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# Critical Investigations on Two-Stage Mixing to Increase Early Strength of Cements with Slag and Limestone

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**ABSTRACT**
Clinker- and resource-efficient composite cements with their great variety of concrete technology advantages suffer mostly from early compressive strength. Literature postulates that the early reaction of cement can be increased by more intensive two-stage mixing.
To which extent various two-stage mixing processes can increase the early hydration reactions and thus accelerate the compressive strength development of ternary cements with granulated blast furnace slag and limestone was systematically investigated up to 56 days. Additionally, influences of a reduced w/c ratio were determined.
Results show that reducing the w/c ratio increases both early and late compressive strength much more significantly than energy-intensive and more complex two-stage mixing processes.

**KEYWORDS:** *Composite cement, two-stage mixing, compressive strength, w/c ratio*

## 1. Introduction

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 their significantly reduced clinker content. However, with reducing the clinker content the early strength of concrete decreases, which is often considered as a disadvantage in construction practice.
It was therefore investigated whether the early strength can be increased by an amplified conversion of cement constituents into reaction products via application of intensive two-stage mixing, as described for example in Baumert and Garrecht (2010). According to this, in the first mixing stage, a suspension of water and cement and sometimes admixtures is produced at very high rotational speeds of the mixing tools of up to e.g. 10,000 rotations per minute (rpm). With such highly intensive mixed suspension, the aggregate is mixed at usual tool speeds in the second mixing stage.
If a so-called suspension mixer is used to produce the suspension, the particles are subjected to greater mechanical stress due to large centrifugal and shear forces as a result of the much higher tool speeds than in so-called intensive mixers, or especially in ordinary forced mixers. According to Reschke (1998), this deagglomerates the particles and distributes them more homogeneously in the suspension. As a result, cement suspensions are more reactive, since the particles, which are more isolated, thereby have a larger surface area and are wetted with water on all sides (Houlsby 1990). As per Juilland (2012), ions detaching from the cement particles' surfaces are shifted to a greater extent into the bulk aqueous solution due to the stronger mechanical stress. The interface therefore remains undersaturated for a longer time and more ions go into the solution. The stronger mechanical cement particle contacts could promote the conversion into reaction products, since crystal nuclei and/or first hydrates are dissolved from the surface and are distributed more regularly in the suspension, and the interfaces are then once more available for water influx or further

reaction (Kravetz 1959). In composite cements, softer limestone particles could be refined by harder constituents, such as granulated blast furnace slag. The same may apply to all cement constituents as a result of the higher tool speeds, and the refined cement would then be more reactive.

## 2. Materials and methods

To classify the influences of two-stage mixing processes, the compressive strength development of conventionally, i.e. single-stage mixed standard mortars acc. EN 196-1 was first determined. For this purpose, fresh mortar with 1350 g CEN standard sand, 450 g cement (c) and 225 g deionised water (w), i.e. w/c ratio = 0.50 (“050”), was produced in a commercial mortar mixer (“MM”). 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”) was used as clinker-efficient composite cement. 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. Properties of the cements are given in Table 1.

**Table 1. Cement properties.**

| | Blaine[1)] cm²/g | x‘ [2)] µm | n[3)] - | IST[4)] min | compressive strength[5)], MPa 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 |

[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.

For comparison, the compressive strength development of single-stage mixed mortar with a w/c ratio of 0.35 (“035”), 500 g cement and 1350 g CEN standard sand was determined. A commercially available PCE-based superplasticiser was added to the suspension so that its consistency was fluid and the mortars had a comparable spread of (150 ± 20) mm according to EN 1015-3. The water contained in the superplasticizer was deducted from the water added.

