Development of rapid set mortar for additive manufacturing

B Nespor¹, M Bohac¹ and M Nejedlík¹

¹Research Institute for Building Materials, Hnevkovskeho 65, Brno 61700, Czech Republic
Email: nespor@vustah.cz

Abstract. The study presents the development results of blended cement mortars for additive manufacturing. The goal was to achieve a balanced rheological behaviour of the fresh mixture through optimal granulometry, suitable grain shape and the choice of micro-admixtures. The article closely describes the granulometric and rheological characterization of the proposed ternary and quaternary blended mortar mixtures with various SCM’s. The print quality and shape stability of the promising mortars and the researched 3DP mixes were evaluated during incremental layering for comparison. The performed experiments confirmed that the mixtures containing blast furnace slag, quartz powder and metakaolin are more plastic and allow faster layering in height. The slaked lime-enriched mixture has excellent plasticity and is able to resist deformation during overlaying, the printed layers are without surface defects. The small addition of polypropylene fibre (0.08 wt.%) improves the plasticity and shape retention ability.

1. Introduction
Concrete is the single most widely used material in the world, after water, with a usage of about 13 billion tons per year. A primary reason for its popularity as a building material stems from the fact that it goes naturally from a fluid to a solid state – being able to flow and fill a mould, and upon hardening sustains a load. This gives great flexibility in terms of material handling and placement, something that has yet to be fully exploited in the world of digital fabrication [1].

Digitization of production is one of the pillars of the industry 4.0 initiative, which is considered the fourth industrial revolution. This includes 3D printing (3DP), a subset of digital fabrication, and a technology that is still at the nascent stage of realization in architecture and construction, notwithstanding the growing attention in recent years [2–6]. The future seems to be in the connection of 3D printing and so-called 4D materials, i.e. materials with properties that change depending on the change of boundary conditions (e.g. time, temperature, stress, dynamic effects, etc.), or digital materials to enable user programming of functional properties [7–8].

Cement mortars for 3DP technology have the potential to help the necessary digitization of construction industry and thus enable the unlimited implementation of computer-optimized designs of structure elements and buildings. In the future, it is possible to anticipate the gradual replacement of a significant part of current construction technologies by additive manufacturing. The 3DP technology or additive manufacturing or also incremental production technology is a relatively new, progressive, rapidly developing area of development in the construction industry in recent years. Additive manufacturing allows the creation of architectural models, building elements and buildings based on a digital design using a machine 3D printer. A suitable material is gradually applied by the printhead layer by layer. It is a computer-automated manufacturing process based on a 3D model.
This technology significantly speeds up construction, reduces labour costs and enables creation of a wide range of modern architectural works of any shape without restriction.

By using progressive cement-based binders with SCM’s (supplementary cementitious materials), CO₂ emissions and energy consumption in the production of Portland clinker can be reduced. A suitable ratio of ternary or quaternary binders can improve the granulometry of the densely filled polydisperse system, the rheology of the 3DP mortar and the printability interval. 3DP mortars should achieve relatively high flow limits and low plastic viscosities to achieve print quality and dimensional stability.

The use of recycled materials is also very promising, as they can make a significant contribution to saving raw materials and energy in conjunction with additive manufacturing technology. Utilization of the fine fraction of recycled material is often problematic and the use of recycled materials for additive manufacturing is a new solution for the recovery of this waste.

2. Experimental

2.1. Materials and methods

Limiting the use of chemical additives was a leitmotif in designing 3DP mixtures. The aim was to achieve a balanced rheological behaviour of the mortar mixture through optimal granulometry, suitable grain shape and the choice of micro-admixtures. The design of the composition of the quick-drying mortar mixture for 3D printing was based on a previous study; see Boháč et al [9], in which the role of various aggregates on the rheology of fresh 3D printing concrete was described. One of the key admixtures was the crushed recycled concrete from the recycling centre, which, with a suitable dose of fines, does not affect the plasticity of the mortar mixture, and at the same time, increases the required yield stress and adhesion of the fresh material.

The ternary blended binder of the reference mixture (TBM) is composed of Portland cement (C) CEM I 52.5 R (Cement Hranice), fly ash (FA) (Veolia Energie ČR, plant Přerov) and silica fume (SF) Elkem 971 (Elkem) in proportions 40:40:20 wt.%. Special quartz sand B30 (Tvarbet Moravia, sandpit Bzenec) of fraction below 1 mm with the fine fraction of recycled concrete aggregate (RCA) (Ditton) were used as aggregate. The unpolluted fine fraction of crushed RCA below 0.355 mm was used as a partial replacement (4 wt.%) for sand. The ratio of binder to aggregates was 1:1.7. Polycarboxylate superplasticizer (SP) Glenium ACE 446 (Basf) was used for all mixtures. The used water-binder ratio was 0.3 to 0.43 due to the use of fibre and concern for the various water demands of SCM’s.

