Influences of Accelerators on Compressive Strength Development of Composite Cements

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Abstract

Low-clinker composite cements often have the disadvantage of lower early compressive strength. Hardening accelerators can increase the early compressive strength of Portland cement at the expense of reduced late strength.

The extent to which different hardening accelerators influence the compressive strength development of low-clinker composite cements containing granulated blast furnace slag and limestone was systematically investigated using compressive strength test, ultrasound transmission experiments and heat flow calorimetry.

The results show that the accelerator must always be adapted to the particular composite cement in order to increase the early compressive strength. Synergetic effects of cement constituents besides clinker can partly compensate for the reduced late strength of accelerated systems.

Keywords

composite cement, granulated blast furnace slag, limestone, concrete admixture, accelerator, compressive strength, microstructure, ultrasound velocity, heat flow calorimetry

1 Introduction

In order to achieve climate neutrality and to conserve natural resources, there is no alternative to the use of cements with several main constituents (so-called composite cements or blended cements) with a significantly reduced clinker content. However, reducing the clinker content decreases the early compressive strength of concrete, which is often seen as a disadvantage in construction practice.

The early strength can be increased by using concrete admixtures that accelerate cement hardening. The addition of nanoparticles significantly increases the surface for heterogeneous nucleation due to their very large specific surface area [1]. This promotes nucleation during the hydration of Portland cement clinker and shortens the induction period. The acceleration period starts earlier and progresses faster due to the increased number of nuclei.

Pozzolanic reacting nanoparticles are also nuclei initially. As a result of the pozzolanic reaction, they form additional C-S-H phases and consume calcium hydroxide [2] already after the first day of hydration [3].

In contrast, as to [2,3], the addition of synthetic crystallisation nuclei, i.e. C-S-H seeding, supports the nucleation process and C-S-H phases grow up already in the “pre-induction period”. As a result, the strength after the first day of Portland cement hydration is significantly higher than

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with the addition of nanosilica and, due to the lack of pozzolanic reaction, post-hardening is less intensive from the third day [3]. According to [4-6], seeding can also accelerate the initial reaction of composite cements and can compensate for the early strength loss due to a reduced clinker content.

The addition of very small amounts of triethanolamine (TEA) to Portland cement can accelerate the conversion of the C_3A by consuming calcium sulphate to AFt hydrates [6] and the compressive strength after the first day of hydration is higher [8]. Higher doses of such organic accelerating substances can have retarding effects [7,9].

As to [9], triisopropanolamine (TIPA) primarily complexes iron and thus reduces the formation of Fe(OH)3, which in particular allows C_4AF to dissolve to a greater extent from the second day of Portland cement hydration [10]. In the presence of limestone, the reaction of C_4AF is accelerated and intensified by TIPA, resulting in higher contents of carbo-AFm hydrates with corresponding AFt stabilisation and microstructure refinement as well as higher compressive strengths [11]. Diethanolisopropanolamine (DEIPA) is more effective than TIPA or TEA and also accelerates the reaction of granulated blast furnace slag [12].

The aim of this study was to increase the early compressive strength of low-clinker ternary composite cements containing granulated blast furnace slag and limestone to a level comparable with Portland cement using commercially available concrete hardening accelerators recommended for composite cements. It was also investigated how the latent hydraulic reaction of blast furnace slag and synergies with limestone can counteract a potential decrease in the late strength.

2 Materials and methods

2.1 Accelerators

Properties of the two commercial hardening accelerating admixtures (“BE”) are shown in Table 1.

Table 1 Properties of the accelerators (BE)

Parameter	Unit	BE1	BE4
colour	–	colourless	colourless
MEC1)	–	CSH seeds	min. salts7)
density2)	g/cm³	1.16	1.33
content3)	mass %	27	54
pH4)	–	11.2	4.9
dosage5)	mass % of c	0.1 – 5.0	0.1 – 5.0
max. dos.6)	mass % of c	–	3.0

[1] main effective component acc. product sheet; [2] absolute density acc. ISO 758; [3] conventional dry material content acc. EN 480-8; [4] pH value acc. ISO 4316; [5] dosage range acc. product sheet; [6] maximum recommended dosage acc. product sheet;

[7] nitrates and thiocyanates; –: not stated

2.2 Cements

A commercial Portland cement CEM I 52,5 R (“PZ”) acc. EN 197-1 was used as a reference and as the base component for the production of the composite cements.

