The hydration of fast setting spray binder versus (aluminum sulfate) accelerated OPC

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Abstract The (early) hydration mechanisms of two different binder systems used for shotcrete were investigated: the so far almost unexplored low sulfate binder (spray binder), used in the field of dry-mix shotcrete; and ordinary Portland cement, accelerated by aluminum sulfate, widely used for wet-mix shotcrete. The basis for the fast setting of the spray binder is the rapid dissolution of C_3A and the subsequent formation of flaky CO_3-AFm phases. Thereby induced high aluminum concentrations in the pore solution lead to a blockage of alite dissolution during the first hours of hydration. At later stages, higher amounts of portlandite are formed in the dry-mix, compared to the wet-mix system. The lower calcium availability for portlandite formation in the wet-mix system is explained by an enhanced formation of C–A–S–H phases with a higher Ca:Si ratio. Additionally, wet-mix systems show lower porosity and higher compressive strength after 1 d of hydration and beyond.

Keywords Shotcrete · Hydration · Accelerator · Pore solution

1 Introduction

Shotcrete, also known as gunite or sprayed concrete, is a widely used material for underground constructions, slope stabilizations, temporary pit supporting, construction overhauling and fire protection layers. Large amounts of shotcrete are used for tunneling in combination with the new Austrian tunneling method (NATM) [1]. A proper adhesion on the rock surface and a rapid development of early strength are mandatory in this field of application to ensure safety and cost-efficiency during the cyclic tunnel excavation process.

Nowadays two main techniques of shotcrete application are available: the so called wet- and dry-mix processes. In the wet-mix process, fresh concrete is supplied with a truck mixer to the construction site and filled via hopper into a mobile spraying device. The concrete is pumped to the nozzle, where compressed air and liquid setting accelerator are added. The
addition of the setting accelerator allows, together with the high speed shooting process, for the shotcrete to stick on the surface where it is applied and to reach the required early strength development during the first minutes and hours of hydration [2]. Due to their low impact on final strength and their beneficial safety profile (due to moderate acidic pH values) [3, 4], alkali-free setting accelerators based on aluminum sulfate, are nowadays preferred in many countries. The main benefits of the wet-mix process are the good controllability of the water/binder ratio, and the high spraying capacity. In the dry-mix process, a dry ready-mix (binder and aggregates) is transported via compressed air to the nozzle, where water is added as controlled by the nozzleman. The small size of the spraying equipment and the use of a dry ready mix allows the application of dry-mix shotcrete even at construction sites with limited space or far from concrete plants. The fast setting and hardening can be achieved in this case with the use of powdery setting accelerators (added to the binder and aggregate mix) or with the use of special rapid setting cements, so called ‘spray-binders’, which are mainly characterized by a low sulfate content in comparison to ordinary Portland cement (OPC). Despite the frequent use of spray binder for dry-mix shotcrete applications in the Alps region, the scientific knowledge regarding the hydration process is almost inexistent. Therefore, the objective of the present research is the investigation and elucidation of the (early-) hydration mechanisms of dry-mix shotcrete with spray binders and compare it to the phase assemblages of a wet-mix system, with OPC and aluminum sulfate based setting accelerators. By following the hydration in the solid and liquid (pore solution) phases of the systems, starting right after water addition, this study highlights the mechanisms that govern (early-) strength and consequently play decisive roles on the durability properties of dry- and wet-mix shotcrete.

1.1 Hydration of dry-mix systems with spray binders

To the authors knowledge only one study investigating the hydration of spray binders has been published until now [5]. Generally speaking, this type of binder is mainly composed of cement clinker. Therefore, the knowledge about the hydration processes in spray binders is mostly based on the hydration of the major cement clinker phases C₃A and alite in the absence of calcium sulfate.

1.1.1 Hydration of C₃A in the absence of calcium sulfates

In the absence of calcium sulfates C₃A (3CaO·Al₂O₃) reacts very fast with water, producing high heat (see Fig. 10 in the Appendix) and forming flaky Al₂O₃-Fe₂O₃-mono (AFm) phases, with the general formula [Ca₂(Al,Fe)(OH₆)]X·nH₂O, where X represents one formula unit of a single charged anion or a half formula unit of a double charged anion. In OPC systems, the most important anions are OH⁻, SO₄²⁻ and CO₃²⁻, forming hydroxy-AFm (OH-AFm), monosulfate (SO₃-AFm) and carboaluminate (CO₃-AFm) phases, respectively [6, 7].

In OPC systems the hydration of C₃A is mainly controlled by calcium sulfates, which are known for their retarding effect. The blockage of active C₃A dissolution sites by coupled calcium and sulfate ions is responsible for the retardation [8–12]. The sole adsorption of sulfate ions on the C₃A surface is only likely below a pH of ~12 and the pore solution of cementitious systems is usually above this value [9].

The influence of alkali sulfates in pure C₃A-water systems has been only investigated in few studies. It was found that sodium sulfate (Na₂SO₄) does not significantly change the C₃A dissolution rate [13] and heat of hydration [14] even at high concentrations ≥100 mmol/L. Potassium sulfate (K₂SO₄) [15] and magnesium sulfate (MgSO₄) [13, 15] solutions were shown to lower the C₃A dissolution rate to a certain extent, depending on the concentration. However, the effect is smaller compared to that of calcium sulfate and the experiments performed by [13, 15] to show this effect used moderate pH values (<12), so the results may not be fully applicable to common cementitious systems.

1.1.2 Hydration of alite in the absence of calcium sulfates

C₃S (3CaO·SiO₂), also known as alite, is the major constituent of OPC clinker. Due to its importance regarding early age and long-term hydration properties of cementitious systems, the hydration of C₃S/alite has been investigated in numerous studies in the past. In pure C₃S-water pastes, C₃S hydrates to form
calcium-silicate-hydrates (C–S–H) and portlandite (Ca(OH)₂) [16].

However, there is a major difference between pure C₃S and the actual alite present in OPC systems, as well as most synthetic alite samples used for experiments. Aluminum- and magnesium oxides are frequently used as dopants to stabilize the monoclinic structure of alite, which is similar to the alite present in OPC [17]. Beside the crystal structure, the dopants also affect the hydration process of alite. In particular, aluminum can potentially influence the dissolution–precipitation process during alite hydration [18–23], and it is also incorporated into C–S–H phases (C–(A)–S–H) [24, 25].

The hydration process of alite can be divided into several stages, following the heat of hydration by isothermal calorimetry (Fig. 11 in the Appendix). The initial period starts upon contact with water and is characterized by a large heat production, originating from: (a) heat released by wetting the powder [26], (b) alite dissolution [26–28] and (c) early precipitation of C–(A)–S–H nuclei [11, 29–32]. The initial period is followed by a severe decrease in the heat of hydration which initiates the slow reaction or ‘dormant’ period. In this period the heat of hydration is very low, but it never goes down to zero. According to Juilland et al. [33], this period is coupled with a decrease of undersaturation in the pore solution with respect to alite.

After the end of the dormant period, the main hydration of alite, with formation of C–(A)–S–H and portlandite starts. This period is often subdivided in an acceleration (up to the maximum of the main peak) and a subsequent deceleration period [34]. A recent study from Ouzia and Scrivener [35] explains the slowdown of heat evolution after the main hydration peak with the C–(A)–S–H growth theory, originally proposed by Bazzoni [36] in 2014. According to this theory C–(A)–S–H ‘needles’ start to grow after the end of the dormant period perpendicular to the alite grain (outer C–(A)–S–H). At the beginning of the main hydration period, the number and length of those needles increase fast, resulting in a strong increase of the heat of hydration. Once the alite surface is almost fully occupied with C–(A)–S–H, a slowdown of the C–(A)–S–H growth rate occurs, which corresponds to the slowdown of heat flow after the main hydration peak. Towards the end of the main hydration period the formation of inner C–(A)–S–H (in the gap between the outer C–(A)–S–H and the reacting grain) starts.

At later age (> 1 d) the role of available water and space becomes predominant: once the degree of hydration exceeds a certain value, no more external water is available and the growth of the outer product stops [11, 37]. Additionally, the crystallization in smaller pores requires higher ion concentrations in the pore solution than in bigger pores [11]. Both mentioned effects contribute to the further decrease of the alite hydration rate with progressing hydration time.

1.2 Hydration of wet-mix systems accelerated by aluminum sulfate based setting accelerators

Al³⁺-ions (from the accelerator) are immediately transformed into Al(OH)₄⁻-ions at the alkaline conditions in the cement paste and react with SO₄²⁻-ions (from the accelerator and/or the pore solution) and Ca²⁺-ions (from the pore solution) to form ettringite, which is responsible for the fast setting [2, 38, 39]. The rapid formation of ettringite, together with the acidic nature of the setting accelerator, reduces Ca²⁺-level and pH in the pore solution, promoting alite and C₃A dissolution. This in turn leads to an increased supersaturation with respect to calcium–(aluminum)–silicate–hydrates (C–(A)–S–H) and consequently to the precipitation of nuclei of these phases [25]. Sulfate ions (SO₄²⁻) adsorb preferably on these early C–(A)–S–H nuclei [40], leading to an earlier sulfate depletion in the pore solution, compared to non-accelerated systems. This earlier sulfate depletion can cause an ‘uncontrolled’ C₃A reaction before or during the main alite hydration, compromising the formation of strength giving C–(A)–S–H phases due to consumption of extra Ca²⁺-ions needed for the hydration of C₃A to form AFm phases (e.g. monosulfate).

