Sulfate resistance and phase composition of shotcrete

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ABSTRACT

Shotcrete is often in direct contact with groundwater containing sulfate. The resistance to sulfate attack of modern sprayed concretes produced with non-alkali aluminate-based accelerators in combination with different cement types is related to their microstructure, transport properties, porosity and phase composition. A characterization of these properties allows a comprehensive assessment of the sulfate resistance of shotcrete with the identification of the relevant physical and chemical influencing factors.

As with conventional concrete, the cement type and the water to binder ratio are also decisive for the sulfate resistance in shotcrete. On the one hand, capillary porosity and diffusion coefficient show cement-specific differences, and accordingly the sulfate solution uptake and the sulfur profile in the test specimen with cement type and w/b also are different. On the other hand, the type of cement defines the potential for ettringite formation and thus for damage to the concrete. Sulfate expansion is caused by the conversion of monocarbonate/hemiacetate/hemisulfate (AFm phases) to ettringite. The application of sulfate-resistant cements does not guarantee the sulfate resistance of sprayed concretes in each case. Their use, however, minimizes the damage potential.

In the sulfate resistance tests, damage in shotcrete causing a drop in the dynamic modulus of elasticity occurs at a higher sulfate expansion compared to conventional concrete due to the higher volume of hardened cement paste and the smaller maximum aggregate size.

The studied alkali-free accelerators, currently used in practice, are found to have no direct adverse effect on the sulfate resistance in the dosage investigated and behave more favorably than the aluminate based alkali-containing accelerators. However, the accelerators influence the sulfate resistance indirectly by causing higher porosity and permeability and thus by an increased sulfate solution uptake of the shotcrete.

1. Introduction

The application of sprayed concrete (shotcrete) is a widely used and efficient placement technique in tunneling and mining. Principally, two different application techniques can be distinguished: wet and dry spraying. In this study, only wet spraying is considered. In the wet spraying technique, the concrete is premixed in a standard concrete mixer, then pumped to the nozzle, where it is accelerated physically by compressed air so that it can be sprayed with high velocity to a tunnel wall, where it is compacted. Furthermore, through the injection of a set accelerator at the nozzle, its chemical hydration is also accelerated. Hence, set accelerators are an important ingredient of shotcrete. In the recent years a strong trend towards alkali-free set accelerators has been observed. They are based on mixtures of aluminum sulfate/hydroxide/formate, calcium formate or calcium sulfoaluminate. Contrary to the traditional set accelerators like alkali silicates (e.g. water glass), alkali aluminates, alkali carbonates or hydroxides, the alkali-free systems have significant advantages regarding early and late strength, work hygiene/safety and sintering of drainage systems. The set accelerators significantly influence the phase composition of the hydrated concrete which also applies especially for alkali-free set accelerators owing to their aluminate or sulfate components (Salvador et al., 2016; Xu and Stark, 2005).

Little is known about the interaction of shotcrete with sulfate ions in ground water. Studies of the damage mechanisms through the interaction between shotcrete and ground water show that in most cases a sulfate attack is involved (Romer et al., 2003; Leemann and Loser, 2010). A sulfate attack may lead to the secondary formation of the sulfate phases ettringite, gypsum or thaumasite and hence to a high crystallization pressure (Taylor and Gollop, 1997; Scherer, 2004). The
aluminum that is necessary for ettringite formation is present in the clinker phases Ca3A and Ca3AF and their hydrate phases. In the case of shotcrete, the set accelerators based on aluminum compounds may become thus an additional aluminum source (Paglia et al., 2002, 2003). A higher risk regarding a sulfate attack is possible due to a different cement phase composition arising from increased aluminum and sulfate contents introduced by the accelerators. Furthermore, the generally higher paste volume of shotcrete, required due to the lower maximum aggregate size, also may lead to a lower sulfate resistance.

In order to investigate such possible risks, the influence of alkali-free set accelerators on the sulfate resistance of shotcrete was examined and compared to an alkali-based reference accelerator. Their interaction with different cement types is studied. A new method recently developed to evaluate the sulfate resistance for conventional concrete (Loser and Leemann, 2016), based on cyclic drying and subsequent storage in a sulfate solution, is now applied to shotcrete. In a comprehensive study (Kaufmann et al., 2019), the hydrates present in the shotcretes are analyzed. The present paper summarizes some of the results obtained in a recently finished project (Kaufmann et al., 2019).

2. Materials and methods

Three different commercial set accelerators were studied. The chemical composition determined by ICP-OES (inductively coupled plasma optical emission spectrometry) of the applied set accelerators is presented in Table 1. One set accelerator was alkali-based (Na-aluminate-based, BE1) and two were alkali-free (aluminum sulfate/hydroxide based, BE2/BE3).

