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Influences of Accelerators on the Compressive Strength of Clinker-Efficient Composite Cements with Slag and Limestone

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ABSTRACT
Clinker- and resource-efficient composite cements with their multiple concrete technology advantages can have an early strength that is too low for some applications. Hardening accelerators can increase the early compressive strength of Portland cement at the expense of decreased late strength.
To which extent two commercial admixtures influence the compressive strength development of ternary composite cements with granulated blast furnace slag and limestone was systematically investigated using compressive strength tests, ultrasound transmission experiments and heat flow calorimetry.
The accelerator must always be adjusted to the particular composite cement to be able to increase the early compressive strength. Cement constituents besides clinker can contribute to compensating for the reduced late strength of accelerated systems.

KEYWORDS: *Composite cement, hardening accelerating admixture, compressive strength, retardation*

1. Introduction

To achieve climate neutrality and conserve natural resources there is no alternative to the use of cements with several main constituents (so-called composite cements or blended cements) with their significantly reduced clinker content. However, with reducing the clinker content the early strength of concrete decreases, which is often considered as a disadvantage. It is generally known that admixtures which accelerate the initial hardening, i.e. hardening accelerating admixtures, can increase the early compressive strength of concrete with Portland cement, which mostly results in a decreased late compressive strength.
The aim was therefore to increase the early compressive strength of ternary cements with granulated blast furnace slag and limestone to a level comparable with Portland cement, using commercially available hardening accelerators recommended for composite cements. How the latent hydraulic reaction of blast furnace slag and synergies with limestone can counteract the decrease in late strength was also investigated.
According to John (2018), nanoparticles significantly increase the interface for heterogeneous nucleation due to their very large specific surface areas. This promotes nucleation during the hydration of Portland cement and shortens the induction period. The acceleration period therefore starts earlier and proceeds faster due to the higher number of nuclei. Pozzolanic reacting nanoparticles are also nuclei at first. As a result of the pozzolanic reaction, they form additional C-S-H phases and consume calcium hydroxide (John 2019) already after the first day of hydration (Land 2012). In contrast, as to John (2019) and Land (2012), the addition of synthetic crystallisation nuclei, i.e. C-S-H seeding, largely replaces the nucleation process and C-S-H phases already grow in the "pre-induction period". Thus, the strength after the first day of Portland cement hydration is significantly higher than with nanosilica addition, and due to the lack of pozzolanic reaction, post-hardening is slower from the third day (Land 2012). According to Ferrari (2019), Land (2015)

and Marazzani (2012), seeding can also accelerate the initial reaction of composite cements and can compensate for the early strength loss due to the reduced clinker content.

2. Materials and methods

A commercial Portland cement CEM I 52,5 R ("PZ") served as reference. A CEM II/B-M (S-LL) 52,5 N ("PZ-20S-10LL") and a CEM II/C-M (S-LL) 42,5 R ("PZ-30S-20LL") were used as clinker-efficient composite cements. The PZ-20S-10LL was produced in the laboratory from ≈ 70 mass % PZ, ≈ 20 mass % blast furnace slag ("S"), ≈ 10 mass % limestone ("LL") and some anhydrite dotation to optimise setting and hardening. The PZ-30S-20LL contained ≈ 50 mass % PZ, ≈ 30 mass % S, ≈ 20 mass % LL and the anhydrite dotation. Properties of the cements are given in Table 1.

Table 1. Cement properties.

	Blaine[1)]	x‘ [2)]	n[3)]	IST[4)]	compressive strength[5)], MPa	
	cm²/g	µm	-	min	2 days	28 days
PZ	4530	13.0	0.93	110	47.5 ± 0.7	69.4 ± 0.7
PZ-20S-10LL	4540	13.6	0.89	115	32.8 ± 0.4	63.7 ± 0.6
PZ-30S-20LL	4190	15.0	0.88	135	25.2 ± 0.2	56.1 ± 0.5

[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] compressive strength acc. EN 196-1

The cements' clinker consisted of ≈ 75 mass % alite, ≈ 8 mass % belite, ≈ 10 mass % aluminate and ≈ 5 mass % ferrite. The glass content of S was ≈ 98 % and its fineness 3580 cm²/g acc. EN 196-6. The calcite content of LL was ≈ 89 mass %. The remains consisted mainly of quartz with some feldspars and mica. The LL fineness was 4390 cm²/g acc. EN 196-6.
Table 2 shows properties of the two commercial hardening accelerating admixtures ("BE") used.