3DP mortars from literature review – SM1–5 [10–14] (see table 1), differed in the ratio of ternary binders, mainly by the increasing amount of Portland clinker, but also by the proportion of binder to aggregate, the dose of mixing water and plasticizer, or the use of reinforcement. These compositions were slightly modified from the original. A fine fraction of RCA was used as a partial replacement (4 wt.%) for sand. To eliminate cracks caused by plastic shrinkage and plastic settling, the reference mixture was enriched with polypropylene fibres with a length of 3, 6 or 8 mm (PFRM 1–5).
Table 1. Mix design of printing mortars.

| Prescription | C | SCM | Aggregates | Reinforcement | SP | w/b |
|--------------|---|-----|------------|---------------|----|-----|
| **3DP mixtures from literature review** | | | | | | |
| TBM Bohac et al 2018 | 40 | 40 | 20 | 163.2 | 6.8 | 1.0 (b) | 0.3–0.4 |
| SM 1 Tay et al 2016 | 50 | 38 | 12 | 153.6 | 6.4 | 0.3 (b) | 0.4 |
| SM 2 Nerella et al 2019 | 55 | 30 | 15 | 172.8 | 7.2 | 2.0 (b) | 0.3 |
| SM 3 Nerella et al 2016 | 55 | 22 | 23 | 152.6 | 6.4 | 1.3 (b) | 0.3 |
| SM 4 Le et al 2012 | 70 | 20 | 10 | 144.0 | 6.0 | 0.15 (b) | 2.0 (b) | 0.28 |
| SM 5 Anell 2015 | 80 | 10 | 10 | 132.5 | 5.5 | 0.14 (b) | 1.4 (b) | 0.27 |
| **Fibre-reinforced mortars** | | | | | | |
| PFRM 1 | 40 | 40 | 20 | 163.2 | 6.8 | 0.08 (b) | 1 (b) | 0.37 |
| PFRM 2 | 40 | 40 | 20 | 163.2 | 6.8 | 0.08 (b) | 1 (b) | 0.40 |
| PFRM 3 | 40 | 40 | 20 | 163.2 | 6.8 | 0.08 (b) | 1 (b) | 0.39 |
| PFRM 4 | 40 | 40 | 20 | 163.2 | 6.8 | 0.15 (b) | 1 (b) | 0.43 |
| PFRM 5 | 50 | 12 | 38 | 170.9 | 7.1 | 0.14 (b) | 0.5 (b) | 0.40 |

The blended binder of the reference mortar was further modified with various admixtures. The main goal was to optimize print quality and shape stability of 3DP mixture and mainly to reduce the cost of the binder. Microsilica is replaced by ground granulated blast furnace slag SM Š 400 (BFS) (Cemix, plant Kotouč Štramberk), finely ground limestone (L) Vitošov 7000 (Vápenka Vitošov), metakaolin (MK) Mefisto K05 (České lupkové závody, plant Nové Strašeci), quartz powder (MD) Mikro-Dorsilít 120 (Gebrüder Dörflner). Different doses of slaked lime (SL) High purity lime (Research institute for building materials) were tested to improve plasticity. The mix designs QBM 1–7 are given in table 2.

Table 2. Mix design of quaternary blended cement mortars for 3D printing.

| Prescription | C | SCM | Aggregates | SP | w/b |
|--------------|---|-----|------------|----|-----|
| **QBM 1**   | 40 | 40 | 10 | 10 | 163.2 | 6.8 | 1 (b) | 0.4 |
| **QBM 2**   | 40 | 40 | 10 | 10 | 163.2 | 6.8 | 1 (b) | 0.30.4 |
| **QBM 3**   | 40 | 40 | 10 | 10 | 163.2 | 6.8 | 1 (b) | 0.4 |
| **QBM 4**   | 40 | 40 | 10 | 10 | 163.2 | 6.8 | 1 (b) | 0.3–0.4 |
| **QBM 5**   | 31 | 31 | 16 | 22 | 124.8 | 5.2 | 0.8 (b) | 0.64* |
| **QBM 6**   | 35 | 35 | 18 | 12 | 144.0 | 6.0 | 0.9 (b) | 0.59* |
| **QBM 7**   | 37 | 37 | 19 | 6 | 153.6 | 6.4 | 0.9 (b) | 0.55* |