The Al₂O₃/SO₄²⁻ molar ratio present in the accelerator is also crucial for the hydration of C₃A and alite: if the Al₂O₃/SO₄²⁻ molar ratio is higher than in ettringite (0.33) then the consumption of sulfate phases, present in the ordinary Portland cement, is favoured to ensure ongoing and stoichiometric ettringite formation. This also leads to a more rapid depletion of SO₄²⁻-ions in the pore solution, with subsequent impacts on C₃A and alite hydration.

At later stages of hydration, Al₂(SO₄)₃ accelerated mixes show a reduced portlandite content in comparison to conventional OPC or dry-mix systems. It is
hypothesized that the consumption of Ca\(^{2+}\)-ions due to the massive ettringite formation is responsible for this behaviour [38, 41].

2 Experimental

Figure 1 presents the experimental program of this study. Tests were performed with mechanically mixed (not sprayed) mortar and paste samples. The mixing procedure of both sample types is explained in Sect. 2.3 (Mortar/paste preparation). Mechanical mixing was chosen for this lab- study, even though it does not completely reproduce sprayed shotcrete. Spraying leads to slightly faster (C\(_3\)A) hydration reactions due to higher shearing conditions compared to mechanical mixing [17, 40, 42]. Nevertheless, heat of hydration and phase development are very similar for both sample types [42], ensuring a good applicability of the results shown in this study also for sprayed shotcrete.

2.1 Materials

For the experiments a CEM I 52.5 R cement according to EN 197-1 [43], and a spray binder, according to the Austrian Guideline for shotcrete [4] were used. The cement, from now on called ‘CEM I’ and the spray binder, from now on called ‘SpB’ were provided from the same cement producer. The mineralogical composition (Table 1) of CEM I and SpB was determined by X-ray diffraction (PANalytical X’Pert PRO, Co tube, 40 kV, 40 mA, 7–80° 20, step size 0.017° 20, time per step: 40 s), and subsequent Rietveld [44] analyses. The chemical composition, obtained with X-ray fluorescence analysis, of CEM I and SpB was provided by the manufacturer (Table 2). Following physical parameters were measured of CEM I and SpB: (i) dry particle density (using a pycnometer and isopropanol), (ii) grain size distribution (laser diffraction with dry dispersion: sympatec Helos H2395 & Rodos) and (iii) Blaine surface according to EN 196-6. Results are given in Table 3.

For the mortar samples, a carbonate sand (34 wt% CO\(_2\)) with grain fraction 1–4 mm was used. For wet-mix specimens (mortar and paste) a commercial

| Table 1 | Mineralogical composition of CEM I and SpB  |
|---------|------------------------------------------|
| Phase (wt%) | CEM I | SpB |
| Alite (C\(_3\)S) | 62.9 | 67.6 |
| C\(_2\)S | 8.8 | 9.4 |
| C\(_3\)A (cubic) | 2.6 | 1.1 |
| C\(_3\)A (orthorhombic) | 8.5 | 9.7 |
| C\(_4\)AF | 7.3 | 6.3 |
| Anhydrite | 3.4 | – |
| Arcanite | 0.4 | 0.6 |
| Bassanite | 1.5 | 0.9 |
| Gypsum | 0.3 | – |
| Dolomite | 1.6 | – |
| Periclase | 2.7 | 3.8 |
| Portlandite | – | 0.2 |
| Lime | – | 0.4 |

Fig. 1 Diagram showing the experimental program of this study.
liquid, alkali-free setting accelerator, commonly used for wet-mix shotcrete applications was used. The properties of the accelerator are shown in Table 4. All samples were mixed with tap water at a temperature of 20 ± 2 °C.

Table 4 Accelerator (acc.) characteristics, according to the supplier

|                        | CEM I | SpB |
|------------------------|-------|-----|
| Al₂O₃/SO₄²⁻ molar ratio| 0.33  |     |
| Total Al₂(SO₄)₃ content| ~ 35 wt%|   |
| Total H₂O content      | ~ 65 wt% |
| pH                     | 2.4 (14.4 °C) |
| Density                | ~ 1.4 kg/dm³ |

2.2 Mix design

In Table 5 the mix composition of the dry- and wet-mix samples is shown. The water/binder (w/b) ratio was 0.5 for all mixes. In the accelerated wet-mix samples, the accelerator dosage equals 7% by weight of CEM I.

2.3 Mortar/paste preparation

The standard mixing regime for mortars, according to EN 196-1 [45] is not appropriate for the conducted mixes due to the fast setting after adding either the setting accelerator to the wet-mix or the water to the dry-mix. Therefore, a more adequate process of mixing and compaction was carried out. Dry-mix mortar samples were prepared as follows: 300 g water were added to a 5 l Hobart mixer. Then the whole amount of pre-mixed solids (600 g binder + 1200 g aggregates) was added by means of a 1510 ml flat aluminum scoop during 5 s mixing at about 150 rpm. After that, the mixing speed was increased to 300 rpm for 25 s. For dry-mix paste samples, the SpB and water were mixed with a Vortex-mixer (Velp Scientifica ZX4) at 3000 rpm in a standard calorimetry container (~ 120 ml) for 30 s. For wet-mix samples the procedure is described in detail in [25].

For additional tests with SpB mixes (see Fig. 12 in the Appendix), either a 0.2 M KOH or a 0.1 M K₂SO₄ solution was used as ‘mixing water’.

2.4 Setting time

The setting time was determined on paste samples via a modified Vicat test, based on EN 196-3 [46]. The preparation of the dry-mix (SpB + water) was carried out as follows: 250 g of SpB were hand-mixed with water (w/b 0.5) for 60 s and the paste was immediately poured into the Vicat cone. The time of water addition was noted as time zero. For the wet-mix samples the preparation was as follows: 250 g CEM I were hand mixed with water (w/b 0.5) for 90 s. After a rest period of 10 min the calculated amount of accelerator (17.5 g) was added to the mix, while intensive hand-mixing for 30 s. Thereafter the accelerated paste was quickly transferred into the Vicat cone and compacted by beating the filled cone several times on a table surface. The time of accelerator addition was noted as time zero.

The initial setting time was taken when the Vicat needle (300 g) did not drop to the bottom of the sample for the first time. Final setting was attained at the time when the penetration depth was < 1 mm. The tests
were carried out under standard laboratory conditions of 65% ± 5% RH and 20 ± 2 °C.

2.5 Compressive strength tests

Specimens were prepared as follows: the mortar was rapidly poured into steel prism molds (40 × 40 × 160 mm) while vibrating for 30 s. The prisms were then covered with a glass plate and stored at 100% RH and 20 °C (wet storage) for ~ 6 h. The specimens were then demolded and kept under wet storage. Compressive strength tests on mortar prisms were carried out after 6 h, 1 d and 28 d of hydration. After 6 h and 1 d the compressive strength was determined with a displacement-controlled testing machine (Shimadzu, 100 KN max load) with a testing speed of 1 mm/min. The 28 d compressive strength tests were performed by the use of a force-controlled testing machine (Toni Tec, 300 KN max load), according to EN 196-1 [45].

2.6 Hydration stoppage

The hydration of accelerated cement pastes and SpB-water mixes was stopped by solvent exchange with isopropanol [47] at certain times in the period from ~ 5 min to 28 d after water/accelerator addition. For this purpose, the sample was gently ground with a mortar and pestle and subsequent drained by means of vacuum filtration while rinsing several times with isopropanol. The sample was then dried at 40 °C for ~ 4 h and stored air-sealed.

2.7 Thermogravimetric analysis (TGA, DTA)

TGA measurements were carried out on stopped paste samples in a Netzsch STA 409EP equipment with a heating rate of 10 °K/min, from 30 to 1050 °C under nitrogen atmosphere. For the determination of bound water in the hydrated samples, the mass loss between 30 and 600 °C was considered.

2.8 Quantitative X-ray diffraction (QXRD)

Phase development during hydration was determined on stopped dry- and wet-mix paste samples. Measurements were performed on a PANalytical X’Pert PRO diffractometer (Co tube, 40 kV, 40 mA, 7°–80°, step size 0.017, time per step: 40 s). Phase quantification was carried out by means of the Rietveld refinement method [44] with the use of the HighScore Plus Software (Malvern Panalytical, v. 3.0.4). The amorphous content was calculated by means of the G-factor method [48] with the use of an alumina powder (NIST SRM 676a) as external standard.