Table 2. Accelerator properties.

	colour	MEC[1)]	density[2)] g/cm³	content[3)] mass %	pH[4)] -	dosage[5)] mass % of c	max. dosage[6)] mass % of c
BE1	colourless	C-S-H seeds	1.16	27	11.2	0.1 – 5.0	−
BE4	colourless	min. salts[7)]	1.33	54	4.9	0.1 – 5.0	3.0

[1] main effective component acc. product sheet; [2] absol. density acc. ISO 758; [3] convent. dry material content acc. EN 480-8; [4] pH value acc. ISO 4316; [5] dosage range acc. product sheet; [6] max. recommended dosage acc. product sheet; [7] nitrates and thiocyanates; −: not stated

To classify the effect of the accelerators, the compressive strength development of accelerator-free mortar was first determined. For this purpose, mortar with 1350 g CEN standard sand, 500 g cement (c) and 175 g deionised water (w), i.e. w/c ratio = 0.35, was produced in a mortar mixer according to EN 196-1. The mortar consistency was adjusted to a spread of (150 ± 20) mm according to EN 1015-3 by adding a commercially available PCE-based superplasticiser. The water contained in the superplasticizer was deducted from the water added. The mixing regimes for mortar without and with accelerator are given in Table 3.

Table 3. Mixing regimes for mortar without and with accelerator.

without accelerator			with accelerator		
action	speed[1)]	duration	action	speed[1)]	duration
mixing of c and w	low	60	mixing of c and w	low	60
adding PCE and mixing	low	30	adding PCE and mixing	low	30
adding sand during mixing	low	30	adding sand during mixing	low	30
mixing	high	60	adding BE and mixing	high	60

[1] low: (140 ± 5) rpm rotation and (62 ± 5) rpm planetary movement; high: (285 ± 10) rpm rotation and (125 ± 10) rpm planetary movement

Preliminary tests showed that adding BE together with PCE or BE first and then PCE does not have a measurable effect on the early compressive strength. 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 complied with EN 196-1.
The microstructure formation 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. With an isothermal conduction calorimeter TAM Air from TA Instruments, the hydration kinetics of the cement paste was measured. Here, the deionised water (w/c = 0.35) was added volumetrically to the cement using the AD-MIX-AMPULLE with two syringes. One syringe contained half of the water and the other a solution of the second half of the water, the PCE and the accelerator if added. After the substances had been tempered in

the device to 20 °C, the internal stirrer was started. The water was added first and then the admixture-water-solution. The subsequent stirring time was 60 s.

3 Results

The compressive strength development of mortar with PZ, PZ-20S-10LL or PZ-30S-20LL without the addition of an accelerator (“0BE”) is shown in Figure 1.

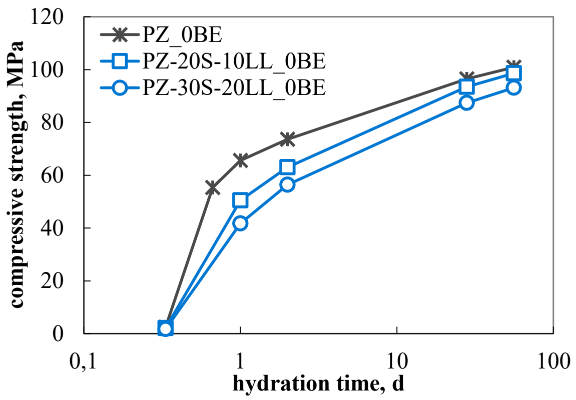
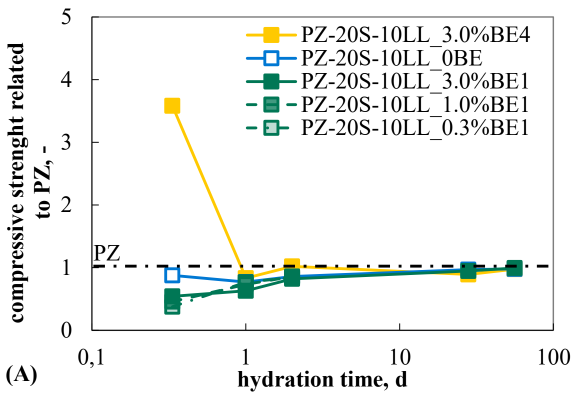


Figure 1. Compressive strength of accelerator-free mortar with Portland cement PZ or composite cement PZ-20S-10LL or PZ-30S-20LL as a function of hydration time.

As expected, the compressive strength of the accelerator-free mortars up to two days of hydration decreased with decreasing clinker content in the respective cement (Figure 1). In the further course of hydration, the compressive strengths of the mortars with clinker-efficient composite cement approached the compressive strength of the Portland cement mortar mainly due to the latent hydraulic reaction of the slag.
Figure 2 A and Figure 2 B shows the ratio of the compressive strength of mortar with PZ-20S-10LL or PZ-30S-20LL without and with up to 3 mass % accelerator BE4 or BE1 to the compressive strength of the accelerator-free PZ mortar shown in Figure 1.