Table 1

| Component | BE1 (alkali-based) | BE2 | BE3 |
|-----------|--------------------|-----|-----|
| Aluminum mass-% | 11.95 | 5.62 | 6.9 |
| Sulfates mass-% | 0 | 28.5 | 28.2 |
| Na2O eq. mass-% | 17.1 | 0 | 0.5 |
| Magnesium mg/kg | 9 | 974 | 826 |
| Silicium mg/kg | 116 | 1395 | 1743 |
| Lithium mg/kg | 0 | 2 | 1 |
| Potassium mg/kg &lt; 0.8 | 0.4 | 0.8 |
| Calcium mg/kg | 0 | 5041 | 52 |
| Sodium mass-% | 12.69 | 0.03 | 0.35 |
| Iron mg/kg | 3 | 75 | 37 |
| Phosphorus mg/kg | 16 | 11 | 12 |
| Diethanolamine mass-% | &lt;0.4 | 1.7 | 1.4 |
| Triethanolamine mass-% | &lt;0.8 | &lt;0.8 | &lt;0.8 |

Table 2

| Component | CEM I | CEM II/B-M | CEM III/B |
|-----------|-------|------------|-----------|
| SiO2 mass-% | 19.02 | 25.27 | 31.28 |
| Al2O3 mass-% | 4.69 | 6.19 | 9.26 |
| Fe2O3 mass-% | 3.3 | 2.89 | 1.29 |
| Cr2O3 mass-% | 0.007 | 0.012 | 0.006 |
| MnO mass-% | 0.078 | 0.080 | 0.209 |
| TiO2 mass-% | 0.25 | 0.339 | 0.725 |
| P2O5 mass-% | 0.161 | 0.229 | 0.086 |
| CaO mass-% | 64.45 | 55.76 | 48.45 |
| MgO mass-% | 1.75 | 3.18 | 5.24 |
| KO mass-% | 0.84 | 0.96 | 0.73 |
| Na2O mass-% | 0.19 | 0.27 | 0.23 |
| SO3 mass-% | 2.65 | 3.40 | 2.83 |
| L.O.I. mass-% | 2.39 | 1.23 | –0.58 |
| Total mass-% | 99.77 | 99.81 | 99.76 |
| Total C mass-% | N.A. | N.A. | N.A. |
| CO2 mass-% | 1.69 | 0.99 | 0.66 |
| free lime mass-% | 1.50 | 1.05 | 0.39 |
| density g/cm³ | 3.14 | 3.05 | 2.98 |

Table 3

| Component | kg/m³ |
|-----------|-------|
| Cement (Silica fume) | 450 (414) |
| Silica fume | (36) |
| Water | 202.5 / 216 |
| w/b | 0.45 / 0.48 variable (2.25–4.5) |
| Superplasticizer | 0.9 |
| Retarder | 0.9 |
| Set accelerator | 27/36 |
| Sand 0.1 mm | 553 |
| Sand 1.4 mm | 436 |
| Gravel 4.8 mm | 688 |

Four different binders were used and combined with the different set accelerators. The oxide compositions of the binder components as found by X-ray fluorescence analysis are presented in Table 2. The underlying shotcrete mix design is given in Table 3. The superplasticizer (poly-carboxylate-based) dosage was adapted accordingly in order to reach a predefined slump flow of about 600 mm. A retarder (based on tri-carboxylic and citric acid) was added to guarantee similar flow properties during the whole application process. Concretes were mixed in a planetary mixer (capacity: 2 m³) for 5 min and then the fresh concrete was transported (5–10 min duration) to the spray equipment (Meyco supreme), pumped to the nozzle and finally sprayed. The accelerator dosage was set to 6 mass-% (in some samples also 8 mass-%) of the binder content. The air pressure was maintained at 5 bar.

For one mixture pure Portland cement CEM I 42.5 N was used. In order to test a denser system Portland cement was blended with 8% of silica fume (417 kg/m³ CEM I 42.5 N + 33 kg/m³ silica fume). The silica fume (–SF) as used in this work was added in the form of a dry powder of compacted amorphous silica composed of extremely fine (0.1 µm) particles, so that 50% of its volume consisted of particles with a diameter larger than 50 µm. The dosage used (8% by mass of the CEM I cement) is based on the usual practice. By the application of the CEM III/B cement a similar compaction effect and a dense cementitious matrix was envisaged. For some mixtures the water to binder ratio w/b was varied (w/b = 0.48 instead of generally w/b = 0.45).

The shotcrete was produced at the Hagerbach test galleries in Flums (Switzerland) under full-scale conditions. Square slabs of 600 × 600 × 100 mm³ were sprayed for further testing. The slabs remained covered by plastic sheets for 18 days on-site at about 16 °C and were then transported to Empa and stored until the age of 3 weeks at 20 °C/90% (uncovered) in a climate chamber. At this age, sampling took place. The sampling scheme is given in Fig. 1. Afterwards, the derived samples were stored at 20 °C/90% RH until an age of 28 days, at this age the different test routines were initiated. The control samples were stored at the same climate until the date of the end of the sulfate resistance test (age 112 days).

2.1. Fresh concrete properties of the delivery mixtures

Concrete slump flow was measured according to EN 12350-5 (2019) and air void content according to EN 12350-7 (2019).

2.2. Compressive strength

Compressive strength was determined on drill cores (height = diameter = 50 mm) according to the European standard EN 12504-1 (2017). The cores were polished in parallel prior to testing. Three cores for each shotcrete variation were measured. The exact extraction position of each drill core was recorded.

