Drying and shrinkage of cement paste for 3D printable concrete

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Abstract. The article presents the results of the study of drying and shrinkage of three compositions of cement paste different in the content of microsilica and superplasticiser within the range of variation typical for 3D printable concrete compositions. Plate samples kept in the environment with RH = 20, 30, 50, 70 % were used to simulate different drying conditions of material in thin layers of 3D printing structures. Rates of mass loss and shrinkage of hardened cement paste are compared with criterial parameters of their structure. It is shown that increased dosage of microsilica and superplasticiser ensures the reduction of total volume of pores, increase of the content of nanopores, while simultaneously the area and energy activity of solid phase surface increases. These factors secure the ability of cement paste to better retain the water in the structure under all drying conditions. As a result, reduction of absolute values of mass loss by 3 - 4 times and shrinkage by 2 times in comparison with reference system is ensured for cement paste with maximally dense structure. At the same time, there is a twofold increase of relative deformability on each percent of mass loss, which may lead to significant tension in 3D printing structures due to moisture gradient.

1. Introduction

3D concrete printing (3DCP) is one of the emerging technologies that can minimize the supply chain in the construction process by automatically producing building components directly from digital model without human intervention and complex formwork. Potential advantages of this process include ability to get multicomponent materials of different functionality directly on the construction site, to print the freeform constructions without formwork, to reduce materials consumption and building work content [1 - 3]. One of the most complex problems in the implementation of the abilities of 3D printing in different fields of construction is the problem of creating mixtures with functional characteristics that correspond to their using. Active development of the research has allowed achieving quite a wide range of effective mixtures for 3D printable concrete. When it comes to optimisation of mixture compositions, researchers usually focus their attention on such issues as rheological behaviour, extrudability, buildability and structural build-up of concrete [4 - 18]. However, the problems of 3D printable concrete behaviour during working-time remain unexplored. The problem of drying shrinkage may be one of the most significant among them, since intensive drying of the material may take place in the thin layers of 3D printing structures and lead to formation of cracks in the structures.

As a rule, high-performance printing concrete is obtained from low water/cement ratio (0.2 - 0.3), efficient plasticisers, ultradisperse fillers (microsilica and nanosilica, metakaolin, etc.), which allow forming solid high-density structure of composites. The experience of studying similar high-
performance cement-based materials has shown [19 - 26] that the process of their shrinkage is different from the development of shrinkage of ordinary cement-based materials. This article is dedicated to the study of processes of drying and shrinkage of high-performance cement paste in the conditions simulating drying in 3D printing structures and correlation of characteristics of these processes with parameters of material structure.

2. Theoretical framework
Drying shrinkage of cement-based materials is defined by joint impact of various types of water differing in connection strength with the structure on its development. According to the existing perceptions [27 - 30], it is supposed that at the initial stage of drying in the range of relative humidity of the environment RH = 80 – 95 % capillary water is removed from large pores r > 100 nm. Capillary pressure in these pores is relatively low, thus the values of shrinkage stress and deformations are small. When RH decreases in the range from 80 to 40 %, water is removed from the pores in radius of 20 nm < r < 100 nm, at the same time the value of capillary pressure grows and, correspondingly, drying shrinkage increases. After capillary water is removed from the pores, adsorption water is removed from the surface of solid phase (RH < 40 %). It is known that adsorption water compensates for a part of excess surface energy of solid phase. In the process of desorption solid phase particles begin to be affected by growing forces of surface tension, for which reason their volume reduces.

The value of drying shrinkage of the material is defined by the level of drying which depends on humidity of environment and structure’s ability to retain water. The latter is determined by quantitative ratio of different types of water in the material. This ratio depends on the following parameters of cement-based materials structure:

- volume and structure of hard phase, as its surface area and surface energy determine the effect of contraction forces when adsorption water is removed;
- volume and size of pores defining the value of capillary forces.

High-performance printing concrete usually has high-density fine-dispersed structure different from the structure of ordinary cement-based materials in characteristics criterial for the development of shrinkage. Therefore, comprehensive study and comparison of the structure and parameters of moisture shrinkage of cement paste as a shrinkage carrier in cement structure is required for predicting operational deformative behaviour of high-performance printing concrete.