A composite cement CEM II/B-M (S-LL) 52,5 N (“PZ-20S-10LL”) was produced from about 70 mass % PZ, about 20 mass % blast furnace slag (“S”) and about 10 mass % limestone (“LL”) in the laboratory. A composite cement CEM II/C-M (S-LL) 42,5 R (“PZ-30S-20LL”) with about 50 mass % PZ, about 30 mass % S and about 20 mass % LL was produced likewise. Anhydrite was added to the composite cements to optimise setting and hardening. The homogeneity of the cements was confirmed by means of X-ray fluorescence analyses.

Properties of the used cements are shown in Table 2. The clinker of the cements consisted of about 75 mass % alite, about 8 mass % belite, about 10 mass % C_3A and about 5 mass % C_4AF (determined by X-ray diffraction with Rietveld refinement). The glass content of S was about 98 % acc. [13] and its fineness 3580 cm^2/g acc. EN 196-6. The calcite content of LL was about 89 mass %, the remainder being mainly of quartz with some feldspars and mica. The fineness of LL was 4390 cm^2/g acc. EN 196-6.

Table 2 Cement properties

Parameter	Unit	PZ	PZ-20S-10LL	PZ-30S-20LL
Blaine$^{1)}$	cm^2/g	4530	4540	4190
x’ $^{2)}$	µm	13.0	13.6	15.0
n$^{3)}$	-	0.93	0.89	0.88
IST$^{4)}$	min	110	115	135
2 d$^{5)}$	N/mm^2	47.5	32.8	25.2
28 d$^{6)}$	N/mm^2	69.4	63.7	56.1

[1] Blaine fineness acc. EN 196-6; [2] position parameter and [3] slope of RRSB particle size distribution; [4] initial setting time acc. EN 196-3; [5] and [6] compressive strength acc. EN 196-1 at 2 days (d) and 28 days

2.3 Mortar composition, mixing and storage

In order to classify the effects of the accelerators, the compressive strength development of mortar without accelerator was determined first. For this purpose, fresh mortar was produced in a mortar mixer according to EN 196-1 with 1350 g CEN standard sand, 500 g cement (c) and 175 g deionised water (w), i.e. w/c ratio = 0.35. The consistency of the fresh mortar was adjusted to a spread of (150 ± 20) mm according to EN 1015-3 by adding a commercially available superplasticiser based on polycarboxylate ether (PCE). The water contained in the superplasticizer was subtracted from the water added.

The mixing regimes for mortar without and with the addition of accelerator are given in Table 3.

Table 3 Mixing regimes for mortar without and with accelerator (BE)

Action	Duration
Mix c and w at low speed[1)]	60 s
Add PCE, mix at low speed	30 s
Add sand at low-speed mixing	30 s
Add BE[2)] and mix at high speed[3)]	60 s

[1] (140 ± 5) rpm rotation and (62 ± 5) rpm planetary movement; [2] for mortars with accelerators; [3] (285 ± 10) rpm rotation and (125 ± 10) rpm planetary movement

Preliminary tests have shown that the order of BE addition (BE together with PCE or BE first and then PCE) had no measurable effects on the early compressive strength development. The dose of BE4 was 3 mass % of c ("3.0%"). BE1 was dosed at 3.0, as well as 1.0 and 0.3 mass % of c ("1.0%" and "0.3%"). Mortar compaction, storage and testing were in accordance with EN 196-1.

2.4 Microstructure and hydration kinetics

The formation of the microstructure of cement paste (w/c = 0.35, PCE addition and mixing acc. Table 3 without sand addition) was determined using an ultrasound testing device IP8 from UltraTest.

The hydration kinetics of cement paste was measured with an isothermal conduction calorimeter TAM Air from TA Instruments. Here, deionised water (w/c = 0.35) was added volumetrically to the cement using the ADMIX-AMPULLE with two syringes. One syringe contained half of the water and the other contained a solution of the other half of the water, the PCE and the accelerator, if added. After tempering the substances in the device to 20 °C, the internal stirrer was started and the plain deionised water was added first, followed by the admixture-water-solution. The subsequent stirring time was 60 s.