2.3. Water absorption & porosity

Porosity and water absorption were determined on drill cores
(height = diameter = 50 mm) according to Swiss standard SIA 262/1, appendix A (2013). The samples first were dried for 2 days at 50 °C and then immersed 3 mm deep in water at one end face. Water uptake after 24 h was measured. The water absorption coefficient \( w_{\text{cap}} \) was calculated by division with the root of time (24 h). After this procedure, the samples were completely immersed in water for 4 days. The capillary porosity \( P_{\text{cap}} \) was calculated by subtraction of the masses per volume after the drying at 50 °C from the ones obtained after the water immersion. Finally, the samples were dried during 3 days at 110 °C. The air content \( P_{\text{air}} \) was determined by complete saturation under vacuum. Three cores for each shotcrete variation were measured. The exact extraction position of each drill core was recorded.

### 2.4. Sulfate resistance test

The sulfate resistance of the concretes was determined according to the Swiss standard SIA 262/1, appendix D (2013), (Loser and Leemann, 2016) on a series of six cores \( \varnothing \) 28 mm and length 148 mm. The cores were taken perpendicular to the spray direction. The drill cores were first subjected to four drying / immersion cycles (5 days drying at 50 °C, 2 days immersion in 5% sodium sulfate solution) to accelerate the sulfate solution penetration. During the subsequent additional storage of 8 weeks in the same sodium sulfate solution, the expansion \( \Delta l_s \) was measured, which is used as a criterion for assessing the sulfate resistance of a concrete. In addition, the sulfate solution uptake \( \Delta m_s \) was determined by weight measurement. According to the Swiss standard SN EN 206:2013+A1 (2018), a limit of \( \Delta l_s \leq 1.0\% \) applies to a concrete with high sulfate resistance.

### 2.5. Dynamic elastic modulus

The resonance frequency of the first fundamental mode as identified by transit time measurements for longitudinal ultrasound pulses was used to calculate the dynamic modulus of elasticity on the basis of the standards ASTM C 215-08 (2008) and DIN EN 14146 (2004). The software RITA (“Resonance Inspection Techniques and Analysis®”, Los Alamos National Laboratory, USA Dept. of Energy) was used to record the measured values and to evaluate the data sets. Each drill core was measured twice and the average of these two measurements was used as a single value for the further calculations. Three drill cores with a diameter of 28 mm and height 148 mm were analyzed. As a result, the percentage change in the dynamic modulus of elasticity of samples as function of the duration of the sulfate exposure (additional storage) in relation to reference samples (same age but stored at 20 °C/90%RH) was derived.

### 2.6. Oxygen diffusion

The oxygen diffusion coefficient \( D_{O2} \) was measured by applying an oxygen flow on one side and a nitrogen flow on the other side of cores with diameter of 100 mm (height of 50 mm) at identical gas pressure on both sides. Then the oxygen content in the nitrogen flow was monitored until reaching equilibrium. The samples were stored at 35% relative humidity during 7 days before the measurement. The exact procedure and calculation of the diffusion coefficient was as described in Villani et al. (2014). Three drill cores were tested for each batch.

### 2.7. X-ray diffraction analysis (XRD) and thermogravimetry (TGA)

For the analysis two disks of 5 mm height were taken from drill cores as used for the sulfate resistance test after the test had ended as well as from control samples stored at 20 °C/90% RH (having the same age). The samples were crushed to a particle size of several millimeters, then hydration was stopped by solvent exchange with isopropanol and diethylether. Then the pieces were gently ground and larger particles were removed using a sieve with mesh size of 125 μm. The fraction below 125 μm was ground using a pestle and a mortar, until all particles passed a sieve with mesh size of 63 μm. The obtained powder was used for XRD and TGA analysis.

X-ray diffraction data was collected using a Panalytical X’Pert Pro MPD diffractometer in a \( \Theta - \Theta \) configuration using CoKα radiation, a fixed divergence slit of 1/2° and a rotating sample stage. The samples were scanned between 5 and 90° with the X’celerator detector. Thermogravimetry was carried out on about 50 mg at a heating rate of 20 K/ min in the temperature range 30–980 °C. A Mettler Toledo TGA / SDTA 851e was used.

### 2.8. Scanning electron microscopy

For scanning electron microscopy, a slice of concrete was cut perpendicular to the longitudinal axis out of the middle part of selected test pieces used for the determination of the sulfate resistance and dried in an oven at 50 °C for three days. Afterwards, the samples were impregnated with an epoxy resin under pressure, thereafter polished, carbon coated and examined by scanning electron microscope (SEM). A FEI Quanta 650 with an acceleration voltage of 12 kV, a spot size from 4.5 and a pressure of 3.0–5.0 × 10⁻⁶ Torr were used. Chemical analysis was performed by energy-dispersive X-ray spectroscopy (EDS) with a Thermo Noran Ultra Dry 60 mm² detector and Pathfinder X-Ray Microanalysis Software.
Table 4
Fresh concrete properties of the delivery mixtures.