3. Experimental programme and methods

3.1. Materials and mix design
Portland cement CEM I 52.5, microsilica (specific surface 24500 m²/kg, SiO₂ content ~ 70%); superplasticiser (SP) of trademark Sika ViscoCrete 20HE based on polycarboxylic ethers were used to produce the samples of cement paste.

Ordinary cement paste (Table 1) of reference content and high-performance cement pastes of MB-8 and MB-30 series were studied. The change of structure of high-performance cement pastes was ensured by variation of the dosage of microsilica and plasticiser. Consistence of cement paste was assumed as a fixed factor for the experiments (slump 180 mm for other compositions).

| Material         | Mass/ mass cement loss Control | MB-8 | MB-30 |
|------------------|--------------------------------|------|-------|
| Cement           | 1.0                            | 1.0  | 1.0   |
| Microsilica      | -                              | 0.08 | 0.3   |
| Plasticiser      | -                              | 0.005| 0.018 |
| Water/cement ratio | 0.40                          | 0.34 | 0.24  |
3.2. Experimental procedures

Sample plates 10 × 40 × 160 mm in size dry in the environments with different humidity were used in assessment of deformations and mass loss to simulate humidity conditions of material usage in thin layers of 3D printing structures. Series of cement paste samples (6 in each series) were produced for experimental research from one batch of each of the studied mixtures. Series of cement paste samples hardened during 24 hours in moulds. Then the samples were put in dessicators above saturated salt solutions with humidity RH = 20; 30; 50; 70 %. Maturing in dessicators was carried out with constant temperature (20 ± 2)°C until stabilisation of their mass and linear dimensions. Deformations were determined by a comparator with indicating gage with division value of 0.01 mm. Mass and sizes were monitored within 1, 3, 7, 14, 28 days since the moment of placement into dessicators and then after every 14 days. Sample weighing error accounted for ± 0.1 g, error of sample length change accounted for ± 5 µm. Within-run variability ratio in assessment of deformations and moisture losses accounted for 8 - 10%.

Simultaneously, structural characteristics of cement paste were monitored. Assessment of specific surface, total volume of pores as well as the volume of pores in radius of less than 20 nm (this radius is considered to be the border of effect of capillary forces) of cement paste was carried out through four-point nitrogen adsorption BET method on SoftSorbi-II ver.1. Surface energy of hard phase was estimated by calorimetric method by heat of wetting the prepared sample of cement paste at t = 20°C in Calvet calorimeter C80 using mixing cell with circulation. Phase composition of cement paste was controlled by X-ray diffraction method (CuKα radiation, λ = 1.541788 Å, diffractometer ARL X'TRA). At the same time the degree of cement hydration in the content of alite phase was evaluated. Scanning probe microscope JEOL JSM-7001F was used to assess the morphology of cement paste structure.

4. Experimental results and discussion

4.1. Structural characteristics

Combined application of microsilica and superplasticiser additives results in the change of hardened cement paste structure by parameters the values of which are presented in table 2. The thickest structure is typical for MB-30 system. Total volume of pores in cement paste structure is characterised by minimal values of the volume of pores (0.24 m³/m³) with up to 60 % of pores in radius of less than 20 nm from their total volume; specific area of the surface reaches maximum value of 51.3 m²/g for the studied systems. MB-8 system containing small amounts of microsilica and plasticiser is similar to control system in the values of density and porosity and to MB-30 system in the values of specific area of solid phase surface. Such change of parameters of solid phase and porosity is naturally caused by parameters of the cement substance of the studied systems. Morphology of the particles of the studied systems is evaluated according to the data of electronic microscopy (Figure 1).