* The water to binder ratio includes the water required for slaking of lime

2.2. Granulometric characterization

Coarse RCA was crushed and sieved to 0.355 mm (crushed RCA), the oversize fraction was grounded and sieved to 0.355 mm (ground RCA). The effect of preparation of RCA on the shape factor was observed with optical microscope Nikon Eclipse LV100ND in linearly polarized light at 500× magnification.

Particle size distribution (PSD) of cement, various SCM’s, sand, crushed and ground RCA was determined by a sieve analysis (above 0.4 mm) and CILAS 920 laser particle-size analyser with a range of 0.3–400 μm. Before the measurement, particles were dispersed in isopropyl alcohol using sonication for 60 seconds.

The optimal dose of selected microsilica substitutes was designed using Elkem Materials Mixture Analyzer (EMMA). Input data from PSD were uploaded into EMMA particle packing. The cumulative
PSD curves of the quaternary blended cement mortars were compared with the ideal grain size curve according to the modified Andreassen model for ideal packing density with the distribution coefficient 0.38 as in equation (1).

\[ CPFT = \frac{D_P^q - D_S^q}{D_L^q - D_S^q} \times 100 \]  

where, CPFT = the cumulative (volume) percent finer than, DP = the particle size, DS = smallest particle size, DL = largest particle size, \( q \) = the distribution coefficient or exponent.

The distribution coefficient (fine to coarse particle ratio) was proposed with concern for extrudability and shape-retention-ability of fresh mortars. Densely packed polydisperse systems have \( q = 0.2 \) – 0.4. If the exponent increases, it means an increase of the coarse materials, and if it decreases, the amount of the fine materials is increased [15]. Due to the slope of the cumulative curves of the studied mixtures, the distribution coefficient of 0.38 was chosen.

2.3. Rheological characterization
Each blended binder was thoroughly homogenized by a laboratory homogenizer for 30 minutes. Dry components (binder and aggregates) were dry-mixed for 2 minutes in the mixer, then water with superplasticizer was added and mixed for another 3 minutes.

Rheological characterization of mortars was carried out using a TA Instruments Discovery Hybrid Rheometer DHR-1 under standard laboratory conditions at 25°C. Flow characteristics were monitored in a range of 1–150 s\(^{-1}\) using the geometry of concentric cylinders (DIN). Yield stress and plastic viscosity were calculated from flow curves by Bingham model equation (2).

\[ \tau = \tau_0 + \eta \gamma \]  

where \( \tau \) = shear stress (Pa), \( \tau_0 \) = yield stress (Pa), \( \eta \) = viscosity (Pa.s), \( \gamma \) = shear rate (s\(^{-1}\)).

Thixotropy or rheopexy (time-dependent viscosity) were evaluated from hysteresis loops. All mixtures were pre-sheared at a constant shear rate of 10 s\(^{-1}\) for 10 s.

The shape stability of freshly printed mortars was simulated using a rheometer with parallel-plate geometry in the axial mode. The increase in axial force was monitored as the upper geometry approached. During one cycle, the geometry approaches 20 μm at a speed of 2 μm/s. The geometry approach was set in minute intervals. The number of cycles indicates stability when layering the material during 3D printing. More cycles mean less stability of the fresh mortar mixture.

Buildability (resistance to deformation) was assessed using a rheometer in oscillatory mode by amplitude sweep test in a log strain ramp from 0.001% to 1%, which was within the linear viscoelastic region (LVER). The LVER indicates the area in which the sample resists the applied deformation without destroying the structure. The LVER of storage modulus (\( G' \)) and loss modulus (\( G'' \)) was determined. The visco-elastic behaviour was characterized by the complex modulus (\( G^* \)), which is expressed by the vector sum of individual moduli (3).

\[ |G^*| = \sqrt{(G')^2 + (G'')^2} \]  

where: \( G^* = \) complex modulus, \( G' = \) storage modulus, \( G'' = \) loss modulus.

The physical stability of the samples was monitored using critical strain (\( \gamma_c \)), which determines the upper limit of the LVER. The critical strain can be read from the stress-strain curve as the onset of the decrease in complex modulus.