| batch | cement       | binder [kg/m³] | w/b | plasticizer [kg/m³] | slump flow [mm] | dry density [kg/m³] | air [vol-%] measured |
|-------|--------------|----------------|-----|---------------------|-----------------|---------------------|---------------------|
| BG 1  | CEM I 450    | 0.45           | 4.52| 570                 | 2349            | 2.5                 | 0.42                | BE1/2/3             |
| BG 2-1| CEM I + 8%SF | 0.45           | 5.40| 520                 | 2278            | 5.6                 | 0.44 (0.41)         | BE3                 |
| BG 2-2| CEM I + 8%SF | 0.45           | 5.86| 610                 | 2359            | 2.2                 | 0.48 (0.44)         | BE1/BE2             |
| BG 3  | CEM I + 8%SF | 0.48           | 4.59| 580                 | 2318            | 2.6                 | 0.49 (0.45)         | BE2/3               |
| BG 4  | CEM II/B-M   | 0.45           | 3.58| 580                 | 2340            | 2.4                 | 0.45                | BE1/BE2             |
| BG 5  | CEM III/B    | 0.45           | 4.10| 670                 | 2315            | 2.7                 | 0.43                | BE1/BE2             |

Table 5
Summary of the shotcrete testing results.

| cement | w/c (w/b*) | accelerator | f_c,28 [MPa] | d_28d [kg/m³] | P_cap [vol-%] | P_air [vol-%] | w_24 [kg/m² h²] | D_o2 [10^-8 m²/s] | Δm_s [kg/m³] | ΔL_s [%] | ΔE_s [%] |
|--------|------------|-------------|--------------|---------------|---------------|---------------|-----------------|-----------------|--------------|---------|---------|
| CEM I  | 0.45       | –           | 49.5         | 2243          | 7.7           | 6.7           | 0.49            | 2.38            | 407          | 1.24    | N.A.    |
| CEM I  | 0.45 (0.42)| BE1 / 6%    | 27.5         | 2301          | 9.0           | 3.2           | 0.62            | 3.10            | 534          | 16.62   | –84.42  |
| CEM I  | 0.45 (0.42)| BE2 / 6%    | 53.9         | 2284          | 8.2           | 3.0           | 0.46            | 2.11            | 455          | 2.97    | –4.88   |
| CEM I  | 0.45 (0.42)| BE3 / 6%    | 53.9         | 2297          | 8.3           | 3.4           | 0.46            | 1.99            | 451          | 3.62    | –23.99  |
| CEM II/B-M | 0.45 | –           | 65.6         | 2318          | 6.3           | 3.9           | 0.32            | 0.67            | 348          | 0.47    | N.A.    |
| CEM II/B-M | 0.45 (0.45)| BE1 / 6%    | 38.5         | 2299          | 8.2           | 2.5           | 0.48            | 1.30            | 496          | 10.60   | –26.02  |
| CEM II/B-M | 0.45 (0.45)| BE2 / 6%    | 59.0         | 2295          | 7.5           | 3.4           | 0.42            | 1.22            | 450          | 1.28    | 7.45    |
| CEM II/B-M | 0.45 (0.45)| BE3 / 6%    | 57.2         | 2280          | 7.7           | 3.4           | 0.38            | 1.39            | 449          | 1.51    | 6.37    |
| CEM III/B | 0.45       | –           | 53.9         | 2273          | 5.4           | 6.6           | 0.26            | 0.20            | 294          | 0.47    | N.A.    |
| CEM III/B | 0.45 (0.43)| BE1 / 6%    | 50.9         | 2258          | 7.2           | 3.4           | 0.43            | 0.37            | 381          | 0.67    | 23.04   |
| CEM III/B | 0.45 (0.43)| BE2 / 6%    | 48.8         | 2252          | 7.4           | 4.2           | 0.40            | 1.08            | 395          | 0.47    | 11.39   |
| CEM III/B | 0.45 (0.43)| BE3 / 6%    | 54.4         | 2258          | 7.7           | 4.1           | 0.41            | 1.12            | 407          | 0.44    | 11.4    |
| CEM I + SF | 0.45      | –           | 46.0         | 2132          | 7.9           | 10.5          | 0.44            | 3.25            | 420          | 3.90    | N.A.    |
| CEM I + SF | 0.45 (0.44)| BE1 / 6%    | 35.3         | 2305          | 8.3           | 2.3           | 0.52            | 1.69            | 540          | 26.85   | –91.76  |
| CEM I + SF | 0.45 (0.44)| BE2 / 6%    | 54.6         | 2291          | 8.3           | 2.7           | 0.43            | 2.25            | 433          | 0.73    | 11.07   |
| CEM I + SF | 0.45 (0.44)| BE2 / 8%    | 50.9         | 2284          | 8.5           | 2.5           | 0.47            | 2.29            | 467          | 1.02    | N.A.    |
| CEM I + SF | 0.48 (0.49)| BE2 / 6%    | 54.9         | 2269          | 9.3           | 3.4           | 0.52            | 2.28            | 431          | 4.18    | N.A.    |
| CEM I + SF | 0.45 (0.41)| BE3 / 6%    | 55.7         | 2298          | 8.1           | 3.8           | 0.42            | 2.10            | 429          | 0.94    | 9.16    |
| CEM I + SF | 0.45 (0.41)| BE3 / 8%    | 46.9         | 2278          | 8.8           | 2.5           | 0.45            | 2.70            | 474          | 3.76    | N.A.    |
| CEM I + SF | 0.48 (0.45)| BE3 / 6%    | 51.4         | 2257          | 8.9           | 3.4           | 0.50            | 2.49            | 447          | 7.36    | N.A.    |

*) water to binder ratio as measured on the fresh concrete.

f_c,28: compressive strength 28d; d_28d: dry density 28d; P_cap: capillary porosity; P_air: air porosity.

w_24: water absorption coefficient; D_o2: oxygen permeability coefficient.

