Sulfate resistance testing of shotcrete – Sample preparation in the field and under laboratory conditions

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HIGHLIGHTS
• Sulfate resistance testing of shotcrete.
• New method for test sample preparation in the laboratory without spraying.
• Comparison of laboratory-prepared with real on-site shotcrete.
• Chemical phase assemblage of shotcrete before and after sulfate interaction.
• Effect of alkali-free accelerators and different cement types on the sulfate resistance of shotcrete.

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ABSTRACT
When shotcrete is in contact with sulfate containing ground water, there is a risk of a drastically reduced service life. In this case, the use of sulfate-resisting cement is recommended. Since physical characteristics of the cement matrix of shotcrete differ from conventional concrete, sulfate-resisting cements do not always guarantee sufficient shotcrete durability. Thus, testing of the sulfate resistance in accelerated tests is necessary. Providing test samples from on-site (real) shotcrete is time consuming and demanding. In this study, the sulfate resistance and physical properties such as compressive strength and transport properties of samples produced in the laboratory without spraying are compared to the properties of field samples. A new compaction method is proposed, which is apt to allow high accelerator dosages. For different alkali-free set-accelerators and cement types, the laboratory-produced samples not only reveal similar sulfate resistance test results as on-site shotcrete, but also exhibit comparable porosity, transport properties and chemical phase assemblage.

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1. Introduction
Wet spraying of concrete (shotcrete) is an efficient way especially in underground construction to secure the uncarved rock walls and protect the obtained tunnel space against the inflow of ground water. In this type of application the concrete is premixed (delivery mixture) and then pumped to a nozzle where it is accelerated through pressurized air and finally sprayed. Shotcrete differs from conventional concrete in addition to the special application technology in terms of mix proportions and the addition of high levels of admixtures, especially of set accelerators. Compared to conventional concrete, shotcrete generally displays a smaller largest grain size (approx. 8 mm) and in addition sufficiently low viscosity facilitating the pumping of the delivery concrete and the passage through the nozzle. The smaller maximum grain size demands a higher binder volume to achieve an adequate workability. At the same time, usually lower water/binder ratios apply for sprayed concrete in order to achieve higher early strengths and denser microstructures. Hence, the mix designs of shotcretes comprise higher binder dosages than conventional concrete of about 420 to 460 kg/m³. In order to reduce the viscosity, water reducing agents (in dosages of about 0.5 to 1.5 mass-% of binder) are typically used.

The addition of a set accelerator at the nozzle leads to a rapid solidification and hardening of the shotcrete and, accordingly, to a high early strength and improved adhesion to the substrate. Usually, rather high accelerator dosages of 5–10 mass-% of the cement dosage are used. A strong trend towards alkali-free accelerator systems has occurred in recent years. Generally, these accelerators are chemically based on mixtures of aluminum and sulfate based chemical compounds. Because of the special application technique, especially for thick shotcrete layers of several decimeters when
application is in multiple rounds, spraying often results in a layered structure. The layer boundaries can present pathways for the penetration of harmful fluids like sulfate containing ground water. As a result, the durability of the shotcrete then may reduce seriously. Sulfate attack on mortar or concrete leads to the formation of expansive minerals like ettringite, gypsum and thaumasite [1–4]. The formation of these minerals through solution and precipitation processes can produce high crystallization pressures [5,6]. Thus, testing and designing of the shotcrete regarding its sulfate resistance is an important issue with respect to a long service life. Sulfate resistance testing, like in a recently improved accelerated test [7] requires the production of representative samples. For this purpose, shotcrete has to be produced on-site requiring the use of large machines such as concrete mixers, ready-mixed concrete vehicles, pumps and spray equipment. In addition, relatively large quantities of materials (binders, aggregates and admixtures) compared to typical laboratory tests are necessary. For meaningful studies, it is necessary to produce at least 1–2 m³ of shotcrete per batch [8]. Furthermore, the space requirement for the spray process is considerable, as the initial adjustments of the spray parameters normally involve a large test area. A significant amount of concrete (>10 mass-%) rebounds from the application surfaces partly at high speed and thus requires some safety distance. Therefore, research and optimization experiments in practice are often carried out as part of the realization of large construction objects. Due to the great effort, it is clear that a systematic and wide variation of test parameters is a rare exception.

There are ways to spray small amounts of concrete in the laboratory scale. However, limitations with regard to the usable largest grain size (usually only mortar with maximum grain size <2 mm) and the maximum possible accelerator dosages, due to rapid hardening, have to be accepted [9,10]. Such tests may deliver useful information regarding the efficiency of binders and chemical admixtures, but are not prone to produce large quantities of shotcrete as is required for durability testing. Thus, the presented study evaluates a laboratory method regarding its ability to serve as an alternative to on-site spraying for sample preparation.