2.9 Total porosity calculation

The total porosity ($P_t$) of dry- and wet-mix samples was calculated based on the volumes of the CEM I or SpB ($V_{CEM I/SpB}$), the solid content of the accelerator, if present ($V_a$), the water ($V_w$) and hydrates formed ($V_{hydrates}$) before ($t = 0$) and during ($t$) cement hydration, according to Eq. 1 [49, 50]. The chemical shrinkage and porosity due to cracks and/or air voids is not taken into account in the calculations [49, 50]. Volumes were computed based on QXRD and TGA results. The specific densities of the cement and hydration products were taken from ICSD Database [51] and are given in Tables 7 and 8 in the Appendix. The XRD amorphous content was assumed to correspond to C–(A)–S–H phase with an approximated density of 2.2 g/cm³ [52].

$$P_t = \frac{V_{CEM I/SpB,t=0} + V_w + V_a - V_{CEM I/SpB,t} - V_{hydrates,t}}{V_{CEM I/SpB,t=0} + V_w + V_a}$$

2.9.1 Isothermal calorimetry

Paste samples were immediately transferred after water (dry-mixes with SpB) or accelerator addition (wet-mixes with CEM I) to an isothermal calorimeter
CO$_3^{2-}$ in the pore solution was calculated as follows: for the dry-mix sample the CO$_3^{2-}$ originating from the mixing water (5 mmol/L) and an assumed additional carbonate source of 220 mmol/L minus the amount of CO$_3^{2-}$ bound in CO$_3$-AFm phases, according to QXRD analyses, was taken into account. Detailed information regarding the necessity of an external, soluble carbonate source, is given in Sect. 4.1. For the wet-mix sample the CO$_3^{2-}$ originating from the mixing water (5 mmol/L) was considered. Charges were balanced by K$^+$-ions.

2.9.4 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses

Morphology and chemical composition of early age hydrates (15 min after water addition) of a dry-mix paste sample were analyzed by means of a field emission scanning electron microscope (FESEM) model TESCAN MIRA3 equipped with the EDAX EDX detector. The specimens were sputter-coated with carbon using an SCD 050 Sputter Coater, BAL-TECH device with a current of 1.5 A under vacuum $\sim 5\times10^{-2}$ mbar.

For the determination of the chemical composition it was assumed that the early age hydrates of the dry-mix sample did not contain silicon (Si). The amount of Si measured was assumed to originate from intermixtures with the cement clinker phases alite (C$_3$S) and belite (C$_2$S). Therefore, the amounts of calcium (Ca) and oxygen (O) in the hydrates were corrected, according to Eqs. 2 and 3. The factor 2.88 represents the weighted average elemental ratio of Ca/Si of both C$_3$S and C$_2$S and the factor 3.0 describes the elemental ratio of O/Si in C$_3$S and C$_2$S in the cement clinker.

$$C_{a\text{corr}} = C_{a\text{meas}} - S_{i\text{meas}} \times 2.88$$

$$O_{\text{corr}} = O_{\text{meas}} - S_{i\text{meas}} \times 3.0$$

3 Results

3.1 Setting time & compressive strength

The setting times (initial, final) of both, dry- and wet-mix samples are given in Table 6. The setting of the dry-mix happened a lot faster than in the wet-

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(I-Cal 4000 HPC). The acquisition rate was 6/min during the first 2 h and 1/min until 48 h.

2.9.2 Pore solution extraction/analysis

The pore solution of mortar samples was squeezed out at various times during the first 24 h of hydration. About 400–600 g of mortar were placed into a custom made squeezing apparatus. Up to 600 MPa pressure was applied within 2–6 min by an electronically controlled testing machine (L. Kissling & Co. VPC-21). To remove any solids, the obtained solution was filtered through a 0.25 μm cellulose acetate filter. The pH was measured by a WTW 7110 pH meter and WTW senTix 940 pH electrode. Electrical conductivity (EC) measurements were carried out using a Thermo Scientific Orion Tristar device and an Orion 013005MD conductivity cell.

Additional pH analyses during the first sec/min after water/accelerator addition were carried out with the use of photometric electrodes, as described in [53]. This method allows for in-situ monitoring of the pH in the system without having to squeeze out the solution. The pH probes were introduced in the samples just after water/accelerator addition and the pH values were recorded every 5 s. The influence of the accelerator on the pH in the wet-mix sample was monitored by combining two datasets (before and after accelerator addition).

The pore solution was chemically analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optima 8300, analytical error: < 5%) and ion chromatography (IC, Dionex ICS 3000, analytical error: < 3%). The aqueous concentrations of Na$^+$, K$^+$, SO$_4^{2-}$ and Cl$^-$ were determined with IC from diluted (1:200 with ultrapure water, Milli-Q Plus UV, 18.2 MΩ at 25 °C) samples. Additionally, with ICP-OES, the aqueous concentrations of Ca$^{2+}$, Mg$^{2+}$, Si$_{aq}$, Al$_{aq}$ and Fe$_{aq}$ were determined from diluted (1:100 with a 2% HNO$_3$, suprapure) samples.

2.9.3 Thermodynamic calculations

Ion charge balances, aqueous speciation, ionic strength and saturation indices (SI) of the pore solutions with respect to the relevant mineral phases were calculated using the PHREEQC software (v. 3.4.0–12,927) and CEMDATA 18 database [54].
mix sample. Figure 2 shows the compressive strength of mortar prisms of the wet- and dry-mix samples after 6 h, 24 h and 28 d of hydration. After 6 h both mixes showed similar values around 2 MPa. 1 d and 28 d compressive strength values were ~20% higher in the wet-mix than in the dry-mix sample.

3.2 Heat of hydration and phase development

The heat of hydration of the dry- and wet-mix samples, obtained by means of isothermal calorimetry, is shown in Figs. 3a, b and 4a, b together with the development of selected crystalline phases and amorphous content, determined by QXRD. According to the development of heat of hydration and phases, the early hydration of dry- and wet-mix systems was split into several stages.

3.2.1 Dry-mix

I (initial period) Instantly after water addition a large exothermic signal was detected. After ~5 min, during the rapid setting, a kink in the heat flow curve occurred. After this, the heat of hydration increased again until ~15 min after water addition. This peak was followed by a severe decrease of the heat flow which lasted until ~2 h. According to XRD data ~33 wt% of C₃A had dissolved within the first 15 min after water addition and CO₃-AFm (hemicarbonate) had formed. This latter phase may also be partly included in the amorphous content due to its poor crystallinity [55]. In addition, the formation of small amounts of SO₃-AFm (monosulfate) was detected. OH-AFm phases (C₄AHₓ), hydrogarnet (C₃AH₆) or strätlingite were not found in the XRD patterns. During this hydration stage no alite had been dissolved.

II (low reaction period) In this period a low amount of heat (<1 mW/g) was released and neither significant amounts of C₃A or alite dissolved. The increase in the amorphous content (between ~2 and 6 h of hydration) is linked to the precipitation of C–(A)–S–H nuclei before the onset of the main alite hydration period.

III (main alite hydration) This hydration stage was governed by the dissolution of alite and the formation of X-ray amorphous C–(A)–S–H phases and portlandite.

IV (later age) Between 1 and 28 d of hydration almost all residual C₃A was dissolved and more CO₃-AFm phases and monosulfate were formed. Alite hydration was further promoted, but considerable amounts of alite still remained after 28 d of hydration.

In addition to the hydration kinetics of the SpB also the effect on heat of hydration of different modifications of the dry-mix system was tested: (i) the use of a 0.2 M KOH solution (pH 13.3) as mixing water, (ii) the use of a 0.1 M K₂SO₄ solution as mixing water, and (iii) an additional Ca-source (Ca(OH)₂). The results are shown in Fig. 12 in the Appendix. The use of a 0.2 M KOH solution had low impact in hydration stage I, but significantly shortened the low reaction period and accelerated alite hydration. Similar, but less pronounced behaviour was observed with the

| ID      | Initial setting time (min:sec) | Final setting time (min:sec) |
|---------|-------------------------------|-----------------------------|
| Dry-mix | 03:20                         | 05:40                       |
| Wet-mix | 36:40                         | 60:00                       |

Table 6 measured setting times of the dry- and wet-mix samples
0.1 M K$_2$SO$_4$ solution. This means that the effect of the KOH solution on the reaction kinetics of SpB is at least partly related to the higher initial pH value, since both mixes had equivalent potassium concentrations at the beginning of the hydration. The addition of 10% Ca(OH)$_2$ to the SpB increased the heat output in hydration stage I, which is associated with AFm formation. Additionally, the low reaction period was shortened which led to an earlier maximum of the main alite hydration period.

### 3.2.2 Wet-mix

1 (initial period) Instantly after the Al$_2$(SO$_4$)$_3$ accelerator intermixture, massive heat release was measured. Ettringite, amorphous phases (probable C–(A)–S–H nuclei) and small amounts of gypsum were formed. The alite content decreased, while C$_3$A was not affected by the accelerator addition.

II (secondary C$_3$A and main alite hydration period)

After the strong slowdown in the initial period, the
heat of hydration started to increase again at \( \sim 3 \) h after accelerator addition, without an earlier extended slow reaction period. This hydration period is governed by both C3A and alite hydration. Alite hydrated to X-ray amorphous C\( \text{-(A)}\)–S–H phases and portlandite after \( \sim 6 \) h of hydration and beyond. By means of the obtained data, an explicit differentiation between the contribution of C3A and alite to the heat flow curve is not possible, however in the investigated heat curve, two ‘shoulders’, attributed to aluminate reaction [6, 26], are visible. The QXRD data (see Fig. 4a) shows that the first shoulder (between \( \sim 3 \) and \( \sim 8 \) h) is due to the ettringite formation, while the second one (between \( \sim 9 \) and \( \sim 12 \) h) is caused by the formation of monosulfate (AFm).