2.4. Technological tests
Technological tests were performed on the optimized mortars. Determination of normal consistency (paste without liquefaction agent) and determination of initial and final setting time of mortars (paste with 1% liquefaction agent) was performed using a penetration test (Vicat) according to EN 196-3.

The consistency of fresh mortar was determined by Haegerman flow table, using a prescribed metal cone after the prescribed number of vertical shocks, by measuring the diameter of the spilt test specimen according to ČSN 72 2441.
Determination of compressive strength, flexural strength, tensile splitting strength was performed according to EN 196-1 (at the age of 1, 2, 7, 28 and 90 days). Moisture content y and water absorptivity were determined according to ČSN 73 1316.

Durability was determined by a standard freeze-thaw resistance test according to ČSN 73 1322 and an accelerated durability test. The weather changes simulation involves the cyclical alternation of summer and winter dominant factors. The weather model is based on the long-term trend of climate development in the Czech Republic (1961–2021). One model year of external environment simulation consists of cyclic water sprinkling and drying by radiant heat drying by radiant heat (18 cycles) a freezing and thawing (1 cycle). The test specimens (20 × 20 × 100 mm) were subjected to water sprinkling for 170 min. There was a 10-minute delay after each sprinkling, followed by radiant heat stress using 2400 W.m^-2 IR lamps. The radiant heat was supplemented by xenon lamps, which supply a component of UV radiation with an output of about 200 W.m^-2. The surface temperature of the test specimens was about 70°C. The effect time of radiant heat and UV radiation was 170 minutes. There was a 10-minute break before the next water sprinkling cycle. After 18 cycles of the thunder-shower simulation, test specimens were saturated by water at a temperature of 20°C for 2 h. Subsequently, the samples were surface dried and frozen to -20°C for 2 h and then thawed in water (20°C) for another 2 h. After completion of weathering cycles, changes in mechanical properties of reference and cyclically stressed samples were evaluated.

Determination of volume changes was performed using the beam method according to ČSN 73 1320. The test specimens (40 × 40 × 160 mm) were fitted with metal targets. The longitudinal strain was determined according to the formula (4).

\[
\varepsilon_{s,n} = \frac{\Delta Z_n}{Z} \cdot 1000
\]

where: \(\varepsilon_{s,n}\) = longitudinal strain (mm/m), \(\Delta Z_n\) = change in length over original length (mm), \(Z\) = original length (mm). Changes in length were measured after demoulding (1, 4, 14, 36, 39 days) and after determination of freeze-thaw resistance (50, 75, 100 freezing cycles) using a calliper.

2.5. *Pilot plant experiments*

The pilot plant verification of the designed mortars was carried out by Construction 3D printer "AMT" S-6045. Numerous printing experiments were performed using a model design of a circle with a diameter of 500 mm. The material was printed at a speed of 100 mm/s through the print head with a diameter of 40 mm. The layer height was 10 mm. The dimensional conformity of the printed layer with the model 3D design (print quality) and the ability to resist deformations during overlaying (shape stability) were evaluated by optical observation. Surface defects and cracking were also monitored.

3. Result and discussion

3.1. *Granulometric characterization*

The effect of preparation of unpolluted coarse fraction of RCA on the particle size and shape factor is summarized in figure 1. RCA was ground by crushing and grinding to a very similar fineness. The RCA particles are often non-spherical or irregularly shaped and have various shapes, including a rectangle, ellipse, or random shapes with sharp edges. The granulometry of the two RCA is very similar and the particle size does not have to be differentiated when assessing the rheological properties.
Particle size distribution of dry mixtures was routinely carried out by a laser diffraction method. Cumulative PSD curves of the blended cement mortars were correlated with the ideal PSD curve. The effect of SCM’s microsilica substitutes on cumulative particle size curves was monitored, respectively how close it is to the ideal PSD curve. Microsilica was replaced with 5, 10 and 15% wt. of L, BFS, MK and MD. The optimal amount of all SCM’s was close to 10% wt., see figure 2. Compared to the ideal curve, the reference mortar TBM shows higher content of particles below 1 µm. All SCM’s improve PSD below 1 µm. BFS has slightly fewer particles in the range of 1 and 10 µm.

3.2. Rheological characterization
The effect of RCA preparation on flow properties of reference paste is minimal. Small differences are observable at the low shear rates (figure 3), where static yield stress values can be observed.
Figure 3. The effect of RCA preparation on flow properties of pastes, the low shear rates detail (right).

