particles between 2 and 3 μm and 10–30 μm. Mean particle diameters are close to 10 μm. The limestone has a more homogeneous grain size distribution with a maximum between 2 and 4 μm and mean particle diameter of about 2.5 μm.

Nine binder formulations were investigated: They are distinguished by their carbonate contents ($h\overline{C}$ = high carbonate series; $m\overline{C}$ = medium carbonate series; $n\overline{C}$ = series without carbonate) and their M values (Table 2). The formulation with plain CSA clinker (=$n\overline{C}M0$) clinker was only used for compressive strength testing. The applied water/binder ratio was 0.74, considering the whole formulation as the binder. Setting was regulated by the same admixtures in all systems. Mortars were prepared containing 30% binder including the admixtures and 70% quartz sand with a grain size between 0.1 and 0.25 mm. Per 1 kg dry mortar, 220 g water were added.

2.2. Methods

2.2.1. Isothermal calorimetry

Isothermal calorimetry was performed using a Thermometric TAM Air at 20 °C during 7 d. In order to measure the initial heat release, Admix ampoules were used [31]. 2.7 g of binder were mixed inside the calorimetric cell with 2 g water and stirred for 2 min.

2.2.2. Thermodynamic modeling

The phase assemblage in various systems at a hydration degree of 100% was calculated by thermodynamic modeling applying the

Table 1
Chemical and mineralogical composition of the used materials.

X-ray fluorescence analysis (wt%)				Mineralogical phase composition (wt%)[b]	
	CSA clinker	Anhydrite	Limestone		CSA clinker
SiO_2	5.4	0.2	0.4	$C_4A_3\overline{S}$	68.1
Al_2O_3	42.6	0.0	0.2	CA	3.2
Fe_2O_3	1.6	0.0	0.1	CA_2	0.7
Cr_2O_3	0.0	0.0	0.0	$C_{12}A_7$	1.4
MnO	0.0	0.0	0.0	C_2AS	19.4
TiO_2	2.1	0.0	0.0	C_2S	1.7
P_2O_5	0.1	0.0	0.0	CT	3.9
CaO	35.9	41.7	56.6	M	0.6
MgO	1.0	0.5	0.4	MA	1.1
K_2O	0.5	0.0	0.0		
Na_2O	0.0	0.0	0.0	Readily soluble alkalis (g/100 g cement)[e]	
SO_3	8.5	56.2	0.1	Na_2SO_4	0.02
L.O.I.[a]	2.0	1.2	42.2	K_2SO_4	0.31
Total	99.7	99.9	99.9		
Density (g/cm³)[c]	2.75	2.92	2.71		
Blaine (cm²/g)[c]	5080	5130	8080		
CaO_{free} (wt%)[d]	0.06	–	0.1		

[a] Loss on ignition determined at 1050 °C.
[b] Clinker mineralogy as determined by Rietveld refinement.
[c] According to EN 196-6.
[d] According to Ref. [30].
[e] Analyzed by ion chromatography in a 1:10 dissolution.