2. Materials and methods

2.1. Materials

On-site shotcrete and laboratory made shotcrete-analogue (applying a new method) were produced for a selected range of mixtures, varying cement type and accelerator type. Besides an Ordinary Portland cement (CEM I 42.5 N), two blended cements CEM II/B-M 42.5 R (Portland-composite-cement containing reactive aluminosilicates as main constituents besides Portland cement clinker) and CEM III/B 42.5 N (Blast furnace cement) were used. Table 1 summarizes their oxide compositions as derived by X-ray fluorescence (XRF) analysis. Ordinary Portland cement (CEM I) was partly replaced by silica fume (8 mass-% of the cement, labelled "CEM I + SF") in some concretes/shotcretes. The silica fume was added in the form of a dry powder of compacted (50 vol-% frac-tile: d_{50} >50 µm) amorphous fine (with diameters smaller than approx. 0.1 µm) silica particles (SiO₂ content = 94.7 mass-%). Three different alkali-free set accelerators were tested. In Table 2, the chemical analysis as derived from inductively coupled plasma optical emission spectrometry (ICP-OES) is given. The accelerators can mainly be distinguished by their aluminum to sulfate mass-ratio ranging from 0.20 to 0.29 (A1: 0.20, A2: 0.24, A3: 0.29). The underlying concrete mix design is as given in Table 3. In most mixtures, the water to binder ratio (w/b) was 0.45. To achieve a higher w/b of 0.48, the amount of mixing water was increased in some batches. The amount of mixing water was kept constant, increasing the water to cement ratio to 0.49 (resp. 0.52), while the water to binder ratio still was 0.45 (resp. 0.48). For all mixtures, the superplasticizer (polycarboxylate-ether based) dosage was adapted accordingly in order to reach a predefined slump flow of about 600 mm. A retarder (based on trisaccharic acid and citric acid) was added to guarantee constant flow properties during the whole application process. The set accelerator dosage was adjusted to 6 mass-% of the binder dosage (27 kg/m³) in most cases. In some samples, this dosage was increased to 8 mass-%.

| Table 1 | XRF analysis of the cements. |
|---------|------------------------------|
|         | CEM I | CEM II/B-M | CEM III/B |
| SiO₂    | 19.02 | 25.27      | 31.28     |
| Al₂O₃   | 4.69  | 6.19       | 9.26      |
| Fe₂O₃   | 3.3   | 2.89       | 1.29      |
| Cr₂O₃   | 0.007 | 0.012      | 0.006     |
| MnO     | 0.078 | 0.080      | 0.209     |
| TiO₂    | 0.25  | 0.339      | 0.725     |
| P₂O₅    | 0.161 | 0.229      | 0.086     |
| CaO     | 64.45 | 55.76      | 48.45     |
| MgO     | 1.75  | 3.18       | 5.24      |
| K₂O     | 0.84  | 0.96       | 0.73      |
| Na₂O    | 0.19  | 0.27       | 0.23      |
| SO₃     | 2.65  | 3.40       | 2.81      |
| L.O.I.  | 2.39  | 1.23       | −0.58     |
| Total   | 99.77 | 98.81      | 99.76     |
| CO₂     | 1.69  | 0.99       | 0.60      |
| Free lime | 1.50 | 1.05       | 0.39      |
| Density | 3.14  | 3.05       | 2.98      |

*J determined by ion chromatography.

| Table 2 | Chemical analysis (ICP-OES) of the applied set accelerators. |
|---------|---------------------------------------------------------------|
|          | A1                | A2                | A3                |
|          | mass-%            | mass-%            | mass-%            |
| Aluminum | 5.62              | 6.9               | 5.3               |
| Sulfates | 28.5              | 28.2              | 18.0              |
| Na₂O eq. | 0                 | 0.5               | 0.3               |
| Magnesium | 974              | 826               | 29                |
| Silicon  | 1395              | 1743              | 0                 |
| Lithium  | 2                 | 1                 | 7                 |
| Potassium | 21               | 20                | 6                 |
| Calcium  | 5041              | 52                | 34                |
| Sodium   | 0.01              | 0.15              | 0.2               |
| Iron     | 75                | 37                | 9                 |
| Phosphorus | 11              | 12                | 9                 |
| Driethanolamine | 1.7      | 1.4               | 0.2               |
| Triethanolamine | <0.8       | <0.8              | <0.8              |

1) Based on polycarboxylate-ether.
2) Based on trisaccharic acid and citric acid.
3) Laboratory concrete: 0.5 kg/m³, on-site shotcrete: 0.9 kg/m³.
4) River sand and gravel for laboratory concrete was from a different location than for on-site shotcrete.

| Table 3 | Concrete mix design. |
|---------|-----------------------|
|          | Cement kg/m³ | 450 |
| Water   | kg/m³        | 202.5/216 |
| w/b     | kg/m³        | 0.45/0.48 |
| Superplasticizer | kg/m³ | variable (2.25 to 4.5) |
| Retarder | kg/m³ | 0.5/0.5 |
| Accelerator | kg/m³ | 27/36 |
| Sand 0.01 mm | kg/m³ | 553 |
| Sand 1.0-4.8 mm | kg/m³ | 416 |
| Gravel 4.0-8.8 mm | kg/m³ | 684 |