**III (later age)** Hydration of alite continued as in hydration stage II, but at a much slower reaction rate. This transition from fast to slow is tagged at the kink in heat of hydration at \( \sim 16 \) h. Monosulfate was formed through the transformation of ettringite and also by C3A reaction. Small amounts of alite still remained after 28 d of hydration.

### 3.3 Phase assemblage and calculated total porosity

The time resolved phase assemblage and the resulting total porosity of both the dry- and the wet-mix sample is shown in Fig. 5. The initial gain in sample volume in the wet-mix sample is caused by the addition of the accelerator.

The calculated total porosity is at all times higher in the dry-mix than in the wet-mix sample. It is shown that the massive ettringite formation at early age of hydration in the wet-mix sample led to a higher reduction in porosity than the AFm phases (CO3-AFm and monosulfate) formed in the dry-mix sample. At later age, the amount of portlandite was found to be significantly higher in the dry-mix samples, whereas the X-ray amorphous content (mainly C–(A)–S–H phases) was lower in the dry-mix in comparison to the wet-mix.

### 3.4 Pore solution

The measured values of selected elemental concentrations, pH and EC in the pore solutions of the dry- and the wet-mix systems during \( \sim 24 \) h of hydration are shown in Fig. 6a–e and in the Appendix in Table 10. The ion concentrations in solution gives a snapshot of the system that reflects both the effects of dissolution of solid (cement-) phases and the precipitation of hydration products (e.g.: ettringite, AFm-phases, C–(A)–S–H, portlandite). For the dry-mix the first ‘squeezed-out’ pore solution was collected \( \sim 4 \) min after water addition. In the wet-mix, the points in the graphs at 0 h display the state of the pore solution before accelerator addition (after the 10 min rest period). The second points show the data of the first measurement \( \sim 2 \) min after accelerator addition. In addition, the pH development during the first min after water addition of the dry- and wet-mix was measured via photometric electrodes [53].

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Fig. 5 Phase assemblage and calculated total porosity of a dry-mix and b wet-mix systems over 28 d of hydration. AFm phases are shown as the sum of CO3-AFm phases (hemicarbonate, monocarbonate) and monosulfate.
whereby a continuous measurement was possible (Fig. 6a).

In the dry-mix system, the pH values increased strongly during the first seconds after water addition, but stayed below 13 until ~ 1 min. After ~ 30 min the pH reached a plateau of ~ 13.8 and remained at this value until the end of the measurement (24 h).

For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

**Fig. 6** Development of pH a, Ca\(^{2+}\) b, Si\(_{\text{aq}}\) c, Al\(_{\text{aq}}\) d and SO\(_{4}^{2-}\) e concentrations in the pore solution of the dry- and wet-mix. Note that the Al\(_{\text{aq}}\) concentration is plotted in a logarithmic scale.
In the wet-mix system, the addition of the Al$_2$(SO$_4$)$_3$ accelerator led to a drop of pH from ~ 13.5 to ~ 12, followed by an increase up to the initial value (before accelerator addition), after ~ 1 h of hydration. Thereafter, the pH slightly decreased again to 13.07 until ~ 4 h after accelerator addition and subsequently increased until ~ 24 h (not shown).

Dissolved Ca$^{2+}$ in the pore solution is provided by the dissolution of Ca-bearing cement clinker phases (primary C$_3$A & alite) and calcium sulfates. Ca$^{2+}$ concentrations in the dry-mix system were below 1 mmol/L shortly after water addition and did not exceed 5 mmol/L during the measurements. In the wet-mix, the intermixture of the Al$_2$(SO$_4$)$_3$ accelerator and subsequent ettringite formation led to an abrupt consumption of Ca$^{2+}$ ions from the pore solution. After this initial ettringite formation was completed, the Ca$^{2+}$ concentration rose again. This was in turn followed by a decrease in Ca$^{2+}$-ions in solution up to 2 h of hydration. Thereafter Ca$^{2+}$ concentration remained constant until 4 h and subsequently decreased due to ‘secondary’ ettringite and C–(A)–S–H formation.

In the present systems, at early age, dissolved silicon (Si$_{aq}$) in the pore solution originated primarily from the dissolution of alite. Si$_{aq}$ concentrations over 24 h in the pore solution were similar in the dry- and the wet-mix. Accelerator addition in the wet-mix led to a small increase of Si$_{aq}$. In both mixes a distinct drop of Si$_{aq}$ around 4 h of hydration is visible. At the start of the silicate reaction (during ~ 4–6 h), the silicon concentrations strongly increased to around 10 mmol/L.

Aluminum (Al) concentrations in the dry-mix system were around 30–40 mmol/L shortly after water addition and strongly decreased afterwards due to the formation of hemicarbonate. The formation of 1 mol of hemicarbonate requires 2 mol of Al. In the wet-mix, the intermixture of the Al$_2$(SO$_4$)$_3$ accelerator did not lead to a change in the Al-concentration, which implies that the accelerator was completely ‘consumed’ within a few min, mainly through ettringite and C–(A)–S–H formation. Thereafter the amount of Al$_{aq}$-ions in solution remained constant until ~ 2 h of hydration, followed by a sharp drop to 0.024 mmol/L at ~ 4 h. After this decline the Al-concentration in the pore solution rose again to values similar to those present during the initial hydration period (~ 0.5 mmol/L).

In the dry-mix sample SO$_4^{2-}$-ions in the pore solution originate from the rapid dissolution of arcanite (K$_2$SO$_4$) and bassanite present in the SpB. Shortly after water addition, the SO$_4^{2-}$ concentration was about 120 mmol/L. Afterwards it decreased rapidly to lower values and remained below 5 mmol/L until ~ 24 h of hydration. Shortly after the accelerator addition in the wet-mix, the sulfate concentration in the pore solution increased only slightly, in accordance to the very rapid ettringite formation after accelerator intermixture. During ~ 4 h of hydration the consumption of SO$_4^{2-}$ due to ettringite formation and SO$_4^{2-}$ adsorption on C–(A)–S–H phases, and the provision of SO$_4^{2-}$ (due to dissolution of sulfate containing cement phases) was balanced. Afterwards the SO$_4^{2-}$-ion concentration in the pore solution decreased to ~ 10 mmol/L. However, during the 24 h measurement, the SO$_4^{2-}$ and Ca$^{2+}$-concentrations remained high enough to prevent an ‘uncontrolled’ C$_3$A reaction.

The pore solution data was used to calculate the saturation indices (SI) of selected cement clinker phases and hydration products (see Fig. 7a–c and Appendix Table 11). SI values higher than zero indicate potential precipitation, while values below zero indicate possible dissolution of a phase. The descriptions in Fig. 7a–c show the effective dissolution/precipitation processes, according to QXRD data (see Fig. 4a, b and in Tables 7 and 8 in the Appendix).

For both types of mixes (dry- and wet-mix), the clinker phases C$_3$A and C$_3$S were strongly undersaturated, while their main hydration products hemicarbonate (dry-mix) or ettringite (wet-mix) and C–A–S–H phases (both systems) were oversaturated during the 24 h measurement. In the dry-mix system, portlandite is undersaturated during ~ 4 h due to very low Ca$^{2+}$ levels in the pore solution. Thereafter the SI indicates possible precipitation of portlandite. In the wet-mix system, the addition of the setting accelerator and the consequent reduction of the pH value of the pore solution increased the undersaturation with respect to C$_3$A and C$_3$S.

The development of the SI over time can also be used to gain knowledge about the actual dissolution–precipitation processes [56]. For the clinker phases a trend of the SI towards higher undersaturation indicates dissolution and a trend towards lower undersaturation shows in most cases that the dissolution of the corresponding phase is inhibited. For the precipitated
hydration products, a trend of the SI towards lower oversaturation means usually that this phase has precipitated, while a trend towards higher oversaturation indicates no precipitation between two investigated hydration times. For example, this can be clearly seen in the case of ettringite: the first precipitation, after accelerator addition, coincides with an abrupt decrease of the SI. From 15 min up to \( \sim 1 \) h of hydration no ettringite precipitation was observed in QXRD analysis. During this time the SI increased. Thereafter, up to 6 h of hydration, the SI of ettringite decreased as a consequence of ettringite precipitation.

3.5 Microstructural analyses of very early age hydrates of the dry-mix system

The SEM micrographs of hydrated dry-mix paste samples (Fig. 8) show the massive formation of flaky hydration products 15 min after water addition. The elemental ratios of Ca, Al, S and O of these hydrates, measured via EDX point analyses, are in agreement with XRD analyses (Fig. 3a) where hemicarbonate and small amounts of monosulfate (SO\(_3\)-AFm) were found to be the main hydration products a few min after water addition in the dry-mix sample. The presence of sulfate in the early hydrates results from the intermixture of monosulfate among hemicarbonate, since the formation of SO\(_3\)-CO\(_3\)-AFm solid solutions is unlikely to happen [57].

4 Discussion

4.1 Setting mechanism, compressive strength and calculated total porosity

The setting mechanism of the wet-mix system is triggered by the massive instantaneous formation of
needle-like ettringite \[2, 25, 38, 39\]. In depth knowledge of the morphology and chemical composition of the hydrate phases responsible for the setting of dry-mix systems is rare.