Δm_s: sulfate solution uptake; ΔL_s: sulfate expansion; ΔE_s: change of the dynamic elastic modulus. N.A. not available.

Fig. 2. Sulfate expansion of the different cement/accelerator combinations as measured in the sulfate resistance test as function of the additional immersion time in the sulfate solution. Accelerator content was 6 mass-% of binder.
3. Results

3.1. General results

Table 4 summarizes the properties of the fresh concrete of the delivery mixes (concrete without accelerator before spraying). Well sprayable mixtures with slump flows above 500 mm were provided. The amount of water was dosed according to the recipe taking into account the moisture content of the aggregate and its water absorption. Nevertheless, a lower water to binder value than targeted was determined as dosed in the fresh concrete control. This applies to all delivery mixtures with CEM I and especially with added silica fume. It could indicate inaccuracies in the determination of the moisture content of the aggregate or their water absorption, or the degree of drying when testing the fresh concrete, especially in concretes with silica fume. For BG 2–1 a slightly higher air content compared to the other mixtures was detected. This is probably related to the somewhat lower slump flow compared to the other mixtures. Since air is added at the nozzle during spraying, this difference is not essential.

An overview of the properties of the hardened shotcretes is given in Table 5. Results for non-sprayed reference concrete (without accelerator, produced at a different site) are added for comparison. Neither in the porosity nor the transport property results ($P_{\text{air}}$, $P_{\text{cap}}$, $w_{24}$, $D_{\text{O}_2}$) nor in the mechanical properties ($f_{\text{c},28}$) a systematic dependence of the results on the sampling position (top / middle / bottom) was found. This as well indicates a consistently high quality of the test slabs produced.

The usage of the alkali-based accelerator (BE1) leads to a lower compressive strength $f_{\text{c},28}$ (with the exception of CEM III/B) and higher values for the capillary absorption $w_{24}$ compared to the reference (without accelerator) and the samples with alkali-free accelerators. Contrary, compared with the reference, the application of the two alkali-free accelerators has no systematic influence on these values. However, the addition of all accelerators influences the capillary porosity $P_{\text{cap}}$ negatively.

The influence of the type of alkali-free accelerator and the type of cement on the compressive strength at the age of 28 days $f_{\text{c},28}$ is relatively low. On the one hand, the type of cement has a significant influence on oxygen diffusion and the cements with latent-hydraulic or pozzolanic additions (CEM II/B-M and CEM III/B) generally lead to denser concretes as expected. On the other hand, the addition of silica fume does not show the expected structure-compacting effect which is discussed in Section 3.4 in more detail.

3.2. Sulfate resistance

The sulfate solution uptake $\Delta m_s$ and the sulfate expansion $\Delta l_s$ were determined in the sulfate resistance test according to Swiss Standard SIA 262/1 appendix D (2013). Both values as obtained after eight weeks of additional immersion subsequent to the four drying/immersion cycles (5 days drying at 50 °C, 2 days immersion in 5% sodium sulfate solution) are provided in Table 5.

The evolution of the expansion during the additional saturation period for the different accelerator/cement combinations is plotted in Fig. 2. The most striking result is that the application of the alkali-based accelerator leads to significantly larger expansions for all studied cement types with the exception of the CEM III/B, where the expansion generally is much reduced compared to all the other cements. The limit for critical expansion as derived for conventional concrete (not sprayed) of 1‰ is not reached for these very dense cement systems based on CEM III/B. This also applies for the CEM I combined with 8% of silica fume when applying non-alkali based accelerators and the low water to binder ratio (0.45). As shown in Fig. 3, for the silica fume/CEM I combination a higher water to binder value (0.48) leads to a completely different behavior with high expansions. This binder combination is supposed to lead to densified systems which is not found in case of the higher water to binder ratio. Possible reasons are discussed below (Section 4).

The sulfate solution uptake is roughly related to the capillary
porosity of the specimens (Fig. 4). Some deviations from a stronger correlation originate from different water to binder ratios, the cement type (especially CEM II/B-M) and the accelerator type. The relationship between the capillary porosity and the sulfate solution uptake for the shotcretes made with alkali-based accelerator BE1 (empty symbols) seems to be different than the one of shotcretes made with the alkali-free accelerators. The drilling direction of the samples is not relevant for the properties like oxygen permeability and sulfate solution uptake. For practical reasons, and to avoid sample heterogeneities, drilling direction for the sulfate resistance was opposite to the one for the other drill cores. Nevertheless, uptake of sulfate solution increases with increasing oxygen diffusion coefficient, similar to the trend shown in Fig. 4.