1) Based on polycarboxylate-ether.
2) Based on trisaccharic acid and citric acid.
3) Laboratory concrete: 0.5 kg/m³; on-site shotcrete: 0.9 kg/m³.
4) River sand and gravel for laboratory concrete was from a different location than for on-site shotcrete.
2.2. Shotcrete production on-site (wet spraying)

Shotcrete on-site was produced at Hagerbach test galleries (Flums, Switzerland) [11,12] by means of the wet spraying technique. Concrete was first mixed in a planetary mixer (Fig. 1a). The fluid concrete without accelerator (delivery mixture) then was transported to the application site (Fig. 1b). It then was pumped to the nozzle (Meyco suprema pump, Fig. 1c) where the material was accelerated physically by pressurized air (5 bar) and chemically by the addition of an accelerator (Fig. 1d). Then the shotcrete was applied at high speed (Fig. 1e, 6 m³/h) to fill square moulds for sample preparation. Immediately after spraying, the produced square slabs (600 mm × 600 mm × 100 mm) were covered by plastic foils to prevent from water loss by evaporation (Fig. 1f) and stored at the tunnel climate (16 °C/85% RH) before the slabs were transported to Empa (stored at 20 °C/90% RH). As can be seen, the whole shotcrete process implied a high demand regarding machinery, materials and time. Nonetheless, just a few sample square slabs (in this case only one or two per mixture) were produced to provide a sufficient quantity of samples for testing.
Table 4

| Testing scheme with number and dimensions of the specimens. |
|-----------------------------------------------------------|
| **Standard/Reference**                                      | **Specimens**                          |
| Compressive strength 28d                                   | 3 × cylinder: h = 50 mm/d = 50 mm       |
| Water conductivity/porosity 28d                            | 3 × cylinder: h = 50 mm/d = 50 mm       |
| O₂-Diffusion 28d                                           | 2 × cylinder: h = 50 mm/d = 100 mm     |
| Sulfate resistance test                                    | 6 × cylinder: h = 148 mm/d = 28 mm     |
| Dynamic elastic modulus                                    | 4 × cylinder: h = 148 mm d = 28 mm     |
| XRD and TGA                                                | 2 × cylinder: h = 148 mm d = 28 mm     |

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Fig. 3. Sampling scheme for the extraction of drilled cores with diameter of 28 mm (sulfate resistance test, dynamic elastic modulus, TGA/XRD-analysis) - laboratory: parallel to the filling direction, shotcrete: perpendicular to the sprayed direction and diameters 50 mm (compressive strength and porosity) and 100 mm (oxygen diffusion test) - laboratory: parallel to filling direction, shotcrete: parallel to the sprayed direction.

2.3. New method for the preparation of a shotcrete-analogue in the laboratory

Shotcrete production includes the addition of very high amounts of accelerators. These chemical additives strongly accelerate the hydration process, so that the plasticity of the fresh concrete is lost within less than a minute in a way that normal compaction and placing techniques fail. Spraying in the laboratory, especially of typical shotcretes and under typical spray conditions, would require similar demanding equipment as in the field. In order to produce a shotcrete-analogue in the laboratory, a new process which does not require an application with high pressure spraying (Fig. 2) was developed. Typical shotcrete formulations and high accelerator dosages can be used, and samples for e.g. durability testing can easily be extracted by drilling. The method described here was applied for the first time and has the potential to be standardized and automatized. For the production of a concrete similar to shotcrete, first conventional concrete was mixed and produced in a laboratory mixer (approx. 60 l, Eirich R08W mixer) according to the same recipe (without accelerator) as the delivery mixture for an analogous shotcrete. Fluid consistency was chosen (consistency class F5 according to SN EN 206). The required amount of concrete (about 15 kg) for the test specimen production then was filled in a bucket and its weight was measured. Slightly conical plastic buckets with a smallest inner diameter of 290 mm were used and filled up to a filling height of 180 mm. Based on the filling quantity and the targeted dosing, the amount of accelerator was calculated. The content of the filled bucket was then poured evenly over a chute into a second previously empty bucket. This took place within approx. 7 s. At the same time, the accelerator was added continuously, and the concrete now brought into contact with the accelerator was mixed by means of a fixed hand mixer with two counter-rotating stirrers. The stirrers were adapted to turn counterclockwise, so that the filled concrete was pushed downwards during stirring. After the entire amount of concrete was added to the second bucket, further mixing for another 10 s was applied. The filled (second) concrete bucket was then quickly removed from the concrete stirrer by stepping off the pedestal on which it was placed. Due to the high accelerator dosages of up to 8% of the binder content and the accordingly extremely fast setting reaction, it was impossible to extend the mixing times. The concrete was then further compacted in the bucket by a rapid subsequent shock compaction (50 times lifting and subsequent dropping). The filled buckets then were stored at 20 °C/90%RH. The buckets itself hence served as a formwork, in which the concrete continued to harden until the test specimens were taken.

