Effect of Limestone Filler Dosage and Granulometry on the 3D printable Mixture Rheology

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Abstract. The article presents the experimental results concerning the influence of the concentration and a particle size distribution of limestone filler on the rheological behaviour of cement pastes as matrixes of 3D printable concrete. The squeezing test is used in this paper as a rheological behaviour identification tool of cement-based materials in order to evaluate the extrudability and buildability. It has been established that introduction of filler as a factor changing the properties of solid phase in the system “cement + water” is an effective method for plasticity regulation and increasing the 3D printable cement-based materials resistance to load during the printing. Structural stability of cement paste can be improved by 2 times by introduction of filler with efficient ranging of a particle size in dosage of 20 – 40 % by weight of cement. Cement paste with limestone filler having a particle size distribution ranging from 1 to 75 µm is characterized by the optimal plasticity, structural strength and deformability under the load. Using limestone filler with equal particle size impairs these characteristics of cement paste.

1. Introduction
3D build printing is one of the additive manufacturing processes based on a viscoplastic materials deposition via a printing nozzle. 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 top priority problems defining the ability to introduce the innovative 3D-printing into building practice is the problem of creating nomenclature of mixtures ensuring the implementation of this process. Efficiency and buildability of 3D-build printing depend on the complex parameters of the mixtures at all stages of the process. To ensure the required quality and construction time, management of rheological behaviour of mixtures must be done according to the conditions securing fluidity for their pumping, plasticity for extrusion, integrity of surface during multi-layer casting, structural stability for load accommodation of the upper layers. For this reason, researchers focus on the issues of optimization extrudability, firm stability and structural build up mixture compositions, for example [4-14]. As a result, collecting an array of experimental information, numerous mixtures has been received and tested. Relevant materials commonly comprise a combination of cement paste and bulk materials such as natural, manufactured and recycled aggregates and fillers, natural and recycled...
fibres. The obtained mixtures are multi-component, their compositions include superplasticizers, viscosity modifying additives, structural build-up regulators, bulk materials with various chemical-mineral compound and dispersion.

However, there is no systemized information and common approach to explanation of the role of each of the components for regulation the buildability of 3D-printable mixtures. Therefore, it is necessary to conduct system research identifying the influence on the set of rheological parameters of the mixtures of each single component used today in order to obtain them.

Author’s theoretical approach to identifying the main factors of stability of the 3D printable materials is based on the analysis of the 3D printable disperse systems behaviour in dynamic (during pumping and extrusion) and static (during multi-layer casting) conditions of 3D-printing according to point of view of classic structural rheology of disperse systems [15]. In work [16] we have justified basic means of the rheological behavioural management of 3D-printable mixtures considered as a system “solid phase – liquid phase”.

In connection with solid phase, they include its concentration, size of particles and their morphology, chemical-mineralogical composition, physicochemical characteristics of a particle surface. In connection with liquid phase, they include its ionic composition, viscosity, density. According to these means of management, a set of real technological tools has been suggested for management of rheological characteristics of 3D printable concrete. They include the type of binding agent, type and granulometry of filling agents, types and dosages of electrolytes, plastisizers, viscosity modifying additives, etc. For this reason, the main technological means of regulating rheological behaviour of mixtures include three grades of factors. The first one is water/cement ratio as a factor defining the concentration of solid phase in the system. The second one is a concentration and kind of additives as a factor defining the properties of liquid phase. The third one is a concentration, type and granulometry of fillers and aggregates.

This article is dedicated to the study the influence of the concentration and a particle size distribution of limestone filler on the rheological behaviour of cement pastes as matrixes of 3D printable concrete.