The samples with RCA have a lower requirement for mixing water compared to the reference paste without RCA. The measured rheological parameters also correspond to this (Table 3).

Table 3. The effect of RCA preparation on rheological parameters.

| Cement paste   | Static yield stress (Pa) | Dynamic yield stress (Pa) | Plastic viscosity (Pa.s) | Thixotropy (Pa.s) |
|----------------|--------------------------|---------------------------|--------------------------|-------------------|
| Reference paste| 21.99                    | 11.75                     | 1.158                    | 1204              |
| Crushed RCA    | 9.99                     | 7.15                      | 0.97                     | 566               |
| Ground RCA     | 8.69                     | 6.05                      | 0.89                     | 594               |

Fresh mortar mixture for additive manufacturing should have relatively high yield stress and a low value of plastic viscosity. The time-dependent thixotropy is important for this application in terms of gradual layering. A low value of plastic viscosity is necessary due to good pumpability. Yield stress and thixotropy in turn for shape-retention-ability during the next layering. The effect of SCM’s on flow and time-dependent rheological properties after 10 and 30 minutes from the addition of water, as depicted in figure 4.

The mixture with ground limestone is liquid and does not hold its shape. The rheological parameters practically do not change during the first 30 minutes. In contrast to the reference mixture, limestone inappropriately decreases the yield stress of the fresh mixture. The mixture with MK has a significantly higher value of plastic viscosity, which indicates a possible problem with pumpability. The mixture is very plastic and holds the shape well. The fresh mixture has higher water required to achieve the same consistency as the reference mixture. The value of thixotropy decreases with time.

BFS has very similar values as the verified reference mixture, only it has lower values of thixotropy. After 30 minutes, the plastic viscosity value increases, this could lead to pumpability problems. These characteristics can be modified with chemical additives.

The mixture with MD has lower yield stress and a higher plastic viscosity in comparison to the reference mixture. Mikro-Dorsilit is an economically advantageous substitute for microsilica. Rheological properties can be further balanced using chemical additives.
Figure 4. Flow and time-dependent rheological properties of blended cement mortars with 10% replacement of the microsilica by SCM’s, 10 (left) and 30 (right) minutes after addition of water.

The effect of SCM’s on the shape stability and buildability of fresh mortars was studied using an axial squeeze test, see figure 5. Mixtures with a steep increase in axial force are less plastic and therefore more stable during layering. Mixtures containing MK and MD showed the best values of shape stability. The mixture with L and the reference mixture are significantly less plastic than these mixtures. Therefore, it can be assumed that the mixtures containing MK and MD allow faster layering and the possibility of layering in height.

Figure 5. The effect of SCM’s on shape stability and buildability of fresh mortars during layering.

The effect of SCM’s on the rheological stability of fresh mortars was investigated using an amplitude sweep test. The viscoelastic behaviour of mortar mixtures was observed after 10 and 30 minutes after the addition of water. To determine the linear viscoelastic region over which the samples resist the applied deformation, the complex modulus was plotted against the strain amplitude, as depicted in figure 6. The linearity limit or critical strain is characterized as the endpoint of the LVER or also as the onset decrease in the complex modulus. The value of the upper limit of the LVER tends to proportionally correlate with rheological stability. Longer LVER suggest more physical stability of the sample.
Figure 6. The effect of SCM’s on rheological stability of fresh mortars.

The LVER for reference and quaternary blended mortars are very similar. Relatively greater suspension stability can be described for the mixture with MD. The critical strain values after 30 min are lower than after 10 min of hydration, see table 4. In exclusion of the mixture with BFS, a good correlation between critical strain and shape stability results can be observed.

Table 4. The effect of SCM’s on critical strain (physical stability).

| Critical strain γc (%) | TBM ref | QBM 1 10% L | QBM 2 10% BFS | QBM 3 10% MK | QBM 4 10% MD |
|-----------------------|---------|-------------|--------------|-------------|-------------|
| γc 10 min             | 0.042   | 0.041       | 0.034        | 0.048       | 0.066       |
| γc 30 min             | 0.031   | 0.03        | 0.02         | 0.032       | 0.045       |