2.4. Sampling and testing

At the age of 21 days, cores of different diameters and lengths according to Table 4 and Fig. 3, were drilled from the laboratory shotcrete-analogue samples. Drilling of the laboratory specimens was from the filling direction (Fig. 3a). The same amount of samples were taken as well from the on-site produced shotcrete slabs (Fig. 3b). The drilled cores with a diameter of 28 mm for sulfate resistance testing were taken perpendicular to the spray direction. All samples were then stored at 20 °C/90%RH until the start of the different tests at the age of 28 d.

The material properties compressive strength $f_{c28}$ [13] dry density $\rho_{280}$, capillary porosity $P_{cap}$, air content $P_{air}$ [14] and the transport properties oxygen diffusion coefficient $D_{O2}$ [15] and water
Summary of results: Laboratory shotcrete-analogue (L), on-site shotcrete (S, grey) and delivery concrete without accelerator (0).

Sulfate expansion comparison of cement CEM I and accelerator A2 (dosage 6%) of shotcrete, concrete of the same composition produced in the laboratory using the new method and reference concrete without accelerator. For standard deviations the reader is referred to Fig. 12.

The sulfate resistance of the concretes was determined according to the Swiss standard SIA 262/1 [7,16] on a series of six cores Ø 28 mm and length 148 mm. The drill cores were first subjected to four cycles of drying and immersion (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 Δl was measured, which is used as a criterion for the sulfate resistance of a concrete. In addition, the sulfate solution uptake Δm, during drying and immersion cycles was determined by weight measurement. In order to quantify inner damage of the specimens, the dynamic modulus of elasticity was determined [17] and its percentage change of the 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 calculated. The sulfate expansion parallel to the application area (perpendicular to the spray direction) is of most interest. Porosity is widely independent from sampling direction in both production methods. Oxygen permeability and water absorption is somewhat sensitive to preferential transport pathways so that it was decided to drill them from top of the shotcrete panels. The material produced with the new method is uniform in all directions, so that sample drilling direction is a less important factor. These tests are described in more detail in [11,12].

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absorption (suction) coefficient w_{24} (mass uptake in 24 h of samples dried at 50 °C divided by the root of suction time [14,19]) were determined. Samples for the oxygen diffusion and the water suction tests were measured according the test program presented in Table 4.

**Table 5**

| Cement | w/b | Accelerator | f_{28d} [MPa] | ρ_{d28} [kg/m³] | P_{cap} [%] | P_{air} [%] | w_{24} [kg/m²h⁰⁵] | D_{02} [10⁻⁹ m²/s] | Δm₀ [kg/m³] | Δl₈ [%] |
|--------|-----|-------------|--------------|----------------|------------|------------|----------------|----------------|----------------|--------|
| A₀     | 0.45 | -           | 49.5         | 2243           | 7.7        | 6.7        | 0.49           | 2.38           | 407            | 1.24   |
| A₁     | 0.45 | A₂/6%      | 45.9         | 2191           | 8.9        | 8.0        | 0.58           | 4.35           | 453            | 3.84   |
| A₂     | 0.45 | A₂/6%      | 53.9         | 2297           | 8.3        | 3.4        | 0.46           | 1.99           | 451            | 3.62   |
| B₀     | 0.45 | -           | 46.0         | 2132           | 7.9        | 10.5       | 0.44           | 3.25           | 420            | 3.90   |
| B₁     | 0.45 | A₂/6%      | 44.3         | 2171           | 9.8        | 6.8        | 0.63           | 5.38           | 476            | 8.76   |
| B₂     | 0.45 | A₂/6%      | 55.7         | 2298           | 8.1        | 3.8        | 0.42           | 2.10           | 429            | 0.94   |
| C₀     | 0.45 | A₃/6%      | 39.4         | 2103           | 9.8        | 7.8        | 0.66           | 7.77           | 495            | 6.85   |
| C₁     | 0.45 | A₅/6%      | 56.8         | 2287           | 8.3        | 2.9        | 0.43           | 2.21           | 426            | 0.56   |
| C₂     | 0.45 | A₅/6%      | 42.6         | 2152           | 10.3       | 7.4        | 0.58           | 5.13           | 483            | 7.27   |
| D₀     | 0.45 | A₂/8%      | 46.9         | 2278           | 8.8        | 2.5        | 0.45           | 2.70           | 474            | 3.76   |
| D₁     | 0.45 | A₂/8%      | 42.7         | 2165           | 9.6        | 6.8        | 0.64           | 4.34           | 473            | 10.39  |
| D₂     | 0.45 | A₂/8%      | 51.4         | 2257           | 8.9        | 3.4        | 0.50           | 2.49           | 447            | 7.36   |
| E₀     | 0.48 | A₂/6%      | 65.6         | 2318           | 6.3        | 3.9        | 0.32           | 0.67           | 348            | 0.47   |
| E₁     | 0.45 | A₁/6%      | 40.9         | 2234           | 7.2        | 5.8        | 0.40           | 1.37           | 422            | 1.24   |
| E₂     | 0.45 | A₄/6%      | 59.0         | 2295           | 7.5        | 3.4        | 0.42           | 1.22           | 450            | 1.28   |
| E₃     | 0.45 | A₂/6%      | 35.4         | 2234           | 8.1        | 4.6        | 0.41           | 1.21           | 403            | 1.34   |
| E₄     | 0.45 | A₂/6%      | 57.2         | 2280           | 7.7        | 3.4        | 0.38           | 1.39           | 449            | 1.51   |
| E₅     | 0.45 | A₂/6%      | 53.9         | 2273           | 5.4        | 6.6        | 0.26           | 0.20           | 294            | 0.47   |
| E₆     | 0.45 | A₂/6%      | 46.6         | 2252           | 7.3        | 5.3        | 0.36           | 0.71           | 367            | 0.74   |
| E₇     | 0.45 | A₂/6%      | 54.4         | 2258           | 7.7        | 4.1        | 0.44           | 1.12           | 407            | 0.44   |