2. Materials and methods

Five types of 3D-printable cement pastes were studied (Table 1). Portland cement CEM I 42.5 (EN 197 – 1 : 2011), plasticizer of Sika trademark based on polycarboxylate ethers, limestone filler (CaCO₃ content ~ 95%) were used as initial components of the system. Limestone filler had a particle size distribution ranging from 1 to 75 μm.

| Specimen ID       | Components                          | Specimen ID       | Components                          |
|-------------------|-------------------------------------|-------------------|-------------------------------------|
|                   | plasticiser / mass cement (%)       | limestone filler / mass cement (%) |                      |
|                   | different particle size (DLF)       | equal particle size (ELF) | W/C |
| C – W – P (control) | 0.2                                  | -                 | -                                   | 0.24 |
| C – W – P – DLF20 | 0.2                                  | 20                | -                                   | 0.23 |
| C – W – P – DLF40 | 0.4                                  | 40                | -                                   | 0.22 |
| C – W – P – ELF20 | 0.2                                  | -                 | 20                                  | 0.23 |
| C – W – P – ELF40 | 0.4                                  | -                 | 40                                  | 0.22 |

Concentration and granulometry (Table 2) of limestone filler was assumed as a main factor for the change of rheological behaviour of the 3D-printable cement pastes. Consistence of cement paste was assumed as a fixed factor for the experiments.

To evaluate the extrudability and firm stability of cement pastes, the different kind of squeezing tests were used in accordance with the methodology developed in the works [17-20].
Cylindrical samples of fresh cement paste with radius $R$ equal to their height $h_0 = 25$ mm were used for the implementation of the experiment. For squeezing test, the sample was put between two smooth plates diameter of which corresponded to the size of the sample and was loaded into testing system “INSTRON Sates 1500 HDS”. The test was conducted on a fresh sample for all compositions of cement paste directly after their molding.

Table 2. The particle size distribution of limestone filler.

| Limestone filler     | Granulometry  |
|----------------------|---------------|
|                      | volume of particles, % | size (d), µm |
| Different particle  | 10            | 55           |
| size (DLF)           | 10            | 27           |
|                      | 19.8          | 10           |
|                      | 14.2          | 2            |
|                      | 7.8           | 1            |
| Equal particle size | 90            | 74.6         |
| (ELF)                | 10            | $\leq 70$    |

High compression speed test using constant plate speed $v = 5$ mm/s was implemented as the behaviour of the system in the process of extrusion is most adequately modeled with this speed. The curves “compression force $N$ – displacement $\Delta$” obtained during the experiments were interpreted as influence curves of reduced compression load $F^*$ from relative change of height of the sample $h/R$:

$$F^*_i = \frac{Ph_i}{\pi R^2},$$

where $h_i = (h_0 - \Delta)$, $h_0$ is initial height of the sample, $\Delta$ is transfer in the $i$ point of time, value $R$ was taken as constant and equal to the radius of the sample at the beginning of the experiment.

According to the results of the analysis of the received experimental curves for the studied systems values $K_i$, called plastic yield value by N. Roussel and C. Lanos [17,18], were calculated at the inflection point of the $F^*(h_i/R)$ curves between “placing phase” and “perfect plastic response phase” zones (Figure 1):

$$K_i\left(\frac{h_i}{R}\right) = \frac{\sqrt{3}F^*}{2}.$$

The squeezing test was conducted with constant strain rate $v = 0.5$ N/s was implemented as the behavior of the system in the process of multi-layer casting. The strain rate conforms to the average speed of load increase during multi-layer casting of building sites by industrial printers. Methodology of its implementation corresponds to the approaches of A. Perrot [19,20] to evaluation of buildability of the 3D printable mixtures. Squeezing was conducted until the rupture of the samples. The curves “compression force $N$ - displacement $\Delta$” were recorded as a result of the experiments. Based on the obtained experimental curves, structural strength ($\sigma_0$) of cement pastes was calculated for the moments corresponding to the start of deformation ($\Delta = 0.1$ mm), and plastic strength ($\sigma_{pl}$) was calculated at the beginning of cracking. The value of plastic deformations $\Delta_{pl}$ at the start of cracking was determined as a ratio of the displacement $\Delta$ of the plates in the squeezing test to the initial height of the sample $h_0$.