After water addition, the SpB did not set instantly but only after a few min. The fast formation of significant quantities of CO$_3$-AFm phases led to high heat evolution (see Fig. 3a, b) and fast setting. In addition, the calorimetry results indicate that the very early dissolution/hydration of C$_3$A was modified and/or an endothermic reaction took place soon after water addition. Since the hydration of C$_3$A is only exothermic (see Fig. 10 in the Appendix), a possible mechanism for the observed kink in the heat development might be the dissolution of ‘additives’ to control setting times (e.g. organic acids) \[6, 58, 59\], possibly added during or after grinding the cement clinker.

Until \(\sim 4\) h of hydration \(2.5\) g/100 g SpB of hemi-carbonate and \(3.4\) g/100 g SpB monocarbonate were formed. For the formation of these phases \(\sim 7.8\) mmol/100 g SpB of CO$_3^{2-}$ are necessary. The mixing water included \(\sim 5\) mmol/L HCO$_3^-$ (at pH \(\sim 7.5\)), which corresponds to only \(\sim 0.2\) mmol/100 g$_{\text{SpB}}$ of CO$_3^{2-}$ (at pH \(\sim 13\)) at a w/b ratio of 0.5. The difference of \(\sim 7.6\) mmol/100 g$_{\text{SpB}}$ of CO$_3^{2-}$ ions implies that the dissolved carbonates in the mixing water are certainly not enough to form all (early) CO$_3$-AFm phases. Since the samples were hydrated air sealed, the extra carbonate source has to be included in the spray binder formulation (SpB) formulation. However, due to their supposed small quantities and peak overlapping with other phases, a distinct verification was not possible via Rietveld analyses.

The compressive strength of cementitious materials is in a large part linked with their porosity. Generally, the lower the porosity, the higher the compressive strength \[50\]. In comparison to the dry-mix, the wet-mix sample had higher compressive strength values and a lower calculated total porosity after 24 h of hydration and beyond. It is worth to note that although the accelerator contained \(\sim 65\) wt% of water, this had almost no effect on the available water for cement hydration. The added \(7\) wt% of accelerator corresponds to 2.45 g Al$_2$(SO$_4$)$_3$ and 4.55 g H$_2$O per 100 g CEML. With this amount of accelerator \(\sim 9\) g/100 g$_{\text{CEML}}$ ettringite can be formed, which in turn contains \(\sim 4.13\) g H$_2$O. This means that most of the water contained in the accelerator was used up by the ettringite formed as a result of the reaction between the Al$_2$(SO$_4$)$_3$ and the Ca$^{2+}$ from the pore solution. After 6 h of hydration the compressive strength was equivalent in both sample types, while the calculated total porosity was also lower in the wet-mix sample. It can be therefore assumed that at early hydration stages the morphology and mechanical properties of the phases formed are also relevant for the compressive strength of the cementitious matrix. The house-of-cards-like structure of the early formed AFm phases (see Fig. 8) in the dry-mix sample may sustain compressive force more efficiently than the unordered, needle like ettringite. This could at least partly compensate the higher porosity values at early age of hydration.
Regarding the transferability of the mechanical properties to sprayed concrete it should be noted that the mixing procedure may affect the distribution of the aluminate phases (e.g. ettringite) and thus the matrix constitution, its porosity and strength.

4.2 Effect of aluminum on early hydration mechanisms

As already mentioned in the introduction, the presence of Al has a major influence on the hydration kinetics of alite. During the past few years several authors have investigated in depth the impact of Al on the dissolution/precipitation process of C₃S and alite [18–23]. Fundamentally two different mechanisms have been proposed:

(i) According to the ‘dissolution hindrance theory’ Al can lead to a retardation of alite dissolution through binding of Al-species (covalent Si–OH–Al bonds) on active alite dissolution sites at moderate alkaline conditions [18, 21–23]. If the initial pH value (when the alite grains are wetted) is higher than ~ 13, the inhibitory effect of Al on alite hydration is almost cancelled. Furthermore, Nicoleau et al. [21] and Pustovgar et al. [22] showed that once the Al-species passivates the alite surface, a later increase in the pH value only hardly increases alite dissolution rate and heat of hydration. However, the reason for this nonreversible process is not fully understood and still under discussion. According to Nicoleau et al. [21] the covalent Si–OH–Al bonds are preferably formed at low alkaline conditions, Ca²⁺-ions may stabilize these bonds at higher pH values. Another hypothesis is that the mentioned Al-bonds may break up at high pH values but anyway the conditions in the pore solution are not the same anymore as shortly after wetting of the alite grains. Some alite has already been dissolved and the undersaturation in the pore solution may not be high enough to ‘restart’ hydration [22].

(ii) In addition to the inhibitory effect of Al on alite dissolution, a second theory, originally proposed from Begarin et al. [19], claims to explain the apparent impact of Al on alite hydration. According to the authors early C₃A–S–H nuclei are ‘poisoned’ with Al and therefore not able to grow or act as a template for growth, as pure C–S–H (without Al) nuclei do. The progressive formation of new Al-bearing nuclei leads to a decrease in the Al-concentration down to a threshold value for which precipitated C–S–H nuclei are not poisoned anymore and are able to grow. In addition, Wagner et al. [18] stated that Al-ions in solution decrease the supersaturation with respect to C–S–H and therefore the precipitation rates. Under high alkaline conditions they observed equivalent supersaturation of C–S–H in C₃S samples with and without Al. However, other research [56] stated that lower supersaturation would actually lead to an increase of the precipitation rate.

Both theories agree that Al retards alite hydration and that high initial pH values are able to cancel this effect. In the present study, the changes in the pore solution (ion concentrations) can be well coupled with phase development (dissolution of cement phases vs. formation of hydration products) determined via QXRD analysis. In the dry-mix systems, the rapid dissolution of large amounts of C₃A right after water addition led to high Al-concentrations in the pore solution. C₃A provides less Ca with respect to Al (Ca/Al 1.5) than what is needed for the formation of the early AFm phases (Ca/Al 2.0), which implies an excess of Al throughout this reaction. To explain the high aluminum concentration in the pore solution in the first min after water addition, it is assumed that the observed CO₃-AFm (mainly hemicarbonate) and SO₃-AFm phases (monosulfate) start to form after water addition, even if their small size does not trigger setting immediately.

In case of the dry-mix sample both circumstances were met: the pH value was lower than 13 in the first
minute after water addition, and the Al-concentration in the pore solution was high. Even though the solution was strongly undersaturated with respect to C₃S (see Fig. 7b), the two mentioned effects led to a blockage of alite dissolution and the inhibition of C–(A)–S–H and portlandite formation for several hours in the dry-mix system (see Fig. 3b).

It is obvious that the lack of Ca²⁺ plays also a big role in the prolongation of the dormant period: If there was, next to C₃A, another soluble Ca-source (without containing Al) at the beginning of the hydration, then the Al-concentration in the pore solution may not increase so much at the onset of hydration. The extra Ca needed for AFm formation could be provided from this additional Ca-source and no excess of Al in the pore solution would be generated. This could result in lower Al-concentrations in the pore solution at a very early age of hydration and potentially lower impact on alite hydration. This hypothesis was confirmed by the addition of 10 wt% portlandite to the SpB (see Fig. 12 in the Appendix), which led to higher heat evolved at hydration stage I (probably due to more AFm phases formed) and to a shorter dormant period. Portlandite turned out to be an adequate additional Ca-source, since it is undersaturated at the beginning of the hydration (see Fig. 7c) and does not contain Al. Free lime (CaO), which is already present in the SpB, or calcium formate could be suitable additions to shorten the dormant period of dry-mix systems with SpB. The latter one is also known to accelerate C₃S [60] and alite hydration [61].

In the wet-mix sample, the Al-concentration in the pore solution after water addition was significantly lower than in the dry-mix sample, since the dissolution of C₃A was controlled by calcium sulfate. However, also in the wet-mix the pH value was below the crucial value of 13, after intermixture of the Al₂(SO₄)₃ accelerator (see Fig. 6a). This temporary effect might increase the risk of a reduced alite reactivity. On the other hand, the rapid consumption of Ca and the reduction of the pH value during and after accelerator addition increases the solubility of alite [25]. Nicoleau et al. [21] stated that a subsequent reduction of the pH would be able to neutralize the inhibitory effect of Al on alite dissolution and that aluminum–silicate species would form after the addition of an acid. Furthermore, the XRD data (see Fig. 4b) gives also no evidence of a restricted alite dissolution in the first 24 h of hydration, which means that an significant effect of Al on alite dissolution is unlikely in the wet-mix sample. Nevertheless, the formation of portlandite, together with C–(A)–S–H phases, does not start until ~ 6 h of hydration, at approximately the same time as in the dry-mix sample. It is also noteworthy that in both sample types, the Al-concentration decreased dramatically before the start of the main C–(A)–S–H and portlandite formation. This could be interpreted as the ‘turning point’ after which viable C–S–H nuclei are formed and rapid growth of C–S–H phases is possible. However, the resurgence of Al-concentration in the following hours contradicts this argumentation.