The total sulfate expansion is in good correlation with the total sulfate solution uptake during the whole 8 weeks period of the immersion in the sulfate solution (Fig. 5). Hence, it is also widely related to the capillary porosity of the samples, which seems to play an important role regarding the sulfate resistance. The cement type is not directly related to the sulfate resistance, but indirectly by leading to either a denser or a more porous system. As mentioned before, the sulfate expansions of the shotcrete specimens are relatively large so that the usual criteria for a high sulfate resistance (expansion < 2‰) is exceeded for most specimens. Interestingly, the loss of the dynamic elastic modulus, an indicator for internal damage and cracking, is not detectable until a sulfate expansion of larger than 2‰ (Fig. 6). This is discussed in more detail in Section 4.

3.3. Phase composition of shotcrete before and after sulfate interaction

The chemical phase composition of the shotcretes was investigated by X-ray diffraction (XRD) and thermogravimetry (TGA). It should be noted that the large grains of the aggregate are sorted out for the analysis. Nonetheless, a part of the aggregates is still included in the samples. This is the source of the phases quartz, albite, clinohore, muscovite and a part of the calcite in the samples.

The phase composition of shotcrete prepared with the alkaline accelerator BE1 combined with different cements is shown in Fig. 7 (before sulfate interaction) and Fig. 8 (after sulfate interaction). This accelerator has a significant influence on the phase composition of some of the cements even without any sulfate interaction (Fig. 7). The CEM I system forms much less ettringite in the presence of BE1 than an analogue reference sample without accelerator (Kaufmann et al., 2019); only small amounts of ettringite are detectable by XRD. Contrary, larger amounts of AFm phases, especially hemi carbonate, are present.

Reason for the small amounts of ettringite and the comparatively high contents of AFm phases is, on the one hand, the addition of additional aluminate by the shotcrete accelerator, without a sufficient amount of sulfate being present for ettringite formation, which favors the formation of AFm phases. On the other hand, the alkaline accelerator contains large amounts of sodium ions, which lead to pH values in the order of 14 (Salvador et al., 2016). At such high pH, the stability of ettringite is reduced and AFm phases are formed instead (Alahrache et al., 2016). The subsequent sulfate storage of CEM I with BE1 then leads, as expected, to a strong ettringite formation, since the existing AFm phases react with the sulfate salt to form ettringite (Fig. 8). A similar formation of ettringite, however somewhat reduced compared to the CEM I cement, is found for the CEM II/B-M cement as well. Contrary, ettringite formation by sulfate solution immersion in CEM III/B is much less than for the other two systems, and a part of the AFm phases seem still to be present at the end of the sulfate resistance testing. This could result from the lower capillary porosity of shotcretes made with CEM III/B.

The alkali-free accelerator BE2 contains essentially aluminum and sulfate, but significantly less alkalis than BE1. Therefore, it affects the phase contents of the CEM I in a different way compared to the alkali-containing accelerator BE1. Considerable higher amounts of ettringite compared to the alkali-free accelerators can be detected by XRD and TGA (Fig. 9), which are formed mainly of the aluminum and the sulfate of the accelerator, and the calcium ions released by the cement hydration. Portlandite is present in similar quantities for CEM I with and without sulfate interaction (Figs. 7/9 and 8/10) and with the alkaline BE1 and the alkali-free accelerator BE2 as can be seen from the TGA data.

As expected, the influence of the silica fume on the phase development in the system with CEM I + SF and the alkali-free accelerator BE2 is low (Figs. 9/10), since only 8% of the CEM I was replaced by silica fume. The amount of portlandite (TGA) appears to be somewhat lower in the silica fume system, indicating a pozzolanic reaction of some silica fume to form C-S-H phases, which consume portlandite (Lothenbach et al., 2014). Portlandite can hardly be detected in the CEM III/B systems. Since the accelerator BE2 serves as an aluminum source, ettringite and possibly also monocarbonate are increased. After sulfate interaction, monocarbonate has largely disappeared and ettringite shares become more dominant. Portlandite remains (if already available) at the same extent.

3.4. Scanning electron microscopy

In all investigated shotcrete samples, included veins in the cement
paste filled with ettringite can be observed after the sulfate interaction (Fig. 11). This phenomenon is usually not present in conventional concrete exposed to sulfate resistance testing. The reason for this difference is not clear, but could be the result of the production-related, layered structure of shotcrete or the generally higher sulfate uptake of shotcrete. It is assumed that the sulfate uptake leads to ettringite formation in the entire cementitious matrix. This leads to an expansion and finally cracking, preferentially along the boundary region between the aggregate and the cement matrix. Such cracks may then be filled by further secondary ettringite formation.

Microscopy also provides a reason for the unexpected high expansion of the CEM I cement blended with 8% of silica fume. In general, the use of silica fume causes the concrete to gain strength and density. As the results show (Section 3.1), this is not really the case with concrete produced with CEM I + SF. From the microstructure, a clear reason can be derived: a relatively large part of the silica fume is present as agglomerates with a diameter in the range of 20–300 µm. This has two different consequences. On the one hand, these agglomerates, unlike finely dispersed silica fume, are unable to densify the pore system and reduce permeability. On the other hand, the microstructure and the chemical analyzes show that the agglomerates are large enough to cause a damaging alkali-silica reaction (ASR). Fig. 12 shows such a silica fume agglomerate, from which cracks in the cement paste originate that are subsequently filled with silicon-rich ASR reaction products.

