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Influence of fly ash on the hydration of calcium sulfoaluminate cement

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ABSTRACT

The effect of fly ash on the hydration of calcium sulfoaluminate cement was investigated. Increasing fly ash contents accelerated the hydration of calcium sulfoaluminate cement due to the filler effect. Dissolution rims around fly ash particles after 90 days indicated a reaction degree of the fly ash of approximately 20 to 30% as estimated by various independent methods. The contribution of fly ash to the hydration reactions resulted in the formation of C-S-H, in an increase of the strätlingite content and in the destabilization of monosulfate.

The mortar with 7.5 mass-% fly ash reached a higher compressive strength than the reference without fly ash when the water to cement ratio was kept constant. Up to 15 mass-% of fly ash could be added without strength loss.

1. Introduction

Calcium sulfoaluminate cements (CSA) are a potential low CO_2 alternative to ordinary Portland cements [1]. Typically they contain 30 to 70 mass-% ye'elimite ($C_4A_3\bar{S}$) as a clinker constituent together with other phases such as belite and calcium aluminates. Plain ye'elimite hydrates to monosulfate and aluminum hydroxide, and if in addition calcium sulfate is present, also ettringite precipitates. The molar ratio of the calcium sulfate to ye'elimite, generally designated as the "M-value", determines how much ettringite forms [2]. An M-value of 2 results in the maximum ettringite content (see e.g. [3]). CSA cements can also contain significant amounts of belite, which can lead to the formation of strätlingite or C-S-H [4–6].

In order to reduce costs and the amount of CO_2 attributed to the production of CSA, they can be blended with supplementary cementitious materials (SCMs) such as limestone powder [7–9] or industrial by-products (e.g. slag or fly ash) [10,11]. The addition of fly ash to Portland cement (PC) was intensively studied in the past, see e.g. [12–17]. Fly ash in PC serves both as filler and as pozzolan [12–14,16,18–22]. The filler effect [23,24] results in part from the presence of additional nucleation sites related to the extra surfaces provided by the SCMs. Further, the effective water/cement ratio is increased at constant water/solid ratio, which results in an increased hydration of the PC. The filler effect is important at early ages, as the fly ash shows little reaction up to 7 days [12,16,18,25]. The high pH in the pore solution of the PC enables the (relatively slow) dissolution of the fly ash, and the reaction of fly ash with portlandite leads to the formation of additional C-S-H [12,16,18–20].

While the addition of fly ash to PC has been studied widely as indicated above, only a few studies have investigated CSA cements blended with fly ash [10,11,26,27]. Pore solutions of CSA cements have generally a lower pH than PC at early hydration times [1,6,28,29] implying that fly ash dissolution is expected to proceed even slower than in PC systems. In addition, portlandite, the main reaction partner of fly ash in hydrating PC, is generally not formed during the hydration of CSA cements. However, in the case C-S-H is present in the hydrated CSA cement, it could supply calcium ions by transforming into a C-S-H with lower Ca/Si ratio as observed in Portland cements blended with fly ash [14,20].

The addition of 5 to 15 mass-% fly ash to CSA cements has been reported to increase the compressive strength by up to 3–6 MPa after 28 days, while the presence of higher fractions of fly ash decreases compressive strength [10,11,26]. Fly ash promotes the early formation of ettringite in CSA cements [10,26] whereas strätlingite is observed only after 180 days at high w/c ratios, which was interpreted as very limited reaction of the fly ash [10].

As up to now only limited information regarding the reactivity of fly ash in CSA cements is available, the present study will investigate the reaction fly ash under the conditions present in hydrated CSA (lower pH than in PC, absence of portlandite) and characterize the Si-containing hydrates (strätlingite and/or C-S-H) formed upon reaction of the fly ash. The experiments were carried out using a CSA cement containing added calcium sulfate at a fixed M-value of 0.8. It was blended with fly ash using replacement levels of 7.5, 15, 30 and 45 mass-%. Hydration was investigated by isothermal calorimetry, thermogravimetric

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Table 1
Chemical and mineralogical composition of the used binder components.