The data obtained in the present study agree with the ‘dissolution hindrance theory’ whereby Al leads to a blockage of alite dissolution in mildly alkaline mixing conditions. The effect is then neutralized by the addition of an acidic setting accelerator. No evidence was found about the ‘poisoning’ of early C–(A)–S–H nuclei with Al in the investigated systems.

4.3 Portlandite content

In both types of mixes (dry and wet), portlandite plays a crucial role regarding different durability parameters. Portlandite is known as the main pH buffer in concrete. It reacts with CO₂ forming CaCO₃ thereby acting as a ‘brake’, slowing down the progression of the carbonation front. However, portlandite shows distinct negative effects towards sulfate- and thaumasite attack and Ca-leaching [41, 62, 63]. In general, it increases also the porosity of the interfacial transition zone between hardened paste and aggregates [64]. Although the XRD amorphous content after 28 d of hydration, which can be assumed to be primary C–A–S–H, is higher in the wet-mix, the amount of portlandite is significant lower in comparison to the dry-mix (19.1 g/100 g_CEMI vs. 26.0 g/100 g_SpB). The same trend was found also by [41] when analyzing the portlandite content of different dry- and wet-mix
shotcrete specimens, sprayed under real scale conditions. Possible explanations for the lower portlandite content of the Al₂(SO₄)₃ accelerated mixes are: (i) the immediate consumption of Ca after accelerator addition and subsequent ettringite formation. [38]. And (ii) the formation of greater amounts of C–A–S–H phases and/or a higher Ca:Si ratio in the C–A–S–H formed in the wet-mix, compared to the dry-mix system.

Indeed, for the formation of one mol ettringite, 6 mol Ca are needed. Consequently, the addition of 7 wt% (by weight of cement) Al₂(SO₄)₃ accelerator leads to the consumption of 43 mmol/ Ca per 100 g CEMI to form stoichiometric ettringite. This fact could lead to the assumption, that this extra Ca consumption is compensated by a reduced portlandite formation, in accelerated wet-mix systems.

However, according to the XRF and QXRD data the Ca:Si ratio in C–A–S–H in the wet-mix was higher (~ 2.0:1) than in the dry-mix (~ 1.6:1) (for the detailed calculation see Tables 13 and 14 in the Appendix). In addition, the amount of C–A–S–H was higher in the wet-mix than in the dry-mix. These two findings imply, that a significantly higher amount of Ca was bound in C–A–S–H phases in the wet-mix, compared to the dry-mix. Consequently, this extra Ca was missed for portlandite formation, explaining the lower amounts of portlandite in the wet-mix, compared to the dry-mix system.

It is worth noting that the reasons for the observed differences concerning the elemental Ca:Si ratio in C–A–S–H phases are still unexplored. Is it the presence of the accelerator which increases Ca:Si ratio and also the amount of total C–A–S–H phases or is it the ‘nature’ of the dry-mix system which decreases those values? Further research, comparing both mixes to a non-accelerated CEM I system may give the answer to this question.
4.4 Conceptual model of the hydration mechanisms of dry- and wet-mix systems

A conceptual model, illustrating the governing hydration mechanisms of both investigated systems, the dry- and the wet-mix system, is shown in Fig. 9. The model is based on results from the literature [6, 11, 18, 21–23, 25, 35, 36, 38, 41], supplemented with the results and discussed mechanisms from this study.

5 Conclusion

In this work we investigated the hydration of two different cementitious systems used for shotcrete applications. A low sulfate Portland cement, called ‘spray binder’, which is used for dry-mix shotcrete applications and an ordinary Portland cement, accelerated by means of 7 wt% of an aluminum sulfate based setting accelerator, widely used in the field of wet-mix shotcrete. The hydration of both systems was followed right after water addition by means of various methods (isothermal calorimetry, X-ray diffraction, pore solution analysis, SEM/EDX analysis, setting time and compressive strength tests). The findings made allow us to draw the following conclusions:

- In dry-mix systems (spray binder + water) rapid setting within the first few min after water addition is caused by the rapid formation of flaky CO$_3$-AFm phases (hemihydrate). A rapidly soluble, carbonate source (e.g. alkali(hydrogen)carbonates) has to be a component of the spray binder formulation to supply sufficient CO$_3$, in addition to the small amount of CO$_3$ which is inherently present in common mixing water (tap water).
- High aluminum concentrations in the pore solution in combination with moderately alkaline conditions (pH below 13) lead to a blockage of alite dissolution which can last for several hours. In case of the investigated spray binder these conditions are met in the first seconds/ minutes after water addition.
- In wet-mix systems, accelerated by means of Al$_2$(SO$_4$)$_3$ based products, lower amounts of portlandite are formed. The hypothesis that the consumption of Ca during ettringite formation in wet-mix systems is responsible for a reduced portlandite formation could not be confirmed in this study. In contrast, the higher amount of C–A–S–H and the higher Ca:Si ratio in wet-mix systems seem to be behind the difference in portlandite contents.
- Wet-mix systems, with usual accelerator dosages (around 7% by weight of binder) show lower total porosity and higher compressive strength at later stages of hydration, compared to dry-mix systems with the same water/binder ratio.
- The development of new binders with enhanced early- strength and durability parameters should include in-depth knowledge on the formation of hydrated phases and the pore solution chemistry, especially the availability of aluminum and calcium.

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Appendix

See Figs. 10, 11 and 12.
See Tables 7, 8, 9, 10, 11, 12, 13 and 14.

Fig. 10 Heat evolution rate obtained by isothermal calorimetry of $C_3A$ at a water/solid ratio of 0.4 at 20 °C as a function of time. Figure taken from [14] and adapted

Fig. 11 Rate of alite hydration as a function of time given by isothermal calorimetry measurements. Figure taken from [26] and adapted with findings from [11, 36]

Fig. 12 Effect of (i) an initial pH value > 13 by means of a 0.2 M KOH solution as mixing water, (ii) a 0.1 M $K_2SO_4$ solution (equivalent potassium concentration in comparison to (i)) as mixing water and (iii) an additional Ca-source by the addition of 10 wt% portlandite (Ca(OH)2) on the hydration kinetics of SpB. Water/binder (w/b) ratio = 0.5 for all mixes. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.
Table 7  Results from QXRD analysis (g/100g_{CEMI/SpB}) of dry and wet-mix samples during 28 d of hydration

| Mix-ID | Age (h) | Alite (M1 + M3) | C2S (α + β) | Dolomite | C3A (c + o) | C4AF | CaO | Anhydrite | Bassanite | Gypsum | Arcanite | Periclase |
|--------|---------|-----------------|--------------|-----------|-------------|------|-----|------------|-----------|--------|----------|----------|
|        | Density (g/cm³) | 3.18 | 3.30 | 2.87 | 3.04 | 3.74 | 3.39 | 2.96 | 2.74 | 2.31 | 2.68 | 3.57 |
| Dry-mix Unhydr. | 67.6 | 9.4 | 0.0 | 10.9 | 6.3 | 0.4 | 0.0 | 0.9 | 0.3 | 0.4 | 3.8 |
| 0.083 | 68.3 | 9.1 | 0.0 | 9.9 | 6.4 | 0.0 | 0.0 | 0.0 | 0.8 | 0.0 | 4.7 |
| 0.250 | 68.8 | 8.5 | 0.0 | 7.3 | 3.9 | 0.0 | 0.0 | 0.0 | 2.9 | 0.0 | 3.4 |
| 0.833 | 68.7 | 7.8 | 0.0 | 6.6 | 3.6 | 0.0 | 0.0 | 0.0 | 2.0 | 0.0 | 3.1 |
| 2.00  | 68.4 | 7.1 | 0.0 | 6.9 | 4.2 | 0.0 | 0.0 | 0.0 | 1.9 | 0.0 | 3.6 |
| 4.17  | 68.6 | 6.6 | 0.0 | 6.9 | 3.8 | 0.0 | 0.0 | 0.0 | 0.4 | 0.0 | 3.1 |
| 6.00  | 66.7 | 7.1 | 0.0 | 6.5 | 3.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.5 |
| 24.0  | 30.1 | 8.6 | 0.0 | 6.7 | 2.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.0 |
| 672   | 15.9 | 8.8 | 0.0 | 1.0 | 2.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.8 |
| Wet-mix Unhydr. | 62.9 | 8.8 | 1.6 | 11.1 | 7.3 | 0.0 | 3.4 | 1.5 | 0.0 | 0.6 | 2.7 |
| 0.000¹ | 62.1 | 8.2 | 1.2 | 9.7 | 6.3 | 0.0 | 2.7 | 0.0 | 0.0 | 0.0 | 2.4 |
| 0.050 | 54.7 | 7.3 | 0.9 | 10.6 | 4.8 | 0.0 | 3.1 | 0.0 | 0.0 | 0.0 | 2.1 |
| 0.817 | 56.1 | 6.6 | 1.0 | 9.5 | 5.6 | 0.0 | 1.8 | 0.0 | 0.0 | 0.0 | 2.5 |
| 2.00  | 54.8 | 7.5 | 0.8 | 9.7 | 5.5 | 0.0 | 1.9 | 0.0 | 0.0 | 0.0 | 2.3 |
| 4.00  | 50.1 | 6.6 | 0.6 | 8.6 | 5.5 | 0.0 | 1.2 | 0.0 | 0.0 | 0.0 | 3.0 |
| 6.00  | 48.2 | 8.3 | 0.6 | 8.3 | 5.7 | 0.0 | 0.9 | 0.0 | 0.0 | 0.0 | 2.9 |
| 24.0  | 27.7 | 9.2 | 2.0 | 4.3 | 3.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.9 |
| 672   | 8.3  | 6.5 | 1.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.4 |