f_{28d}: Compressive strength 28d; ρ_{d28}: dry density 28d; P_{cap}: capillary porosity; P_{air}: air porosity. w_{24}: Water absorption coefficient; D_{02}: oxygen permeability coefficient. Δm₀: sulfate solution uptake; Δl₈: sulfate expansion.

**Fig. 4.** Sulfate expansion comparison of cement CEM I and accelerator A2 (dosage 6%) of shotcrete, concrete of the same composition produced in the laboratory using the new method and reference concrete without accelerator. For standard deviations the reader is referred to Fig. 12.

**Fig. 5.** Sulfate expansion comparison of cement CEM II/B-M and accelerators A1/A2 (dosage 6%) of shotcrete, concrete of the same composition produced in the laboratory using the new method and reference concrete without accelerator. For standard deviations the reader is referred to Fig. 12.

**Fig. 6.** Sulfate expansion comparison of cement CEM III/B and accelerator A2 (dosage 6%) of shotcrete, concrete of the same composition produced in the laboratory using the new method and reference concrete without accelerator. For standard deviations the reader is referred to Fig. 12.
3. Results

3.1. General overview

In Table 5 a summary of the results from the different tests is given. Results from shotcrete produced on-site are highlighted (grey fillings). The other results were obtained for laboratory shotcrete as produced with the new method.

For the cements CEM I, CEM II/B-M and CEM III/B and for all accelerator type combinations, the transport properties \(D_{02, w_24}\) and capillary pore contents \(P_{cap}\) are widely independent of the production method (laboratory shotcrete-analogue vs. on-site shotcrete). Air pore content \(P_{air}\) in the laboratory samples is relatively high, even when no accelerator is used and significantly higher than for shotcrete. A reason is certainly the better compaction when spraying.

3.2. Sulfate resistance

The sulfate solution uptake and the sulfate expansion for on-site shotcretes are similar as for the laboratory shotcrete-analogues with the same mix designs with the exception of the mixtures of Portland cement with a partial silica fume replacement (CEM I + SF). In the latter case, the sulfate solution uptake is similar for both production methods (a somewhat lower sulfate solution uptake for on-site shotcrete with the same mix design as for the laboratory shotcrete-analogue is observed). However a signifi-
A higher water to binder ratio (0.48 vs. 0.45; $E_A$ vs. $B_A$ and $E_B$ vs $B_B$) and a higher accelerator dosage (8% vs. 6%; $D_A$ vs. $B_A$) tend to yield higher sulfate expansions. These effects were observed in the binder system with the partial replacement of the Ordinary Portland cement by a condensed silica fume. Possibly the shear forces at higher w/b and higher accelerator dosage are lower, so that a sufficient dispersion of the very fine silica fume particles is

\[ \text{Fig. 8. Chemical phase composition (XRD and TGA) of shotcrete S and concrete produced in the laboratory I by the new process of the same composition with different cements and accelerator A2 after sulfate interaction (dosage 6%, L-CEM II/B-M: data not available). (XRD above, } \text{Al = Albite, Ca = Calcite, Cl = Clinochlore, E = Ettringite, Hc = Hemicarbonate, M = Muscovite, Mc = Monocarbonate, P = Portlandite, Ht = Hydrotalcite, Qz = Quartz). The arrows in the TGA-plots indicate the corresponding axis.} \]

\[ \text{Fig. 9. Relation between sulfate solution uptake and capillary porosity for on-site shotcrete (shotcrete) and its analogue produced in the laboratory applying the new method (laboratory) – additional data from [12] with crossed symbols.} \]
not achieved [11]. The laboratory shotcrete-analogue seems to be more sensitive regarding a possible performance drop in the sulfate resistance for the high w/b and the high accelerator content.