| structural characteristics | control | MB-8 | MB-30 |
|----------------------------|--------|------|-------|
| Density, kg/m³             | 1680   | 1850 | 1970  |
| Total volume of pores, m³/m³| 0.34   | 0.33 | 0.24  |
| Content of pores in radius r, in % of total volume of pores | | |
| r < 20 nm                  | 24     | 53   | 60    |
| r > 20 nm                  | 76     | 47   | 40    |
| Total specific surface of solid phase of the material, m²/g | 29.1   | 49.4 | 51.3  |
| Heat of wetting of solid phase of the material, kJ/kg | 15.2   | 27.1 | 31.2  |
| Characteristic of intensity of diffraction maximums | | |
| d = 4.86 Å, for Ca(OH)₂ | 1265   | 746  | 496   |
| d = 1.76 Å, for C₃S      | 65     | 116  | 100   |
| Hydration degree, %       | 82     | 78   | 64    |
In the formed structure of hardened cement paste there is mostly C-S-H gel of amorphocrystaline morphology. However, the size of the particles of new developing formations in systems MB-8 and MB-30 is significantly smaller than in the control system. The smallest size of particles of C-S-H gel and the densest packaging are typical for MB-30 system. A significant number of plate crystals of Ca(OH)$_2$ is recorded only in the control system. According to the results of X-ray phase analysis (Table 2), it has been established that in systems MB-8 and MB-30 the intensity of diffraction maximums typical for crystals of Ca(OH)$_2$ decreases by 3 - 4 times as related to the control system. The samples of MB-8 and MB-30 series are characterised by high density and extremely low free volume of pores for the development of structure formation processes. Therefore, for them the degree of cement hydration at 28-day age is characterised by lower values than in check samples. It was this transformation of structural characteristics of cement paste that determined the change of energy potential of the surface of hard phase and pore volume. Also, almost twice as higher energy activity of solid phase surface is typical for MB-8 and MB-30 systems. Specific heat of wetting reaches 27 - 31 kJ/kg as against 15.2 kJ/kg in the control system.

4.2. Drying and shrinkage

Our experiments have determined that drying and shrinkage process is directly related to characteristics of the composition and structure of the studied systems. Significant differences in density and porosity, in surface area and solid phase energy have shown that the value of mass loss for the cement paste of the studied series differs approximately by 3 - 5 times (Figure 2) while the value of deformations differs approximately by 2 - 3 times (Figure 3) under different drying conditions.
Figure 3. Drying shrinkage of cement paste under different drying conditions

On drying in the environments with RH = 50% and RH = 70%, where adsorption water is almost not removed, the difference in the values of mass loss of ordinary (control) and high-performance (MB-8 and MB-30) cement paste is especially notable and can reach almost a fivefold value (Figure 3). For instance, moisture loss on dehydration of the control series samples in the environment with RH = 70% accounts for 5.6% by mass, while in the samples of MB-8 and MB-30 series the losses are 3.6% and 1.1% correspondingly. The value of shrinkage of the control system in the environment with RH = 70% where mostly capillary water is removed already reaches 800 μm/m at the early stage of drying. By the end of 28 days the deformation of control cement paste exceeded the shrinkage in systems MB-8 and MB-30 almost threefold, total shrinkage is twice different. The obtained data on the difference in the processes of drying and shrinkage of the samples of the studied series are explained by the difference in binding force of the material and water. Higher values of binding forces of the material and water which retain the water in the structure correspond to the higher values of specific surface and surface energy of solid phase as well as to the smaller radius of pores. As a result, a considerable part of liquid stage happens to be adsorption-related, and the transfer of moisture in high-performance cement paste can be mainly determined by diffusion of adsorbed molecules on the solid phase surface. So, under the drying conditions in thin layers with normal operating humidity the structure of high-performance cement paste can retain moisture better and resist the growth of deformations.

In the environments with RH = 20, 30% when not only capillary, but also adsorption water is removed, deep dehydration is typical for the samples of MB-8 and MB-30 series. For these series the value of mass loss with RH = 20% is 3-5 times higher than with dehydration of RH=70%. The difference in mass loss when drying in the environments with RH = 20% and RH = 70% is only twice for the samples of the control series.