Part I: CEMI/SpB phases

c + o = cubic + orthorhombic

¹Before accelerator addition
Table 8 Results from QXRD analysis and bound water from TGA analysis (g/100 gCEMI/SpB) of dry- and wet-mix samples during 28 d of hydration

| Mix-ID | Age (h) | HC (g/cm³) | MC | MS | Portlandite | AFt | Amorphous | Bound water |
|--------|---------|------------|----|----|-------------|-----|-----------|-------------|
| Dry-mix | **Unhydr.** | 0.0 | 0.0 | 0.0 | 0.0 | 3.5 | 0.1 | 1.98 |
|         | 0.083   | 3.2 | 0.0 | 0.0 | 0.0 | 2.6 | 6.9 | 4.67 |
|         | 0.250   | 3.4 | 0.0 | 0.0 | 0.0 | 0.0 | 7.8 | 5.66 |
|         | 4.17    | 3.2 | 0.0 | 0.0 | 0.0 | 0.0 | 10.3 | 5.42 |
|         | 6.00    | 3.2 | 0.0 | 0.0 | 0.0 | 0.0 | 11.3 | 5.79 |
|         | 24.0    | 2.9 | 0.0 | 0.0 | 0.0 | 0.0 | 40.6 | 17.21 |
| Wet-mix | **Unhydr.** | 0.0 | 0.0 | 0.0 | 0.0 | 4.9 | 4.9 | 2.98 |
|         | 0.050   | 0.0 | 0.0 | 0.0 | 0.0 | 14.8 | 8.4 | 7.18 |
|         | 0.817   | 0.0 | 0.0 | 0.0 | 0.0 | 15.3 | 10.4 | 8.32 |
|         | 2.00    | 0.0 | 0.0 | 0.0 | 0.0 | 15.3 | 11.6 | 8.91 |
|         | 4.00    | 0.0 | 0.0 | 0.0 | 0.0 | 16.2 | 14.8 | 8.99 |
|         | 6.00    | 0.0 | 0.0 | 0.0 | 0.0 | 17.4 | 18.9 | 10.65 |
|         | 24.0    | 0.4 | 0.0 | 2.7 | 9.7 | 13.7 | 46.1 | 19.31 |
|         | 672     | 3.4 | 5.3 | 3.9 | 19.1 | 11.7 | 69.5 | 29.38 |

Part II: hydration products

†Before accelerator addition

Table 9 Phases used for hydrochemical modelling using PHREEQC and CEM-DATA 18 database [54]

| Phase | CEM-DATA18 phase | Chemical formula |
|-------|------------------|------------------|
| C₃A   | C₃A              | (CaO)₃Al₂O₃      |
| C₃S   | C₃S              | (CaO)₃SiO₂       |
| C₂S   | C₂S              | (CaO)₂SiO₂       |
| C₄AF  | C₄AF             | (CaO)₄(Al₂O₃)(Fe₂O₃)₁ |
| Calcite | Cal             | CaCO₃            |
| Ettringite | Ettringite       | Ca₉Al₅(SO₄)₃(OH)₁₂(H₂O)₂₆ |
| C–A–S–H | SCA              | (CaO)₁.₂₅(Al₂O₃)₀.₁₂₅(SiO₂)₁(H₂O)₁.₆₂₅ |
| Portlandite | Portlandite      | Ca(OH)₂        |
| Gypsum | Gp               | CaSO₄(H₂O)₂     |
| Hemicarbonate | Hemicarbonate    | (CaO)₃Al₂O₃(CaCO₃)₀.₅ |
|       |                  | (Ca(OH)₂)₉.₅(H₂O)₁₁.₅ |
| Monosulfate | Monosulfate12    | Ca₄Al₂SO₄(OH)₁₂(H₂O)₆ |
| C₄AH₁₉ | C₄AH₁₉           | Ca₄Al₂(OH)₁₄(H₂O)₁₂ |
Table 10 Measured ion concentrations, pH values and EC of pore solutions

| Mix-ID | Age (h) | Ca (mmol/L) | Si | Al | SO₄ | Fe | Na | K | Mg | CO₃²⁻†‡ | pH (–) | EC (mS/cm) |
|--------|---------|-------------|----|----|-----|----|----|---|----|---------|--------|-----------|
| Dry-mix | 0.067 | 0.906 | 10.2 | 29.0 | 118 | 0.0103 | 160 | 294 | 5.97 | 0.351 | 200 | 13.29 | 52.6 |
|        | 0.233 | 0.506 | 11.4 | 38.6 | 4.50 | 0.0151 | 188 | 320 | 3.38 | 0.339 | 200 | 13.73 | 105.8 |
|        | 0.750 | 0.788 | 11.3 | 4.57 | 5.76 | 0.0163 | 240 | 388 | 1.89 | 0.408 | 200 | 13.81 | 125.6 |
|        | 2.20  | 1.00  | 9.84 | 1.79 | 4.03 | 0.0079 | 265 | 427 | 1.95 | 0.443 | 100 | 13.74 | 127.4 |
|        | 4.41  | 1.50  | 1.37 | 0.228 | 2.29 | 0.0105 | 248 | 400 | 1.18 | 0.414 | 100 | 13.88 | 131.4 |
|        | 6.49  | 2.30  | 8.78 | 0.538 | 2.12 | 0.0219 | 188 | 302 | 0.76 | 0.309 | 100 | 13.88 | 132 |
|        | 23.9  | 3.63  | 9.14 | 0.802 | 6.86 | 0.0124 | 289 | 482 | 1.66 | 0.535 | 100 | 13.80 | 149.6 |
| Wet-mix | 0.000† | 39.9 | 10.9 | 0.549 | 101 | 0.112 | 37.1 | 214 | 4.21 | 0.202 | 5 | 13.25 | 38.2 |
|        | 0.033 | 16.0 | 11.4 | 0.555 | 113 | 0.0242 | 40.5 | 198 | 4.67 | 0.181 | 5 | 12.54 | 24.8 |
|        | 0.175 | 14.2 | 11.5 | 0.563 | 110 | 0.0676 | 42.1 | 200 | 5.46 | 0.177 | 5 | 12.53 | 26.2 |
|        | 1.03  | 41.8 | 9.92 | 0.540 | 102 | 0.0676 | 44.6 | 213 | 5.63 | 0.177 | 5 | 13.31 | 39.3 |
|        | 1.98  | 24.4 | 10.0 | 0.545 | 99.9 | 0.0208 | 47.2 | 224 | 5.50 | 0.197 | 5 | 13.20 | 37.8 |
|        | 4.04  | 23.7 | 0.178 | 0.050 | 107 | 0.0240 | 55.1 | 238 | 5.67 | 0.205 | 5 | 13.07 | 40.4 |
|        | 6.49  | 3.78 | 11.0 | 0.536 | 44.6 | 0.0933 | 69.8 | 264 | 2.98 | 0.229 | 5 | 13.48 | 59.3 |
|        | 24.5  | 3.00 | 4.43 | 0.316 | 7.88 | 0.0107 | 178 | 434 | 2.00 | 0.356 | 5 | 13.84 | 122.4 |

For the wet-mix the CO₃²⁻ originating from the mixing water (5 mmol/L) was considered.

Detailed information regarding the necessity of an external, soluble carbonate source, is given in Sect. 4.1 of the article.

†Before accelerator addition

‡CO₃²⁻ in the pore solution was calculated as follows: for the dry-mix a constant CO₃²⁻ level of 200 mmol/L in the first 2 h of hydration and 100 mmol/L thereafter was taken into account.