The sulfate expansion during the sulfate resistance test is plotted in more detail for three different cement types (CEM I, CEM II/B-M and CEM III/B) in Figs. 4, 5 and 6. Standard deviations partly are given in Fig. 12. On-site shotcrete (labelled shotcrete) is compared with the shotcrete-analogue produced by the new method in the laboratory (labelled laboratory) and the delivery concrete without any accelerator addition (labelled laboratory/no acc.). The results for the laboratory produced shotcrete-analogue and the ones for the on-site shotcrete are almost identical for all the presented cement/accelerator combinations. For both shotcrete types (laboratory or on-site produced) significantly larger sulfate expansions than for the parallel delivery mixture (concrete without accelerator) of cement CEM I and CEM II/B-M are found. However, this is not found in the CEM III/B cement systems. It is well known that generally a dense microstructure is formed in such concretes [20] and hence sulfate solution uptake is small. This is also supported by the lower values of the transport properties (w250, Dmax). Thus, sulfate resistance is much improved, leading to very little expansion for all concretes made with the CEM III/B cement. The relationship between transport properties and sulfate resistance as discussed below in more detail is part of an explanation of the strong influence of the accelerators on the sulfate resistance of shotcrete.

3.3. Chemical phase composition

For a deeper analysis, the chemical phase assemblage of on-site shotcrete is compared with the shotcrete-analogue produced in the laboratory by the new method without spraying. Furthermore, the effect of the sulfate solution immersion on the phase composition was studied by the analysis of non-immersed (stored at 20 °C/90% RH, Fig. 7) and immersed (Fig. 8) samples of the same mixtures. X-ray diffraction (XRD) and thermogravimetry (TGA) data for mixes with accelerator A2 are shown. The sand and gravel sources differed between the on-site shotcrete and its laboratory imitation. The occurrence of phases like clinochlore, muscovite, albite and calcite might hence differ somewhat. As they are not supposed to play any role regarding the sulfate interaction, these phases are excluded from the discussion. In general, laboratory samples (with accelerators) have phase compositions similar to on-site shotcrete.

The phase analyses (XRD and TGA) of various concretes combined with accelerator A2 before sulfate loading and after sulfate loading are shown in Fig. 7 and Fig. 8, respectively. In the laboratory shotcrete-analogues slightly increased levels of the cement hydrate phases portlandite and monocalcium are observed, which are supposed to be preparation artefacts due to the separation of the samples in the laboratory.

As a consequence of the sulfate interaction, mono- and hemi-carbonate phases are reduced, while ettringite contents are increased. The sulfate interaction leads to a reduction of portlandite especially for CEM II/B-M, however this phase does not disappear completely and the reduction is less for CEM I. A reduction of carbonates upon the contact with the sulfate solution is observed, however this is considered to be an artefact caused by the sample preparation as carbonates originating from calcite, hemi- and monocalcium can hardly be distinguished by TGA. Weaker zones around the aggregates resulting from the sulfate attack might have led to easier separation of hardened cement paste from the aggregate and hence less, possibly calcareous, aggregate parts have been introduced to the analyzed samples.

4. Discussion

Relating the sulfate expansion with compressive strength shows no systematic differences between conventional concrete (delivery mixture, no accelerator) and on-site shotcrete resp. its laboratory analogue. As the strength decreases, the risk of a lower sulfate resistance generally increases. Thereby, the type of cement plays a much greater role than the type of concrete (conventional concrete, on-site/lab shotcrete). However, within this project no systematic and broader variations of the w/b values were performed.

Contrary, the sulfate solution uptake during the initial four drying/wetting cycles has a significant proportional relationship with the transport properties (diffusion coefficient) and porosity (capillary porosity) of the concrete (Fig. 5, enhanced with some additional data from [12]). This relationship is stronger for the laboratory produced shotcrete-analogue. The larger scattering for on-site shotcrete may originate from the different sample orientation regarding the spray direction. Contrary to the samples for porosity and transport properties determination, the samples for the sulfate resistance test (and hence the sulfate solution uptake measurement) were taken perpendicular to the spray direction. The typical layered structure of the shotcrete thus may have led to a weaker correlation in the case of real shotcrete than for its laboratory analogue. Since capillary porosity Pcap and diffusion coefficients also have cement-specific differences, the sulfate solution uptake differs correspondingly with the type of cement. In general, concretes made of cements containing supplementary cementitious materials (CEM II/B-M and CEM III/B) have lower values than the CEM I cement [11].