In the first stage of the two-stage mixing processes an intensive mixer (“IM”) EL5 from Gustav Eirich with a star agitator as mixing tool or a suspension mixer (“SM”) Ultra-Turrax T50 from IKA were used. As mixing tools for the suspension mixer, either a high-intensive dispersing head (“DK”) G 45 M or a cutting head (“SK”) W 65 were used. The rotational speeds of the mixing tools of the suspension mixer were up to approx. 9000 rpm (“9000”) and those of the intensive mixer approx. 1644 rpm (“1644”). Standard mixing times were 30, 60 or 120 s (“30”, “60” or “120”). In supplementary tests it was investigated whether the compressive strength of the mortar could be increased by mixing the suspension for a significantly longer time in the first mixing stage of up to 360 s (“360”). In order to be able to mix 360 s and to limit the temperature of the suspension to a maximum of 45 °C, the water to be added (“W”) was cooled to around 5 °C (“5°C”). Otherwise, the materials and equipment were kept at a temperature of 20 °C. After the first mixing stage, 675 g of suspension were transferred to the mortar mixer and mixed in the second mixing stage with 1350 g of standard sand for 30 s at approx. 140 rpm (planetary motion: approx. 62 rpm) and afterwards for 60 s at approx. 285 rpm (planetary motion: approx. 125 rpm). The two-stage mixing regimes for the w/c ratios of 0.5 and 0.35 are given in Table 2.

**Table 2. Two-stage mixing regimes.**

| w/c ratio = 0.5 action | duration | w/c ratio = 0.35 action | duration |
|---|---|---|---|
| Pre-mixing of c and w in MM | 60 | Pre-mixing of c and w in MM | 30 |
| mixing in IM or SM with DK or SK | see text | adding PCE and mixing | 30 |
| mixing with sand in MM | 90 | mixing in IM or SM with DK or SK | see text |
| | | mixing with sand in MM | 90 |

It was also investigated whether the particles of the PZ-20S-10LL were refined by the more intensive mixing. To exclude influences of hydration reactions, the cement was mixed with a non-aqueous medium (isopropanol) instead of water at equal volume. After mixing, the suspension was diluted with approximately three times the amount of isopropanol. Via vacuum filtration with a Büchner funnel and a Blauband filter the cement was separated. After drying and sieving over a 125 µm sieve to deagglomerate the particles, the particle size distribution after and before mixing was determined with a laser diffractometer 1190 from Cilas (dispersed in ethanol, 60 s ultra-sonic, triple determination) and evaluated according to the Fraunhofer theory.

## 3. Results

The compressive strength developments of the single-stage mixed mortars (MM) with Portland cement (PZ) or composite cement (PZ-20S-10LL) at a w/c ratio of 0.50 (050) or 0.35 (035) are shown in Figure 1.

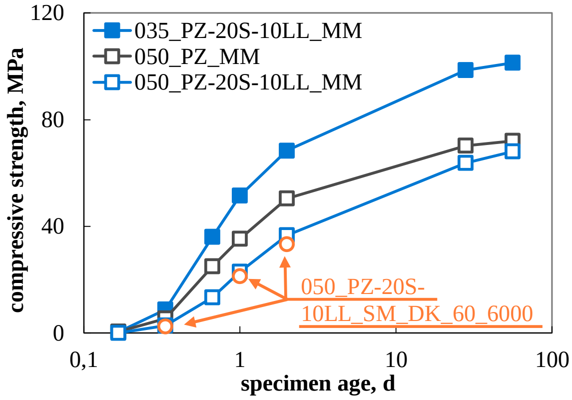


**Figure 1. Compressive strength development of mortar with Portland cement PZ or composite cement PZ-20S-10LL depending on the w/c ratio of 0.5 or 0.35 and the mixing procedure.**

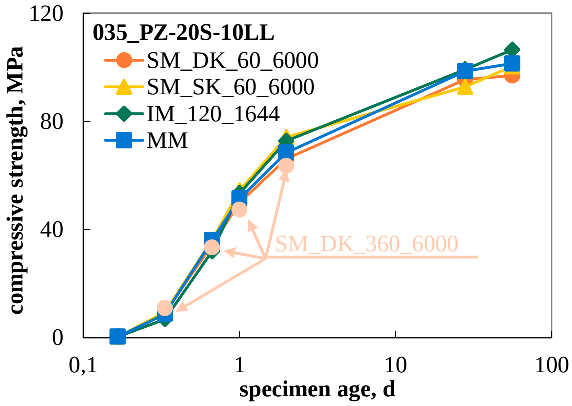


**Figure 2. Compressive strength development of two-stage mixed mortar with composite cement PZ-20S-10LL at w/c ratio of 0.35 compared to single-stage mixed mortar.**

As expected, the compressive strength of the single-stage mixed mortars with PZ-20S-10LL with a reduced clinker content to 70 mass % was around 30 % lower than that of the PZ mortars up to the age of two days (Figure 1). With increasing age, the compressive strength of the mortars with composite cement approached the compressive strength of the Portland cement mortars due to the latent hydraulic reaction of the blast furnace slag.