Table 11 Calculated saturation indices (SI)

| Mix-ID | Age (h) | C3A | C3S | C2S | C4AF | E | 5CA | CH | Gp | HC | MS | C4AH19 |
|--------|---------|-----|-----|-----|------|---|-----|-----|----|----|----|-------|
| Dry-mix | 0.067 | –361 | –151 | –190 | –311 | 215 | 0720 | –125 | –243 | 114 | 0714 | –258 |
|        | 0.233 | –349 | –142 | –156 | –299 | –203 | 0524 | –0648 | –418 | 242 | 0095 | –0881 |
|        | 0.750 | –362 | –133 | –0948 | –310 | –278 | 0674 | –0383 | –398 | 126 | –103 | –195 |
|        | 2.20  | –366 | –129 | –0650 | –318 | –257 | 0833 | –0291 | –382 | 0924 | –120 | –216 |
|        | 4.41  | –364 | –120 | –0426 | –309 | –212 | 0284 | 0409 | –371 | 165 | –0925 | –133 |
|        | 6.49  | –359 | –114 | 0.0279 | –299 | –200 | 111 | 0350 | –381 | 204 | –0600 | –0961 |
|        | 23.9  | –352 | –110 | 0.0585 | –294 | 124 | 142 | 0437 | –301 | 297 | 100 | –0056 |
| Wet-mix | 0.000† | –323 | –892 | 198 | –229 | 137 | 245 | 109 | 0111 | 645 | 705 | 360 |
|        | 0.033 | –366 | –128 | –03049 | –290 | 841 | 0206 | 0816 | 0224 | 107 | 244 | –257 |
|        | 0.175 | –369 | –131 | –0160 | –285 | 787 | 201 | –0917 | –0313 | 0716 | 208 | –294 |
|        | 1.03  | –320 | –868 | 208 | –231 | 139 | 243 | 123 | 0116 | 679 | 733 | 400 |
|        | 1.98  | –334 | –973 | 154 | –257 | 118 | 231 | 0717 | –0149 | 514 | 576 | 219 |
|        | 4.04  | –353 | –116 | –0242 | –273 | 107 | 0339 | 0672 | 0115 | 326 | 409 | 0224 |
|        | 6.49  | –364 | –118 | 0.0271 | –288 | 351 | 155 | –00809 | –0819 | 105 | 0939 | –169 |
|        | 24.5  | –351 | –105 | 0.0754 | –292 | 228 | 126 | 0738 | –270 | 271 | 141 | 0352 |

E ettringite, HC hemicarbonate, MS monosulfate, CH Portlandite

†Before accelerator addition
### Table 12  Standardized (100%) elemental composition and applied voltage of measured EDX spots in the bulk of early age (15 min after water addition) hydrates of the dry-mix sample

| Spot | Ca (at.%) | Al (at.%) | Si (at.%) | S (at.%) | O (at.%) | V (KV) |
|------|-----------|-----------|-----------|----------|----------|--------|
| 1    | 16.2      | 5.83      | 2.01      | 1.61     | 71.3     | 10     |
| 2    | 31.8      | 8.10      | 4.26      | 2.61     | 51.35    | 10     |
| 3    | 18.82     | 6.82      | 3.3       | 1.43     | 65.41    | 10     |
| 4    | 21.84     | 6.58      | 4.47      | 1.39     | 60.94    | 10     |
| 5    | 19.07     | 6.07      | 3.28      | 1.62     | 66.47    | 10     |
| 6    | 17.39     | 5.41      | 2.78      | 2.4      | 67.26    | 10     |
| 7    | 19.17     | 7.49      | 0.91      | 0.94     | 70.7     | 10     |
| 8    | 21.08     | 7.76      | 2.88      | 1.69     | 62.86    | 10     |
| 9    | 30.86     | 10.4      | 3.31      | 2.53     | 47.34    | 10     |
| 10   | 24.74     | 9.21      | 4.13      | 2.37     | 56.28    | 10     |
| 11   | 18.07     | 6.5       | 2.3       | 0.69     | 71.29    | 7      |
| 12   | 16.04     | 7.38      | 1.2       | 1.03     | 73.27    | 7      |
| 13   | 18.5      | 7.72      | 2.24      | 1.32     | 68.65    | 7      |
| 14   | 16.22     | 7.32      | 1.37      | 0.69     | 73.35    | 7      |
| 15   | 21.24     | 6.41      | 2.64      | 1.96     | 64.71    | 7      |
| 16   | 29.14     | 8.53      | 4.41      | 2.23     | 52.94    | 7      |
| 17   | 17.43     | 6.37      | 2.6       | 1.23     | 68.72    | 7      |
| 18   | 30.88     | 7.48      | 4.12      | 3.95     | 45.88    | 7      |
| 19   | 30.28     | 7.87      | 3.87      | 4.05     | 52.46    | 7      |
| 20   | 26.93     | 8.58      | 3.08      | 1.35     | 57.55    | 7      |
| 21   | 20.66     | 7.39      | 2.24      | 1.09     | 66.3     | 7      |
| 22   | 19.48     | 7.99      | 1.64      | 1.36     | 67.52    | 7      |
| 23   | 19.32     | 6.39      | 3.64      | 2.14     | 62.36    | 7      |
| 24   | 18.47     | 7.07      | 1.42      | 0.86     | 70.91    | 7      |
| 25   | 20.77     | 7.02      | 1.51      | 2.11     | 62.36    | 7      |
| 26   | 21.97     | 7.49      | 1.67      | 6.86     | 51.01    | 7      |
Table 13  Calculation of the Ca, Si and Al content in C–A–S–H phases of the dry-mix

| Oxide   | Molar weight (g mol\(^{-1}\)) | Oxide content in binder (g 100 g\(_{SPB}\)\(^{-1}\)) | Ca content (mmol 100 g\(_{SPB}\)\(^{-1}\)) | Si content (mmol 100 g\(_{SPB}\)\(^{-1}\)) | Al content (mmol 100 g\(_{SPB}\)\(^{-1}\)) |
|---------|-------------------------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| CaO     | 56.1                          | 63.2                                            | 1127                            | 0                               | 0                               |
| SiO\(_2\) | 60.1                         | 20.5                                            | 0                               | 341                             | 0                               |
| Al\(_2\)O\(_3\) | 102                        | 5.8                                             | 0                               | 0                               | 114                             |
| Phase   |                               | Phase amount after 28 d in hydrated sample (g 100 g\(_{SPB}\)\(^{-1}\)) |                                           |                                 |                                 |
| C\(_3\)S | 228                          | 15.9                                            | 209                             | 69.7                            | 0                               |
| C\(_2\)S | 172                          | 8.8                                             | 102                             | 51.2                            | 0                               |
| C\(_3\)A | 270                          | 1.0                                             | 11.1                            | 0                               | 9.88                            |
| C\(_4\)AF* | 486                         | 2.4                                             | 19.8                            | 0                               | 10.3                            |
| MS      | 622                          | 4.5                                             | 28.9                            | 0                               | 11.5                            |
| HC      | 564                          | 3.4                                             | 24.1                            | 0                               | 12.1                            |
| MC      | 614                          | 3.8                                             | 24.8                            | 0                               | 12.4                            |
| CH      | 74.1                         | 26.0                                            | 351                             | 0                               | 0                               |
| C–A–S–H |                               | 356                                             | 220                             | 57.8                            |                                 |

The amount of dissolved ions, remaining in the pore solution is not considered.

Ca, Si and Al content in C–A–S–H were determined by subtracting the corresponding amount in the hydrated phases from the total content in the binder.

*For C\(_4\)AF an Al\(_2\)O\(_3\) content of 21.9 wt% was assumed [6]

\(E\) ettringite, \(HC\) hemicarbonate, \(MC\) monocarbonate \(MS\) monosulfate, \(CH\) Portlandite.
Table 14 Calculation of the Ca, Si and Al content in C–A–S–H phases of the wet-mix

| Oxide             | Molar weight (g mol\(^{-1}\)) | Oxide content in binder (g 100 g\(_{\text{CEMI}}\)\(^{-1}\)) | Ca (mmol 100 g\(_{\text{SPB}}\)\(^{-1}\)) | Si (mmol 100 g\(_{\text{SPB}}\)\(^{-1}\)) | Al (mmol 100 g\(_{\text{SPB}}\)\(^{-1}\)) |
|-------------------|-------------------------------|---------------------------------------------------------|--------------------------------|-----------------|----------------|
| CaO               | 56.1                          | 60.6                                                   | 1081                          | 0               | 0              |
| SiO\(_2\)         | 60.1                          | 19.1                                                   | 0                             | 318             | 0              |
| Al\(_2\)O\(_3\) \(_{\text{CEMI}}\) | 102                           | 5.8                                                    | 0                             | 0               | 114            |
| Al\(_2\)(SO\(_4\))\(_3\) \(_{\text{acc.}}\) | 342                           | 2.45                                                   | 0                             | 0               | 14.3           |

Phase                                    | Phase amount after 28d in hydrated sample (g 100 g\(_{\text{CEMI}}\)\(^{-1}\)) |
|-----------------------------------------|--------------------------------------------------------------------------------|
| C\(_3\)S                                 | 228                                                                   8.3                      | 109                          | 36.4            | 0              |
| C\(_2\)S                                 | 172                                                                   6.5                      | 75.6                         | 37.8            | 0              |
| Ett                                      | 1255                                                                  11.7                     | 55.9                         | 0               | 18.6           |
| MS                                       | 622                                                                   3.9                      | 25.1                         | 0               | 12.5           |
| HC                                       | 564                                                                   3.4                      | 24.1                         | 0               | 12.1           |
| MC                                       | 614                                                                   5.3                      | 34.5                         | 0               | 17.3           |
| CH                                       | 74.1                                                                   19.1                     | 258                          | 0               | 0              |
| Dolomite                                 | 184                                                                   1.8                      | 9.76                         | 0               | 0              |
| C–A–S–H                                  | 489                                                                   244                      | 244                          | 67.8            | 0              |

The amount of dissolved ions, remaining in the pore solution is not considered.

Ca, Si and Al content in C–A–S–H were determined by subtracting the corresponding amount in the hydrated phases from the total content in the binder.

_E_ ettringite, _HC_ hemicarbonate, _MC_ monocarbonate, _MS_ monosulfate, _CH_ Portlandite

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