There is a good correlation between the sulfate solution uptake during the initial drying/wetting cycles and the measured sulfate expansion. When comparing these properties it is important to take the binder volume into account. In the presented data set the binder volume (350 l/m³) was widely constant so that concrete (no accelerator) and the laboratory resp. on-site shotcrete can be compared directly. For conventional concrete, the binder volume typically is much lower (about 260 l/m³) and the sulfate expansion should be compared with the sulfate solution uptake per cubic meter of cement paste instead of per cubic meter of concrete. Laboratory-produced shotcrete-analogue and on-site shotcrete show the same relationship between sulfate solution uptake and sulfate expansion (Fig. 10, enhanced with some additional data from [12]). This means, that the use of alkali-free accelerators does not have a direct effect on the sulfate resistance in the test matrix used here. The sulfate resistance is influenced indirectly by the formation of a higher porosity and permeability (higher values for the oxygen diffusion coefficient) and thus an increased sulfate solution.

![Fig. 10. Relation between sulfate expansion and sulfate solution uptake for on-site shotcrete (shotcrete) and its analogue produced in the laboratory applying the new method (laboratory) – additional data from [12] with crossed symbols.](image-url)
uptake by the application of set accelerators in comparison to con-
ventional concrete (no accelerator).

According to the Swiss national appendix of SN EN 206-1 [18] a
limit of $\Delta s \leq 1.0\%$ applies to a concrete with high sulfate resis-
tance. This means that at a higher elongation significant inner
damages are assumed. Damages of the samples were monitored
by the measurement of the dynamic elastic modulus. In the case
of shotcrete and its laboratory analogue, the dynamic modulus of
elasticity increases with low sulfate expansions in the course of
the sulfate resistance test (Fig. 11, with some additional data from
[12]). However, as sulfate expansion increases, the dynamic mod-
ulus of elasticity begins to decrease, indicating damage (micro
and macro cracks). The deterioration in laboratory and on-site
shotcrete starts at sulfate expansions beyond the limit for a high
sulfate resistance (1.0% according to SN EN 206-1). The criterion
originally was elaborated on conventional concrete [7]. In the case
of shotcrete generally higher binder volumes and smaller grain
sizes apply. Hence, the degree of internal constraint is lower for
shotcrete than for conventional concrete. Independent from this,
it is recommended to apply the stronger expansion criterion for
shotcrete as well, as bigger variations and local inhomogeneities
are much more probable during spraying than for casted concrete
and hence a more rigorous tolerance limit should apply for shot-
crete compared to conventional concrete.

The reproducibility of the new production method seems to be
somewhat lower than for real on-site shotcrete. Fig. 12 shows the
standard deviation of the final expansion for the six specimens of
a series after the 8 weeks of the storage in the sulfate solution.
The standard deviation for shotcrete produced with both methods
is significantly higher than for conventional concrete. For on-site
shotcrete this can be explained by the variation of the spray param-
eters and nozzle guidance during the spray process. In on-site shot-
crete application, compaction is done within seconds after the
addition of the accelerators at the nozzle by the impact of the shot-
crete on the rock. The high impact energy even leads to some mate-
rial rebound in the order of 10 to 20 mass-% of the shotcrete [21]
which also may lead to higher scatter than for conventional con-
crete. In the new method, the main problem related to reproducibil-
ity is thought to be related to the compaction method. As the
acceleration of the hydration upon the addition of the highly dosed
accelerators is very fast (within seconds), standard compaction
techniques such as compaction by vibration or shock table could
not be applied. However, the compaction by lifting the bucket is
not well defined in the new method and still may be too slow
regarding the fast action of the accelerators. Some additional de-
velopment regarding the compaction method may be necessary.

In general, the new production method delivers concrete that
shows similar properties, especially similar sulfate expansion as
observed for shotcrete produced on-site. The delivery mixture for
both methods is identically when using the same mixer. However,
the different compaction process, especially the difference in the
compaction energy, has an impact on the microstructure of the
material. The rebound of aggregates, preferentially the larger frac-
tions [21] as observed for on-site shotcrete is not depicted with the
new method, neither is the effect of the additional air that is added
for the (physical) acceleration of the concrete. This air widely is
pressed out of the material upon the impact, but may lead to some
additional large air pores in the hardened shotcrete. Due to the
lower compaction energy, some large air pores also are observed
for the shotcrete made with the new method. However, high sul-
fate swelling pressure is expected in the smaller capillary pores
only [11] that may explain the similarity of the measured sulfate
expansions of both production methods.

Furthermore, the layered structure of the on-site shotcrete,
resulting from its application in many rounds, is not reproduced
with the new method. Weak zones across the diameter of the sul-
fate resistance specimens might influence the sulfate expansion.
However, the sulfate expansion parallel to the application area
(perpendicular to the spray direction) is of most interest in practice
as this may lead to deformations and damage due to restraint. The
drilling of the samples for sulfate testing hence was perpendicular
to the shotcrete direction. This also leads to more uniform test
samples. Regarding the possible sulfate expansions parallel to the
spray direction, higher expansions and a higher risk for local dete-
rioration (spalling) are expected for on-site shotcrete. Such param-
eters and variation were not studied. The materials produced with
the new method are uniform in all directions, so that possible lay-
ering effects cannot be reproduced. Although the new method is
not reflecting all aspects of real shotcrete, its simplicity and cost
efficiency may make it a useful decision making tool for the pro-
duction of samples for sulfate expansion tests.