3.3. Technological tests

The results of determining the technological properties of reference and quaternary blended mortars are summarized in table 5. Normal consistency and setting times were determined by penetration tests. The initial setting time of the mixed cement pastes of normal consistency did not occur earlier than 4.5 hours, the final setting time in 6.5 hours and the case of the mixture with MD in 7.5 hours. To test the consistency of the fresh mixes and to monitor the development of the strength of the cured mortars, the water coefficient was adjusted individually for each mixture so that the quaternary blended cement mortars achieved a similar consistency to the reference mix. The reference mixture had the highest water requirements (w = 0.28). The mixtures containing L, BFS, MK had a lower water-binner coefficient (w = 0.265). The least water (w = 0.255) was used for the mixture with MD. All mortars had a diameter of the slumped cone after shocking of 110 mm on the flow table before and 180 mm after shocking with 15 shocks. Individual diameter in flow table tests did not differ by more than ± 15 mm. All tested specimens showed excellent strength characteristics. SCM’s as a partial replacement (10 wt.%) for microsilica does not have an adverse effect on strength development. Mixtures with L and MK show similar strengths to the reference mixture; however, MK does not have such strength development after 28 days of curing. The mixture with BFS and especially with MD achieves the highest strengths.
Table 5. Technological properties of ternary (reference) and quaternary blended mortars.

|                | Normal consistency (%) | Setting times (min) | Flexural and Compressive strengths (MPa) |
|----------------|-------------------------|---------------------|-----------------------------------------|
|                |                         | Initial Final       | 1 day | 2 days | 7 days | 28 days | 90 days |
| TBM            | 47.5                    | 270 410             | 3.6   | 21.2   | 4.7    | 30.7    | 6.1     | 56.4    | 9.7     | 84.9    | 11.4    | 100.9   |
| QBM 1          | 40.5                    | 270 410             | 4.2   | 22.4   | 4.6    | 32.0    | 6.4     | 57.8    | 7.8     | 81.8    | 11.8    | 102.4   |
| QBM 2          | 39.0                    | 330 400             | 4.6   | 23.6   | 5.1    | 36.8    | 8.6     | 62.3    | 9.8     | 92.5    | 8.7     | 110.4   |
| QBM 3          | 47.5                    | 290 410             | 4.4   | 21.1   | 5.0    | 32.6    | 7.0     | 57.9    | 7.0     | 77.6    | 5.7     | 92.3    |
| QBM 4          | 43.5                    | 320 450             | 4.9   | 25.2   | 4.8    | 37.6    | 4.1     | 64.2    | 12.1    | 100.2   | 13.7    | 114.6   |

The physical properties of selected promising 3DP mixtures for additive manufacturing are summarized in figure 7. These are ternary (modified with PP fibres) and quaternary blended mortars, which have been used in pilot plant experiments. 3DP mortars showed relatively good strength characteristics. The fibre reinforced reference composition and the mixture with BFS and MD averaged compressive strengths of around 40 MPa and flexural strength of 5.5 MPa. The larger amount of fibre, as well as lime, did not have a significant effect on the strengths. The lime enriched mixtures exhibited higher water absorption and lower compressive and flexural strengths of 26 MPa and 4 MPa, respectively.

Figure 7. Physical properties of selected samples of 3DP mortars.

Durability was assessed using the frost resistance test and the accelerated durability test. Changes in the length of 3DP mortars during wet curing and after freezing cycles were continuously measured. These tests were performed on the reference and slaked lime-modified mortars. The impact of freeze-thaw cycles and also weathering changes on the physical properties of 3DP mixtures are presented in tables 6, 7 and figure 8.

During moisture curing, the longitudinal strain was very low in both samples. Comparative (unloaded) specimens of slaked lime-modified mortar had about one-third lower strengths compared to the reference mortar and also higher absorption.

The tested samples are not frost-resistant, the frost resistance coefficient decreased under the value of 0.75. The slaked lime-modified mortar had significantly lower compressive strength and especially flexural strength after freeze-thaw cycles compared to the reference mixture. The sample with SL shows enormous longitudinal strain compared to reference mortar after freeze-thaw cycles.
**Table 6.** The impact of freeze-thaw cycles on physical properties of selected promising 3DP mixtures.

| Freeze-thaw resistance | TBM ref | QBM 7 6% SL |
|------------------------|---------|-------------|
|                        | 28 days | 50 | 75 | 100 | 28 days | 50 | 75 | 100 |
|                        | moist freeze-thaw cycles | moist freeze-thaw cycles |
| Compressive strength (MPa) | 60.0 | 53.4 | 51.5 | 56.0 | 44.0 | 35.7 | 23.8 | 21.4 |
| Flexural strength (MPa) | 9.0 | 5.9 | 5.0 | 5.4 | 7.4 | 1.8 | 0.4 | 1.0 |
| Bulk density (kg.m\(^3\)) | 2060 | 2060 | 2050 | 2060 | 1980 | 2010 | 1990 | 2010 |
| Water absorption (%) | 12.1 | 12.7 | 12.7 | 12.1 | 17.0 | 18.3 | 19.6 | 19.1 |
| Coefficient of frost resistance | - | 0.65 | 0.56 | 0.60 | - | 0.24 | 0.05 | 0.14 |