3. Experimental results and discussion

As a result of interpretation of the squeezing test with constant plate speed, we received experimental curves $F^* = f(h_i/R)$ (Figure 1) which correspond to the similar curves of N. Roussel [18]. Analysis of experimental curves $F^* = f(h_i/R)$ for description of rheological behaviour of cement paste during
squeezing was conducted on the basis of approaches of fundamental structural rheology of disperse systems [15].

![Diagram](image)

**Figure 1.** Tested cement pastes $F^*(h/R)$ curves.

Under the action of low compression stress on the first section of the curve within deformation range $\sim 0.8 < h/R < 1$ the structure maintains stability (“placing phase” according to N. Roussel’s terminology). According to point of view structural rheology of disperse systems, the “placing phase” can be characterized as a viscoplastic fluid with undisturbed structure. When the stress on the second section increases with $0.5 < h/R < 0.8$, the system is plastically deformed while its structure loses its stability (“perfect plastic response phase” according to N. Roussel). This section can be correlated with a viscoplastic fluid with intensively damaged structure in conformity with the structural rheology approach.

The experimental results show the similar kinds of $F^*(h/R)$ curves for all studied cement systems. They have expressed horizontal section of plastic deformation between the two points of inflection. For the systems transfer from stable condition to plastic flow is estimated by load $F^*$ for $\sim 1.0 \div 1.5$ kPa, transfer into the condition of the flow with damaged structure happens with $F^* \approx 1.5 \div 3.5$ kPa. At the same time, rational values plastic yield value $K_i$, which is determined at the beginning of viscoplastic fluid of disperse system with undisturbed structure, are within the range of $0.85 \div 1.20$ kPa (Table 3). These values $K_i$ ensure the best extrability due to their sufficient plasticity and capacity for viscoplastic flow without the damage of the structure under the influence of compression stress. At the same time the mixtures can be extruded through an extruder nozzle with low squeezing force. With values $K_i < 0.85$ kPa cement-based materials would not maintain stability during an extrusion process.

At the same time, the structural strength $\sigma_0$ is calculated on the basis of the quantity load $N$ at the beginning of deformation of viscoplastic mixtures can be considered as the main criterion of their buildability (Table 3). The structural strength $\sigma_0$ characterizes the ability of the system to maintain stability and resist to a deformation during loading.
Table 3. Rheological properties of 3D-printable cement pastes.

| Specimen ID       | Plastic yield value $K_i$ (kPa) | Strength(kPa) | Value of plastic deformations $\Delta_{pl}$ (mm/mm) |
|-------------------|---------------------------------|----------------|--------------------------------------------------|
| C – W – P (control) | 0.86                            | 1.10           | 45.01                                            |
| C – W – P – DLF20  | 1.21                            | 2.41           | 73.18                                            |
| C – W – P – DLF40  | 0.93                            | 2.34           | 69.59                                            |
| C – W – P – ELF20  | 0.95                            | 0.15           | 37.48                                            |
| C – W – P – ELF40  | 0.65                            |                | 0.05                                              |

Analysis of the received experimental data of the curves “compression force $N$ - displacement $\Delta$” (Figure 2) shows two typical zones of rheological behavior. The first one is the zone of plastic deformation. The system’s ability to deform without destruction is evaluated by the quantity plastic strength $\sigma_{pl}$ calculated on the basis of the quantity load $N$ at the beginning of cracking. To characterize buildability, it seems reasonable to evaluate the quantity of plastic deformations on this section $\Delta_{pl}$, which have to be minimized for 3D printable materials. The second one is the zone of cracking and intensively destruction of the structure. The cracking process is characterized by the multi-peak load fluctuations in the second section on “$N$ - $\Delta$” curves.