5. Summary and conclusions

As shotcrete is often in direct contact with groundwater con-
taining sulfates, its resistance to sulfate attack is an important fac-
tor regarding its lifetime and durability. Testing of the sulfate
resistance of shotcrete requires the production of representative
samples, which have to be taken from shotcrete produced on-site
at full scale. On-site spray tests generally require large equipment
and space, hence are expensive, and time consuming. Therefore, it
is interesting to compare laboratory made shotcrete-analogue with
field shotcrete. A new production process in the laboratory, which
allows the use of practical formulations and high accelerator

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Fig. 11. Relation between sulfate expansion and change of the dynamic elastic modulus for on-site shotcrete (shotcrete) and its analogue produced in the laboratory applying the new method (laboratory) - additional data from [12] with crossed symbols.

Fig. 12. Standard deviation (in % of the mean value) of the measured sulfate expansion (6 samples) for different cement types and accelerator A2.

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[Note: The table and graph figures are not transcribed here, as the task requires natural text representation.]
dosages without high pressure spraying, is applied. The main difference to standard laboratory methods is in the way of the accelerator addition and the compaction of such fast hydrating concretes. This new method has the potential to be automated and standardized and could replace the time consuming and demanding large scale sample production for shotcrete testing in general.

In the presented work, shotcretes (sprayed concretes) with alkali-free accelerators based on aluminum and sulfate compounds in combination with blended cements (CEM II/B-M, CEM III/B) were produced by both the laboratory method and on-site under full-scale conditions. Their sulfate resistance and the phase assemblage was analyzed. For the laboratory produced shotcrete-analogue no significant difference from full-scale produced shotcrete was found with regard to the sulfate resistance. Only on concretes with silica fume added, and only when using condensed silica fume, the results were less comparable. Probably the different mixing conditions lead to a different particle dispersion and compaction characteristics and hence a lower sulfate resistance of the laboratory samples compared to the full-scale samples. In practice, silica fume often is added in the form of a suspension (slurry), as an uncompacted powder or as part of the cement (inter-grounded). It is expected that such kind of silica fume addition prevents from the observed particle dispersion effects.

For both, laboratory-prepared samples and real shotcrete, the cement type and the water/binder ratio w/b are decisive for the sulfate resistance. Furthermore, capillary porosity and the oxygen diffusion coefficient show cement-specific differences, and accordingly the sulfate solution uptakes vary in the same manner with cement type and the water to binder ratio w/b. The type of cement defines the potential for ettringite formation and thus the damage to the concrete and sulfate expansion is achieved by converting AFm phases (monocarbonate/hemicarbonate/monsolus phate) to ettringite. Hence, the resulting sulfate expansion of a concrete made of Ordinary Portland cement is generally higher compared to shotcrete made of cements containing supplementary cementitious materials (CEM II/B-M or CEM III/B). Especially the CEM III/B showed an excellent performance which can be explained by its development of very dense microstructure.

Judged on the similarity of the concrete properties, the chosen approach for sample production in the laboratory represents an efficient alternative for the analysis of laborious and expensive concretes with silica fume added, and only when using condensed silica fume, the results were less comparable. Probably the different mixing conditions lead to a different particle dispersion and compaction characteristics and hence a lower sulfate resistance of the laboratory samples compared to the full-scale samples. In practice, silica fume often is added in the form of a suspension (slurry), as an uncompacted powder or as part of the cement (inter-grounded). It is expected that such kind of silica fume addition prevents from the observed particle dispersion effects.

For both, laboratory-prepared samples and real shotcrete, the cement type and the water/binder ratio w/b are decisive for the sulfate resistance. Furthermore, capillary porosity and the oxygen diffusion coefficient show cement-specific differences, and accordingly the sulfate solution uptakes vary in the same manner with cement type and the water to binder ratio w/b. The type of cement defines the potential for ettringite formation and thus the damage to the concrete and sulfate expansion is achieved by converting AFm phases (monocarbonate/hemicarbonate/monsolus phate) to ettringite. Hence, the resulting sulfate expansion of a concrete made of Ordinary Portland cement is generally higher compared to shotcrete made of cements containing supplementary cementitious materials (CEM II/B-M or CEM III/B). Especially the CEM III/B showed an excellent performance which can be explained by its development of very dense microstructure.

Judged on the similarity of the concrete properties, the chosen approach for sample production in the laboratory represents an efficient alternative for the analysis of laborious and expensive production of shotcrete on-site. As such, it facilitates parametric studies and the optimization of mix design.

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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