Figure 1 also shows the compressive strengths of mortars with PZ-20S-10LL at the age of 8, 24 and 48 h, which were mixed in two stages (open orange symbols). These results show by way of example for the different two-stage mixing processes tested (Chapter 2) that the compressive strength of mortar with composite cement at a w/c ratio of 0.50 could not be improved by the two-stage mixing processes applied in this project.

The lower early strength of resource-efficient composite cements with significantly reduced clinker contents and therefore significantly reduced specific $CO_2$ emissions can be increased relatively easily by reducing the w/c ratio. Figure 1 shows that as expected, the compressive strengths of the single-stage mixed mortars with PZ-20S-10LL at a w/c ratio of 0.35 were significantly higher at all test ages than those of the reference mortars with PZ at the w/c ratio of 0.50.

The development of the compressive strength of two-stage mixed mortar with composite cement PZ-20S-10LL at the w/c-ratio of 0.35 is shown in Figure 2 compared to the single-stage mixed mortar. Also, at the w/c ratio of 0.35 the mortar compressive strength could not be significantly increased by the applied two-stage mixing processes. Even the considerably longer mixing of the suspension of up to 360 s (360, filled light orange symbols) did not increase the mortar compressive strength.

The bulk densities of the hardened mortars with PZ-20S-LL10 at w/c = 0.35 ranged from 2270 to 2290 g/dm³. The comparatively uniform bulk densities, despite the clearly different mixing processes, show that the perhaps different amounts of air voids introduced via the various intensive mixing processes were able to be released during the compaction process of the mortars.

The mean values of the particle size distributions of PZ-20S-10LL before and after mixing in isopropanol are shown in Figure 3.

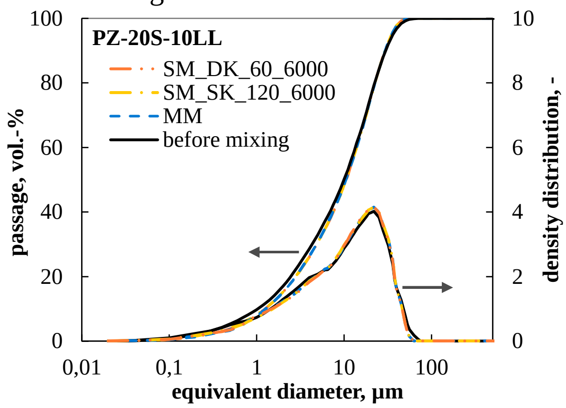


**Figure 3. Particle size distributions of composite cement PZ-20S-10LL before and after mixing in isopropanol with different mixing procedure.**

The particle size distributions show that PZ-20S-10LL was not measurably refined even by the suspension mixer with the high-intensity dispersing head (DK). In consequence, all the results presented show no indication for significantly increased conversion of the cement constituents into more strength-forming hydrates due to the applied two-stage mixing processes.

## 4. Conclusions

Based on the above-mentioned results on the use of two-stage mixing to increase the early compressive strength of clinker- and resource-efficient composite cements, the following conclusions can be drawn:
- two-stage mixing did not increase the early compressive strength of cements tested with w/c 0.5 and 0.35 and did not show any advantages in comparison to ordinary forced mixing
- in contrast to the two-stage mixing, the compressive strength of low-clinker cements could be increased more efficiently by reducing the w/c ratio and the application of a superplasticizer

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## References

Baumert, Chr. and Garrecht, H. (2010) “The Mixing Process of High Performance Concrete” (in German with English abstract) *Beton- und Stahlbetonbau*, 105(6): 371-378

Houlsby, A.C. (1990) “*Construction and design of cement grouting*” New York: John Wiley and Sons, 10-28

Juilland, P. et al. (2012) “Effect of mixing on the early hydration of alite and OPC systems” *Cement and Concrete Research*, 42(9): 1175-1188

Kravetz, G.A. (1959) “Cement and clay grouting of foundations” *ASCE Journal of Soil Mechanics and Foundation Devision*, 85: 109-114

Reschke, A.E. (1998) “The development of colloidal mixer based CRF systems” In: Bloss, M. (ed) *Proceedings of the Sixth International Symposium on Mining with Backfill*, Brisbane, Australia, 14-16 April, 65-70