The origin of insufficient dispersion of the silica fume particles can be attributed to insufficient shear forces during mixing of the concrete, which are not high enough to overcome van-der Waals forces between the very small particles. Reasons for this are the high cement paste volume, the lack of large grains typical for shotcretes, and the relatively low viscosity of the preparation mix that was used in this work. Especially with a higher water to binder ratio (w/b = 0.48 instead of 0.45) insufficient dispersion may become dominant.
Elemental mapping shows a significant chemical difference between the silica fume agglomerates and the rest of the cement paste. Sodium is accumulated in the silica fume agglomerates. Interestingly, the molar sodium content exceeds the molar potassium content by the order of one magnitude, although the molar sodium to potassium ratio in the used cement is in the range of 0.4. When sulfate is consumed by ettringite formation (Schmidt, 2007; Leemann and Loser, 2012), sodium needs a new counter ion to keep charge balance. This counter ion is provided by calcium hydroxide leading to increased pH of the pore solution (Irbe et al., 2019). Consequently, the potential for ASR is increased and the high sodium content in the pore solution is reflected in the observed composition of the ASR products formed in silica fume agglomerates.

4. Discussion

The sulfate expansion of reference laboratory concrete (same mix design but without accelerator) is comparable to that of conventional concrete with identical binder and water to binder ratio (w/b = 0.45, Fig. 12, data from Loser and Leemann, 2013). In contrast, shotcrete (with accelerator application) shows a larger sulfate expansion than the corresponding conventional concretes and the difference increases with increasing sulfate expansion. It therefore appears that shotcrete generally has a higher sulfate expansion than conventional concrete with the same binder content and water to binder ratio (w/b). It is thus more difficult to achieve a high sulfate resistance with shotcrete than with corresponding conventional concrete (no accelerator) when using the same composition (cement type and content, w/b).

There is a relationship between the sulfate solution uptake during the drying and saturation cycles and the measured sulfate expansion, although this is different for conventional (normal) concrete (Loser and Leemann, 2013) and shotcrete or reference concrete produced without an accelerator (Kaufmann et al., 2019). In conventional concrete, sulfate expansion begins to increase at a much lower sulfate solution uptake than in shotcrete or the reference concrete without accelerator. This is

Fig. 8. Phase compositions of concretes with alkali-based accelerator BE1 after sulfate interaction as determined by a) XRD and b) TGA.
mainly due to the higher binder volume of the shotcrete and the reference concrete (about 350 l/m$^3$) compared to conventional concrete (about 260 l/m$^3$). When the sulfate expansion is recorded as a function of the sulfate solution uptake per m$^3$ cement paste volume (instead of per cubic meter of concrete) conventional concrete and shotcrete resp. reference concrete show a similar relationship (Fig. 13).

Sulfate solution uptake during the four drying / wetting cycles has a significant proportional relationship with the transport properties (diffusion coefficient) and porosity (capillary porosity) of the concrete (Fig. 4). It is observed that the spray-application and usage of an accelerator in the case of shotcrete leads to a higher capillary porosity than for the reference concrete (no accelerator) mixed and placed conventionally as is demonstrated in Fig. 14. Hence, the higher sulfate expansion of shotcrete is mainly related to its higher porosity. An efficient transport of sulfate ions is supposed to lead to a higher swelling pressure in the smallest pores, while the additional space due to higher capillary porosity does not reduce expansion significantly (Kunther et al., 2015; Leemann et al., 2010).

Capillary porosity and diffusion coefficient have cement-specific differences and also the sulfate solution uptake differs correspondingly with the type of cement. In general, concretes made of cements containing latent-hydraulic or pozzolanic components (CEM II/B-M and CEM III/B) have a lower capillary porosity, a lower diffusion coefficient and a lower sulfate solution uptake than concretes with the CEM I cement. Reference concrete and shotcrete show the same relationship between sulfate solution uptake and sulfate expansion. This means that the use of alkali-free accelerators does not have a direct effect on the sulfate resistance compared to conventional concrete in the test matrix used here, but only indirectly via the formation of improved pathways and thus increased sulfate solution uptake.

The dynamic modulus of elasticity normally increases with low sulfate expansions in the course of the additional storage of the sulfate resistance test (Fig. 15) possibly due to the ongoing hydration and the densification of the pore system. However, as sulfate expansion

Fig. 9. Phase compositions of concretes with alkali-free accelerator BE2 before sulfate interaction as determined by a) XRD and b) TGA.
increases, dynamic modulus of elasticity begins to decrease, indicating damage (e.g. micro- and macro-cracks). This deterioration begins with conventional concrete at much smaller sulfate expansions than in shotcrete. This means that in the case of shotcrete an expansion well above 1.0‰ is necessary to damage the material in the sulfate resistance test. This is likely to be related to the higher binder volume and smaller size of the aggregates and hence a lower degree of internal restraint.