X-ray fluorescence analysis (mass-%)	CSA clinker	Anhydrite	Fly ash	Fly ash amorphous[b]	Mineralogical phase composition (mass-%)[a]	CSA clinker	Anhydrite	Fly ash
CaO	41.36	42.83	3.38	4.2	Ye'elimite ortho	38.1		
SiO_2	8.05	0.82	55.88	55.3	Ye'elimite cubic	26.2		
Al_2O_3	31.22	0.33	23.03	19.5	Mayenite	2.3		
Fe_2O_3	1.15	0.20	8.14	9.5	Belite (β)	10.6		
MgO	3.78	0.08	1.63	2.0	Alite (M3)	1.5		
K_2O	0.44	0.05	1.88	2.5	Bredigite[f]	3.8		
Na_2O	0.60	<0.03	1.05	1.4	Merwinite[f]	2.8		
TiO_2	0.401	0.019	1.132	1.5	Gehlenite	0.9		
P_2O_5	0.102	0.014	1.050	1.4	Fluorellestadite[f]	7.4		
Cr_2O_3	0.059	0.004	0.023	<0.1	Perovskite	0.9		
MnO	0.163	0.008	0.058	<0.1	Periclase	3.3		0.1
SO_3	10.86	54.83	0.33	0.1	Anhydrite	2.0	97.8	0.4
L.O.I.[c]	0.90	0.77	1.93	2.5	Calcite		1.8	
Total	99.08	99.95	99.51	100.0	Mullite			11.4
					Quartz		0.4	10.5
CO_2 (mass-%)	0.48	0.70	0.33		Hematite			0.5
Free lime[d]	0.05		0.13		Magnetite			0.6
Density (g/cm^3)[e]	2.75	2.83	2.36		Lime			0.1
Blaine (cm^2/g)[e]	5080	3390	3040		Amorphous			76.5
					a) glass phase			75.4
					b) organic C			1.1

[a] As determined by quantitative X-ray diffraction.
[b] Average composition of amorphous part of the fly ash calculated by mass balance based on bulk oxide composition and quantitative X-ray diffraction.
[c] Loss on ignition determined at 1050°C.
[d] According to [30].
[e] According to EN 196-6.
[f] Bredigite = $Ca_7Mg(SiO_4)_4$, merwinite = $Ca_3Mg(SiO_4)_2$, fluorellestadite = $Ca_{10}(SiO_4)_3(SO_4)_3F_2$.

analyses (TGA), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS). In addition, the thermodynamically stable hydrate assemblages were calculated depending on amount and reaction degree of the fly ash using geochemical modeling. Compressive strength was measured in two series, with the mixing water referred either to CSA cement (CSA clinker + anhydrite) or to total binder (CSA cement + fly ash).

2. Materials and methods

2.1. Raw materials and mix design

The materials used are a commercial CSA clinker, a thermal anhydrite and a siliceous fly ash according to EN 450-1. The measured chemical composition and the phase contents as determined by X-ray diffraction using Rietveld refinement are presented in Table 1. The average composition of the amorphous part of the fly ash was calculated based on the bulk oxide composition and the contents of the crystalline phases. 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 particle size distribution of the materials was analyzed using a laser particle analyzer (Malvern Mastersizer X). The powders were dispersed in isopropanol by ultrasound.

The CSA clinker contains approximately 65 mass-% ye'elimite, both in its orthorhombic and cubic polymorph. From the occurrence of fluorellestadite it can be deduced that calcium fluoride was probably used as a mineralizer to produce this clinker. Calcium fluoride is known to lower the formation temperature of alite [31,32], thus traces of alite occur in the clinker. Belite and bredigite are also present as reactive calcium silicates. Finally, the clinker contains 2 mass-% anhydrite. The anhydrite added to make the CSA cement has a purity of >97%. The fly ash used contains approximately 75% amorphous phases.

The CSA clinker shows a broad particle size distribution with a d_{50} of 6 μm (Fig. 1). The fly ash is somewhat coarser with a d_{50} of 17 μm. The

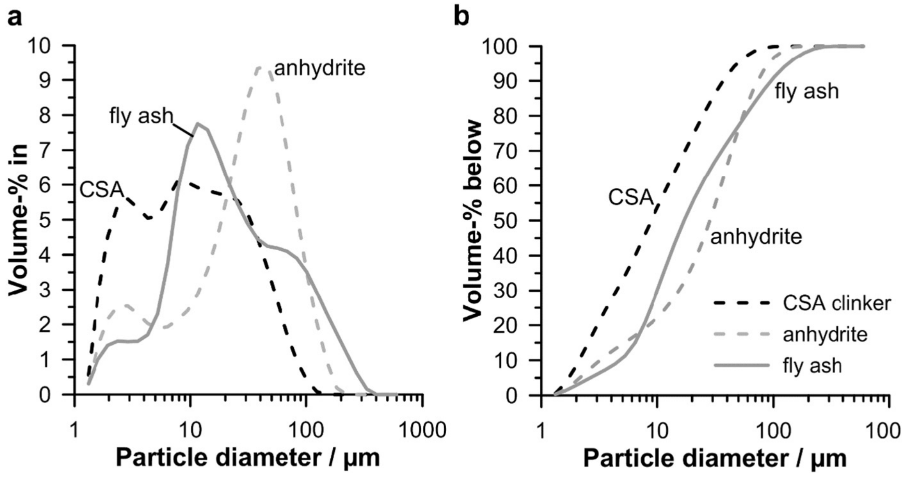

Fig. 1. Particle size distribution of the applied binder constituents. a) Differential and b) cumulative particle size distribution.