Minimal values of shrinkage are noticed for MB-30 system. This system with the largest content of microsilica and SP is characterized by the highest value of specific area and surface energy of solid phase, low porosity and predominance of nanopores r < 20 nm in the total volume of pores. As a result, this does not only prevent from removing water, but also facilitates the reduction of deformation value under all drying conditions. That said, under the change in humidity in the range of RH from 70% to 20% total shrinkage increases by 3.5 times for MB-8, by 2.3 times for the control composition, and by 2.6 times for MB-30 system.

For high-performance cement pastes of MB-8 series in the environments with RH = 20, 30, 50% the value of drying shrinkage almost corresponds to the deformations of cement paste of the control composition. Only in the environment with RH = 70% the value of deformations in MB-8 system is significantly lower than the shrinkage of control series samples. Increased deformability of MB-8 sys-
tem can be conditioned by the following. This system is characterised by the values of area and surface energy of solid phase and relative content of nanopores comparable with MB-30 system. This happens to be the predominant factor of the reduction of deformation value in the environment with RH = 70 % when capillary water is removed. At the same time, MB-8 system is similar to the control one by the value of pore volume, therefore the effect of non-compensated surface forces acts as a factor of deformation growth with removal of water from smaller and smaller pores when drying in the environments with RH = 20, 30, 50%.

So, parameters of the structure of high-performance cement pastes of MB-8 and MB-30 series predetermined the reduction of mass loss when drying by 3 - 4 times as compared to control ordinary cement paste and reduction of shrinkage by 2 times.

4.3. Coefficient of linear shrinkage

Coefficient of linear shrinkage ($\beta$) was used for quantitative criterion evaluation of the value of shrinkage of cement pastes. This relative value physically represents a ratio of material deformations $\varepsilon$ ($\mu$m/$\mu$m) to the measurement unit of its moisture content $\Delta W$ (g/g). Coefficient of linear shrinkage is graphically interpreted as slope ratio of shrinkage curve to the axis of its moisture content change (Figure 4). This index allows quantitatively evaluating the ratio of mass loss value to material shrinkage and can be used for predicting shrinkage stress in the cement volume with humidity gradients.

![Figure 4](image-url)

**Figure 4.** Dependence on drying shrinkage of cement paste on mass losses.

After summarising the aggregate data on the values of moisture shrinkage and moisture losses of cement paste of the studies series with dehydration in the environments with RH = 20, 30, 50,70 %, the design value of coefficient of linear shrinkage accounted for:

- $\beta_{\text{control}} = 0.017$,
- $\beta_{\text{MB-8}} = 0.032$,
- $\beta_{\text{MB-30}} = 0.036$. 
So, relative deformability of high-performance cement pastes happened to be twice higher than in ordinary cement paste. This proves the proposed assumption of the increase of binding force of the structure with water for high-performance cement pastes in relation with the increase of content of nanopores $r < 20 \text{ nm}$, increased dispersion, area, and energy activity of the solid phase surface.

5. Conclusion

Joint employment of microsilica and superplasticiser typical for obtaining high-performance printing concrete is accompanied by significant change of structural characteristics criterial for moisture shrinkage. Total porosity is reduced almost by 1.5 times while the content of pores in radius of less than 20 nm is increased (up to 60 % of total volume); specific surface area and surface energy of solid phase increases almost twice.

Structural changes happen to be a growth factor for the binding force of structure with water. For high-performance cement paste as compared to ordinary cement paste, total reduction of moisture losses when drying reaches a three-fourfold value. And this is a positive factor for the hardening of material in thin layers of 3D printing structures as it helps to preserve moisture for hydration and hardening. If an optimal high-density structure is created, cement paste shrinkage may be reduced twice.

At the same time, quantitative criterial evaluation of deformability potential of cement paste by the coefficient of linear shrinkage $\beta$ has shown that the value of shrinkage for high-performance cement paste under the change of moisture content by 1 % will be twice higher than shrinkage of ordinary cement paste. As a result, the level of internal stresses in thin layers of 3D printing structures may significantly rise even when operating moisture content is slightly changed. Therefore, when it comes to high-performance printing concrete, drying shrinkage can make considerable contribution to the development of stresses in constructions under cyclical moistening-drying during the whole period of operation.

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