Shotcrete generally shows higher expansions in the sulfate resistance test than conventional concrete. At the same time, it can accommodate a higher expansion than conventional concrete in the sulfate resistance test before a decrease in dynamic elastic modulus occurs, which indicates damage. Compared to large on-site structures, the test specimens in laboratory tests are relatively small and expansion with little internal restraint and even without any external restraint is possible. However, on-site sulfate induced concrete expansion can lead to high stress levels due to internal (e.g. spatial distribution of sulfates) or external (e.g. structural) restrained deformations and hence to corresponding damages. Furthermore, the possibility for the occurrence of shotcrete inhomogeneities increases at large on-site structures, promoting localized damage as well. Therefore, any threshold for sulfate expansion in a laboratory test should not be reduced in the case of shotcrete, even if it can accommodate a higher expansion before damage occurs than a conventional concrete.

The higher sulfate expansion of shotcrete has shown to be mainly related to the higher porosity compared to conventional concrete. Due to larger fluctuations in properties compared to conventional concrete, it is therefore in practice even more important than for conventional concrete to apply shotcretes that bear a low expansion risk when an interaction with sulfate containing ground water is possible. This is achieved best by using sulfate resistant cements, which also lead to a dense microstructure with a low porosity. Shotcretes with a low water to binder ratio and the usage of admixtures should additionally contribute to achieve a dense microstructure. The observed higher sulfate expansions alternatively might be accommodated by the introduction of...
artificial joints in the shotcrete applications. Regarding the quality of the shotcrete application, it is essential to aim for uniform spraying and the minimization of inhomogeneities.

5. Summary and conclusions

The sulfate resistance of shotcrete, its phase composition and the relevant physical and chemical influencing factors were assessed by a comprehensive approach including classical laboratory tests as well as X-ray diffractometry (XRD), thermogravimetry (TGA) and scanning electron microscopy. A recently developed sulfate resistance test, which is now standardized in Switzerland, was applied for the first time to shotcrete. Shotcretes produced with different types of cement (CEM I, CEM II and CEM III) in combination with alkali-based and alkali-free accelerators were studied. The sulfate resistance test proved to be suitable for the assessment of shotcrete. Compared to conventional concrete, shotcrete shows the following special characteristics when tested according to the new method:

- Generally, shotcretes show significantly greater length changes when interacting with sulfate solution than conventional concretes of the same water to binder ratio and type of binder.
- A higher length change is in good correlation with a higher porosity and permeability.
- Alkali-free accelerators have only a small influence on the phase assemblage of shotcrete but lead to a significant higher porosity and permeability than for comparable concrete made without accelerators and hence lead to higher sulfate expansion.

Fig. 11. A) Ettringite (blue arrows) along the contact zone of rock and cement paste. Shotcrete with CEM II/B-M, 6% BE3 and w/c = 0.45 B) Silica fume agglomerates with cracks extending radially into the cement paste. Concrete with CEM I + SF, 6% BE3 and w/c = 0.45. The table shows the composition of the silica fume as reacted with the concrete pore solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Alkali-based (aluminate-based) shotcrete shows much higher expansion than alkali-free accelerators. Damage of non-constrained shotcrete, which manifests itself as a decrease of the dynamic modulus of elasticity, occurs at a higher sulfate expansion compared to conventional concrete.

As with conventional concrete, the cement type and the water to binder ratio (w/b) are also decisive for the sulfate resistance of shotcrete. On the one hand, capillary porosity and diffusion coefficient have cement-specific differences, and the sulfate solution uptake in the test specimens differ with cement type and w/b accordingly. CEM III type cement may lead to very dense and durable shotcretes. On the other hand, the type of cement, through its composition, defines the potential for ettringite formation and thus the damage to the concrete. Sulfate expansion occurs by conversion of monocarbonate / hemicarbonate / monosulfate (AFm phases) to ettringite. This is especially the case, when alkali-based accelerators are used, which destabilize ettringite due to high pH and lack of sulfate. However, it is shown that the production of sulfate-resistant shotcrete cannot exclusively be achieved by using sulfate resistant cements, but their application minimizes the damage potential. This is also to be considered with respect to the fact that shotcrete often has an increased probability for inhomogeneities in comparison to conventional concrete.

The present investigation has confirmed practical experience according to which the use of compacted silica fume as additive and/or insufficient dispersion of the added silica fume can lead to a reduction in performance (lower densification of the microstructure) and large expansions due to an additional alkali-aggregate reaction. When using silica fume as an addition, adequate dispersion is to be ensured. Silica fume should hence preferably be used in the form of a slurry, undensified powder or as part of the cement (CEM II with silica fume).

Fig. 12. Comparison of sulfate expansion during the additional storage between conventional concrete and reference samples (laboratory without accelerator) as well as shotcrete (sprayed with accelerator BE3) with identical water to binder w/b value (0.45) and binder type. The dashed line indicates a ratio of 1:1.

Fig. 13. Comparison of sulfate expansion and the sulfate solution uptake (during the additional storage) between conventional concrete (Loser and Leemann, 2013), reference concrete (laboratory concrete without accelerator) and shotcrete (sprayed with accelerator).

CRediT authorship contribution statement

Josef Kaufmann: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Writing - original draft. Roman Loser: Investigation, Methodology, Writing - review & editing. Frank Winnefeld: Investigation, Methodology, Writing - review & editing. Andreas Leemann: Funding acquisition, Investigation, Methodology, Writing - review & editing.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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