**Table 7.** The volume changes of reference and modified 3DP mortar.

| Linear strain (mm/m) | 4 days moisture curing | 14 days moisture curing | 36 days moisture curing | 3 days water curing | 50 | 75 | 100 |
|----------------------|-------------------------|-------------------------|-------------------------|---------------------|-----|-----|-----|
| TBM ref | -0.02 | 0.00 | 0.02 | 0.06 | -0.42 | -0.11 | 0.69 |
| QBM 7 6% SL | -0.04 | -0.02 | -0.08 | -0.06 | 2.93 | 5.63 | 14.69 |

The reference mixture had relatively good durability. After 20 years of weather changes simulation, a 4% loss in compressive strength and a 16% increase in flexural strength was observed. After 20 simulation cycles, the modified mortar had a strength of about one-fifth in both compression and flexure. The values of absorption and bulk density did not change.

**Figure 8.** The impact of weathering changes on physical properties of reference and modified mortars.

### 3.4. Pilot plant experiments

Additive technology on ternary and quaternary blended mortars for 3D printing was verified using a 3D concrete printer. At the first stage, several printing trials of the TBM reference mixtures were carried out. To achieve a satisfactory print quality and shape stability, the water-binder ratio of 0.37 was used. The plastic shrinkage and settling resulted in the formation of cutting cracks through the profile of the printed sample.

Search 3DP mortars (SM) and fibre-reinforced reference mixture (PFRM) were further tested to eliminate cracks or rather for practical comparison with the reference mixture. SM 1 and SM 3 formulations showed excellent print quality and dimensional stability. The fresh mortars had very good viscoelastic properties necessary for additive manufacturing. However, during the setting and hardening of the printed mortars, several cutting cracks were observed. The SM 2 mixture had relatively good print quality and shape stability, showing no surface defects or cracks. SM 4 and SM 5 mixtures with a high cement content inappropriately reduced the yield stress. These mortars had a relatively high content of plasticizing admixture, despite a very low water-binder ratio and the presence of 8 mm polypropylene...
fibres; they were very fluid and did not keep their shape. The rheological parameters of these mixtures are incompatible with additive manufacturing. The formation of cracks on 3DP mortars was successfully eliminated by wetting the printed layers with water mist during the dormant phase of hydration.

Excellent print quality and dimensional stability can be observed in the fibre-reinforced mixtures TBFRM 1 and TBFRM2. The small addition of 3 and 6 mm polypropylene fibre (max 0.08% wt. binder) did not affect the yield stress and improved the plasticity of the mixture. Longer fibres or higher fibre content significantly increased the plasticity of TBFRM 3–5 mixtures. The material was sticking on the worm shaft and also in the funnel. The material was very difficult to push through the print head.

Based on the granulometric and rheological characterization of quaternary blended cement mortars with SCM’, prospective modifications of the reference mixture were selected. Specifically, these were mixtures with BFS and MD that exhibited suitable yield stress and thixotropy values similar to the reference mixture. Different doses of slaked lime were additionally tested to improve plasticity. The mixtures QBM 2 and QBM 4 did not improve the rheological parameters of the reference 3DP mortar. These blends with BFS and MD were more fluid and did not keep the print shape. The individual layers tended to flow. A slight reduction in the water-binder ratio already resulted in a loss of print quality and surface defects. In contrast, slaked lime-modified mortar QBM 7 achieved optimum print quality and dimensional stability. SL as a partial replacement (max 6 wt. %) for microsilica has a positive effect on the plasticity and workability of the reference mortar. The mixture with SL was able to resist deformation during overlaying, the printed layers were free of surface defects, and the edges of each layer were visible and dimensionally consistent.