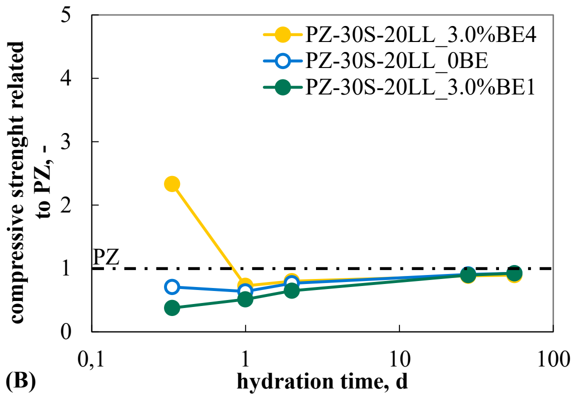


Figure 2. Ratio of the compressive strength of mortar with PZ-20S-10LL (A) or PZ-30S-20LL (B) without and with up to 3 mass % BE4 or BE1 to the compressive strength of accelerator-free PZ mortar show in Figure 1 as a function of hydration time.

At 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 A). With the same dose of BE4 and the decrease of the clinker content to 50 mass % in PZ-30S-20LL, the increase of the early mortar compressive strength was still about 2.3 times higher (Figure 2 B). At one day and two days of hydration, the compressive strengths of the mortars with 3 mass % BE4 tended to be lower than those of the accelerator-free PZ mortars. This confirms general knowledge on the slower post-hardening of accelerated cements. With increasing hydration time, the slower post-hardening was compensated mainly by the latent hydraulic reaction of the blast furnace slag.
Figure 2 A and Figure 2 B also show that 3 mass % BE1 could not increase the early compressive strength of the mortars with PZ-20S-10LL or PZ-30S-20LL to the early strength level of the accelerator-free PZ mortar. The early compressive strength of the mortars with 3 mass % BE1 and PZ-20S-10LL or PZ-30S-20LL was even lower than that of the respective composite cement mortar without accelerator, i.e. retardation.

In order to check if the retardation was due to an BE1 overdose, 1.0 and 0.3 mass % BE1 were added to the PZ-20S-10LL. Figure 2 A shows that the lower BE1 doses also led to the retarding effect. It has to be checked whether or not this retarding effect also occurs in combination with other clinkers.
The retarding effect of BE1 on the early reaction of e.g. PZ-20S-10LL is additionally shown by the delay in the microstructure formation (Figure 3 A) and hydration heat release (Figure 3 B).

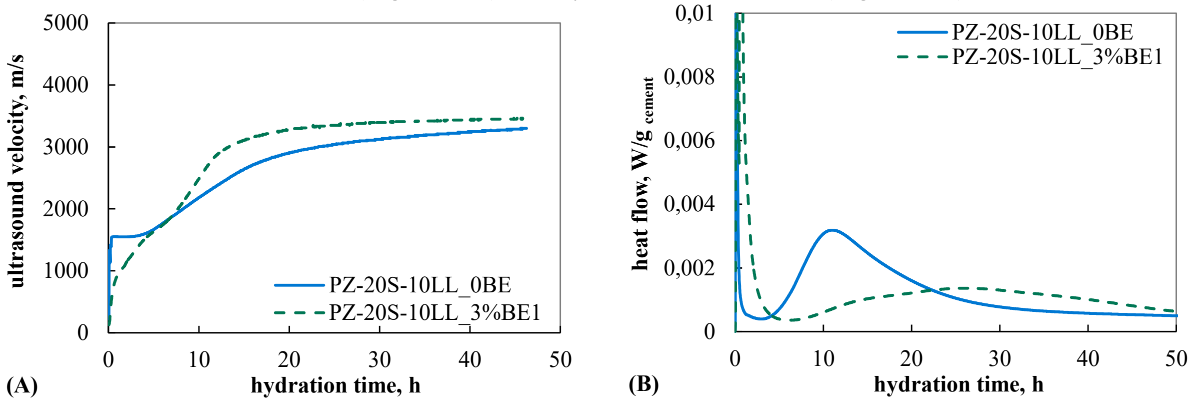


Figure 3. Ultrasound velocity (A) and heat flow (B) of cement paste with PZ-20S-10LL without and with 3 mass % BE1 as a function of hydration time.

3. Conclusions

Based on the above-mentioned results on the influences of commercially available hardening accelerators on the compressive strength of low-clinker composite cements containing blast furnace slag and limestone the following conclusions can be drawn:

- accelerators can increase the early compressive strength of composite cements with 50 mass % clinker to the level of Portland cement or beyond
- the accelerating effect decreased with decreasing clinker content in the cement
- synergetic effects from the other cement constituents besides clinker can partly compensate for the reduced late compressive strength caused by the accelerator addition
- as accelerator BE1 retarded the hydration of the composite cements, accelerators must always be adjusted to the cement and its constituents

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