![Tested cement pastes “compression force $N$ - displacement $\Delta$” experimental results.](image)

The transition between plastic yield value $K_i$, value of structural $\sigma_0$ and plastic $\sigma_{pl}$ strength, plastic deformations $\Delta_{pl}$ is linked to the concentration and a particle size distribution of filler. Analysis of the curves “$N$ - $\Delta$” shows that system C – W – P displays the longest plastic phase zone (Figure 2). Interval of plastic phase zone for system with filler decreases by ~2 times compared with the control systems C – W – P. This effect of decreasing plasticity of cement paste is logically related to the influence of filler. Introduction of filler into disperse system “cement + water” as a regulating factor of solid phase properties changes packing density and molecular interactions.
between solid particles. As a result, flow under stresses becomes difficult for coarser systems containing filler. For systems with DFL (limestone filler with different particle size) plastic yield value \( K_i \), corresponding to the beginning of plastic flow, is in the range from 0.9 to 1.2 kPa, which is more than in the control system without fillers (C – W – P). For systems with EFL (limestone filler with equal particle size) plastic yield value \( K_i \) is in the range from 0.65 to 0.95 kPa.

As a result, the system C – W – P – DLF20, C – W – P – DLF40 have the highest values of structural strength \( \sigma_0 \) and the minimum values of plastic deformations \( \Delta_{pl} \) (Table 3). Introduction of limestone filler with different particle size (DLF) to the cement paste in dosages 20-40% allows to increase the structural strength by 2 times, to reduce plastic deformation by 2 - 5 times in comparison with control systems C – W – P. The system C – W – P – DLF20 has the best indicators such as the highest values of the structural strength \( \sigma_0 = 2.41 \) kPa, the minimum of plastic deformations \( \Delta_{pl} = 0.05 \) mm/mm. The structural strength \( \sigma_0 \) of the system C – W – P – DLF40 is the similar with the system C – W – P – DLF20 but plastic deformations \( \Delta_{pl} \) of C – W – P – DLF40 system is higher by 2 times that plastic deformations \( \Delta_{pl} \) of C – W – P – DLF20. Introduction of limestone filler with equal particle size (ELF) would not possible to ensure rational characteristics of plasticity and structural stability.

Change of rheological characteristics of cement pastes with the introduction of the fillers depends on kind of their granulometry. If fillers have different particle size, their particles locate between cement particles in a rational way. As a result, dense spatial packing of solid particles into cement paste structure is ensured. Such structuring of the cement pastes solid phase ensures the increase of their firm stability and consequently buildability. In contrast, fillers having equal particle size loosen cement paste structure. According to the experimental data, system C – W – P – ELF20 and C – W – P – ELF40 do not have structural stability \( (\sigma_0 < 0.05 \) kPa).

4. Conclusion
Analysis of the study results shows that the use of the squeezing test with constant plate speed is effective tool for evaluation of extrudability. Interpretation of the results of this test from the positions of structural rheology of disperse systems allows categorizing the parameters of plastic yield value \( K_i \approx 1.0 \div 1.5 \) kPa as criterion defining the ability of 3D printable materials to plastically deform without structure destruction and maintain stability during extrusion.

The squeezing test with constant strain rate is effective for the evaluation of buildability. The values of structural and plastic strength, plastic deformations defined by the results of this test characterize the system’s ability to hold its form, resist the deformation under compressions load during multi-layer casting.

It has been established that introduction of filler as a factor changing the properties of solid phase in the system “cement + water” is an effective method for plasticity regulation and increasing the 3D printable cement-based materials resistance to load during the printing. Structural stability of cement paste can be improved by 2 times by introduction of filler with efficient ranging of a particle size in dosage of 20–40% by weight of cement. Cement paste with limestone filler having a particle size distribution ranging from 1 to 75 \( \mu m \) is characterized by the optimal plasticity, structural strength and deformability under the load. Using limestone filler with equal particle size impairs these characteristics of cement paste.

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