3 Results and discussion

The compressive strength development of mortars with Portland cement PZ, composite cement PZ-20S-10LL or PZ-30S-20LL without accelerator ("0BE") is shown in Figure 1.

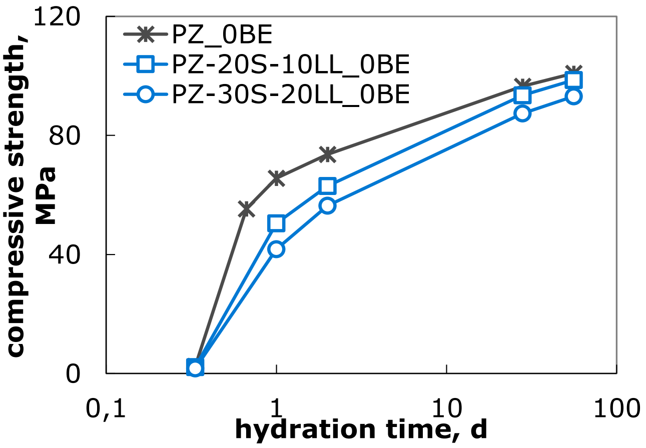

Figure 1 Compressive strength of accelerator-free mortar with Portland cement PZ, composite cement PZ-20S-10LL or PZ-30S-20LL as a function of hydration time

As expected, the compressive strength of the accelerator-free mortars decreased with decreasing clinker content in the cement up to two days (Figure 1). As hydration progressed, the compressive strength of the mortars with the low-clinker composite cements almost approached that of the Portland cement mortar, mainly due to the latent hydraulic reaction of the blast furnace slag.

Figure 2 shows the compressive strength of mortar with PZ-20S-10LL, without and with up to 3 mass % accelerator BE4 or BE1, related to the compressive strength of the accelerator-free PZ mortar shown in Figure 1. Figure 3 shows the equivalent for PZ-30S-20LL.

After 6 h of hydration, the early compressive strength of the mortar with PZ-20S-10LL and 3 mass % BE4 was about 3.6 times higher than that of the accelerator-free PZ mortar (Figure 2). With the same dose of BE4 the mortar with PZ-30S-20LL showed an approx. 2.3 times increase in the early compressive strength (Figure 3).

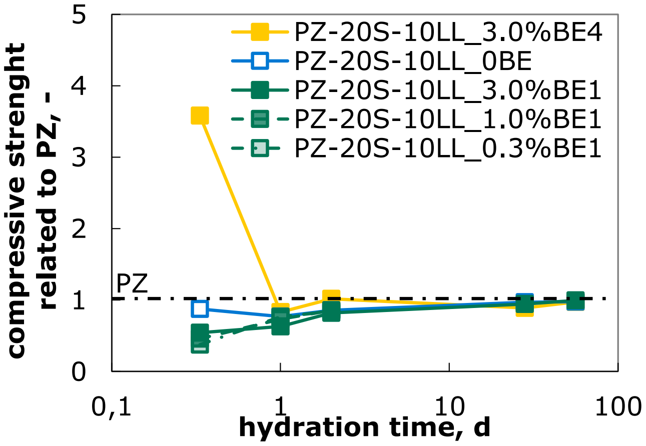

Figure 2 Compressive strength of mortar with PZ-20S-10LL without and with 1 or 3 mass % BE4 and BE1, respectively, related to the compressive strength of accelerator-free PZ mortar show in Figure 1 as a function of hydration time

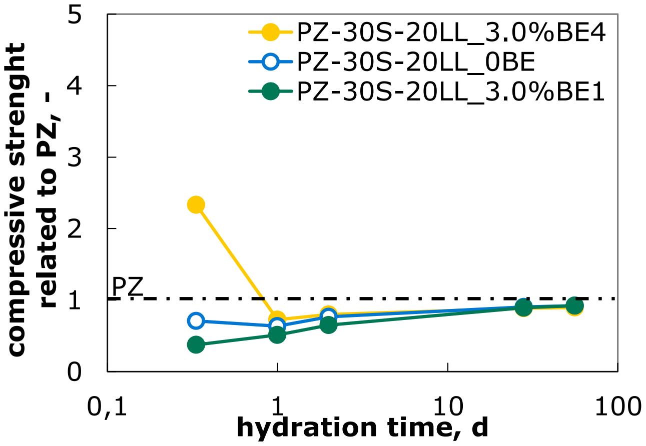

Figure 3 Compressive strength of mortar with PZ-30S-20LL without and with 3 mass % BE4 or BE1 related to the compressive strength of accelerator-free PZ mortar show in Figure 1 as a function of hydration time