4. Conclusions

In this study, several blended cement mortars for additive manufacturing were experimentally verified. The effect of RCA preparation as well as various SCM’s on the granulometric and rheological or physical properties was investigated. The pilot plant verification of the designed mortars was carried out by a construction 3D printer. The dimensional conformity of the printed layer with the model design as well as the ability to resist deformations during overlaying, surface defects and also cracking were monitored and evaluated. The following conclusions can be drawn:

(1) The preparation effect of the unpolluted coarse fraction of RCA on the granulometric and rheological properties was negligible. The granulometry of the crushed or ground RCA was very similar. The effect of RCA preparation on flow properties of reference paste is minimal. The samples with RCA have a lower requirement for mixing water compared to the reference paste without RCA.

(2) The effect of SCM’s substitution (10 wt. %) for microsilica on the flow and time-dependent rheological parameters of fresh mixtures was significant. Quaternary blended mortar with BFS has very similar properties as the reference mixture, only it has lower values of thixotropy. The mixture with MD has lower yield stress and a higher plastic viscosity in comparison to the reference mixture. Ground limestone and metakaolin are not suitable substitutes for silica. Ground limestone inappropriately decreases the yield stress of the fresh mixture. The mixture with L is liquid and does not hold its shape. The mixture with MK has a significantly higher value of plastic viscosity, which indicates a possible problem with pumpability.

The effect of SCM’s on the shape stability and buildability of fresh mortars was noticeable. Mixtures containing BFS, MD and MK were more plastic and it can be assumed that these mixtures allow faster layering and the possibility of layering in height. The mixture with L and especially the reference mixture are significantly more malleable and the possibility of layering in height is thus reduced. All SCM’s had minimal influence on the rheological stability. The reference mortar and mixtures with SCM’ have a very similar linear viscoelastic region in which they resist the applied deformation without destroying the structure.

(3) SCM’s as a partial replacement for microsilica does not have an adverse effect on the strength development. The larger amount of fibre, as well as lime, did not have a significant effect on the strengths. Samples with BFS and MD and also fibre reinforced mortar achieved the highest strengths around 40 MPa and flexural strength of 5.5 MPa. The lime enriched mixtures exhibited higher water absorption and lower compressive and flexural strengths of 26 MPa and 4 MPa, respectively.
(4) Neither reference mortar nor slaked lime-modified mortars are frost-resistant. The slaked lime-modified mortar had significantly lower compressive strength and especially flexural strength after freeze-thaw cycles compared to the reference mixture. The longitudinal strain strength after freeze-thaw cycles was enormous. After 20 years of weather changes simulation, the modified mortar had the strength of about one-fifth in both compression and flexure. In contrast, the reference mortar had very good durability and hardly changed strength.

(5) Reference 3DP mortar TBM by Boháč et al [9] was relatively well designed. The mortar mixture had a balanced rheological behaviour without the use of chemical additives such as viscosity modifying agents, retarders and accelerators. The printed mixture followed the contours of the circle according to the design model and resisted deformation during overlaying. Three layers were printed in 45 seconds. The printed layers exhibited minor aesthetic defects caused by shear forces that occur during extrusion when the material is stressed by compression and shear. The plastic shrinkage and settling resulted in the formation of cutting cracks through the profile of the printed sample. The formation of cracks was eliminated by wetting the printed layers with water mist during the dormant phase of hydration.

Search 3DP mixtures SM 1 by Tay et al [10] and SM 2 and 3 by Nerella et al [11, 12] showed excellent print quality and shape stability, the printed layers were without significant surface defects. The fresh mortars had suitable rheological parameters required for additive manufacturing. The increased amount of Portland clinker in the binder (up to 55 wt. %) had a positive effect on the extrudability, shape stability and adhesion of the fresh mortar. In contrast, the SM 4–5 mixtures by Le et al and also Anell [13, 14] with high cement content were highly liquefied after printing and did not hold their shape. The low yield stress was probably due to the increased dose of superplasticizer. Le et al also used a longer 12 mm fibre and printed the mixture through a 9 mm diameter nozzle.

Fibre-reinforced reference mixtures PFRM 1 and 2 showed an exemplary print quality and shape stability similar to searched 3DP mortars. A small addition of 3 and 6 mm polypropylene fibre (max 0.08% wt. binder) improved the plasticity and shape retention ability of the reference mixture. Longer fibres or higher fibre content significantly increased the plasticity of the mixtures.

Slaked lime-modified mortar QBM 7 achieves optimum print quality and shape stability. Slaked lime as a partial replacement (max 6 wt. %) for microsilica has a positive effect on the plasticity and workability of the reference mortar. The modified mortar was able to resist deformation during overlaying, the printed layers were without surface defects, and the edges of the layers were visible and dimensionally identical.

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