Except for the improvement of the early strength at 6 hours by 3 wt.% BE4, all accelerators affect the further strength development up to an age of about 28 days compared to mortar with Portland cement. This confirms the general knowledge on the lower post-hardening of accelerated cements. With increasing hydration time, the lower post-hardening was mainly compensated by the latent hydraulic reaction of the slag.

Figure 2 and Figure 3 also show that even 3 mass % BE1 could not increase the early compressive strength of the mortars with PZ-20S-10LL and PZ-30S-20LL, but rather decreased it. Lower doses of BE1, 1.0 and 0.3 mass %, also led to a retarding effect. It needs to be investigated whether this retardation also occurs in combination with other clinkers.

The retarding effect of BE1 on the early hydration reactions of e.g. PZ-20S-10LL is additionally shown by the delay in the formation of the microstructure (Figure 4) and the delayed release of the heat of hydration (Figure 5).

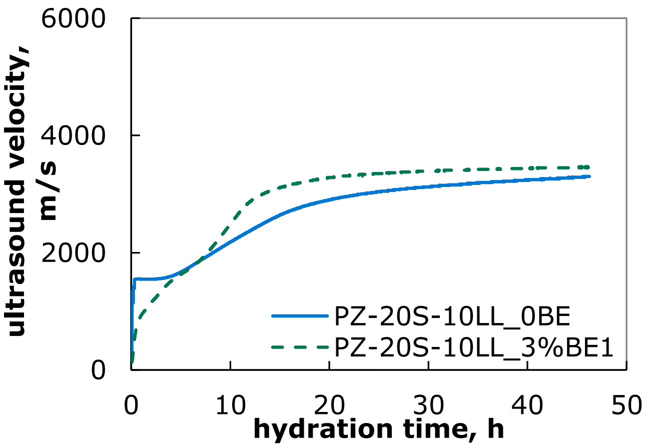

Figure 4 Development of ultrasound velocity as a measure of microstructure formation in cement paste with PZ-20S-10LL without and with 3 mass % BE1 as a function of hydration time

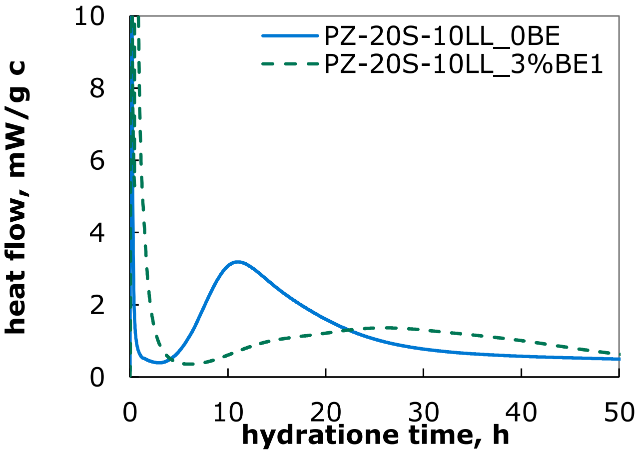

Figure 5 Heat flow of cement paste with PZ-20S-10LL without and with 3 mass % BE1 as a function of hydration time

4 Conclusions

Based on the above-mentioned results on the influences of commercial hardening accelerating concrete admixtures on the compressive strength development of low-clinker ternary composite cements containing slag and limestone the following conclusions can be drawn:

- accelerators can increase the early compressive strength of composite cements to the level of Portland cement or beyond

- the accelerating effect decreased with decreasing clinker content in the cement
- synergetic effects from the cement constituents other than clinker can partly compensate for the reduced late compressive strength caused by the accelerator addition
- as some accelerators can retard composite cement hydration, accelerators must always be adjusted to the cement and its constituents

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