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The effect of using surface functionalized granite powder waste on fresh properties of 3D-printed cementitious composites

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ABSTRACT

The production of low-emission additive manufactured cementitious composites using functionalized rock powders offers promising mechanical properties and significantly reduces cement consumption. The effect of powder functionalization on the rheological properties of the mixture remains unclear, so this study investigated how mechanical and chemical functionalization of granite powder waste affects the viscoelastic properties of a cementitious mixture for additive manufacturing. Compression tests were used to track stress-strain changes over time, while Vane and slug tests measured yield stress in mixes with 20 % and 40 % cement replaced by natural (NGP), sieved (SGP), and carbonated granite powder (CGP). The results showed that all three powders (NGP, SGP, and CGP) increased yield stress compared to the reference mix, with CGP having the smallest effect. The functionalization of granite powder may enable the creation of desirable viscoelastic mixtures using sustainable materials. We observed that functionalizing granite powder (SGP and CGP) accelerated changes in the mixture rheological properties, with yield stress increasing by up to 33 %, while NGP showed minimal impact, similar to the reference mix. Differences between the Vane and Slug test results were also identified and their limitations described.

1. Introduction

Designing the composition of a cementitious mix used for additive manufacturing is a complex process [1–5]. Appropriate selection of ingredients can ensure the homogeneity of the mixture, but this is much more complicated than the selection of ingredients for a traditional concrete mix [6–9].

The 3D printing process of cementitious composites depends on many factors: the composition of the mix, the process parameters, the ambient conditions, and the shape of the object to be printed [10–13]. Fresh properties of the cementitious mixture are therefore crucial for 3D printing. Therefore, methods are being developed to test the cementitious mix used for 3D printing of composites. The problem is so significant that RILEM created a technical committee (303-PFC) dedicated to fresh properties of 3D printable materials, which examined multiple methods for testing these properties. Table 1 presents a literature comparison of publications related to the additive manufacturing of cementitious composites with particular attention to the method of testing the rheological properties, the main findings on this topic and how the mixture was modified with the addition of different types of powders.

The researchers employed various test methods to assess the rheological properties of additively manufactured cementitious

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composites (Table 1). While rheometers were frequently used, they have the drawback of being penetration-based and requiring additional equipment. The viscotester method (shear growth test) is less commonly utilized, making it challenging to compare results. The slug test demonstrates significant potential by measuring rheological properties in real time during the printing process. It is important to note that this article addresses a timely topic, as the reviewed studies date from 2019 to 2022.

The Slug test and the Vane test are two tests recommended by the 303-PFC TC for testing fresh properties of mixes used in additive manufacturing. Ducoulombier et al. [17] described a protocol for conducting the Slug test, while pointing out the practical limitations of this method. Roussel et al. [11] described methods for assessing the fresh properties of cementitious mixes used in 3D printing. They concluded that the Slug test is a simple and robust inline assessment method for the yield stress used during printing. Ducoulombier et al. [18] confirmed that, depending on the rheological model of the mix, the Slug test is a useful tool for testing its printability. The Vane test is a method mainly used in geotechnics to assess yield stresses in the soil. The simplicity and versatility of this method has been recognized by researchers testing cementitious mixtures for 3D printing. Assaad et al. [19] tested the Vane method for analyzing yield stress of cement pastes. They pointed out that when using this method, it is important to consider that different specific surface area of grain may influence the yield stress of the mix. Saak et al. [20] studied the viscoelastic properties of cementitious pastes with use of Vane apparatus and compared it with other methods. They [20] noted that, depending on the method used, the results varied considerably.

For practical reasons, the application of mechanical property testing of fresh cementitious composites seems particularly relevant [21,22]. This is because these parameters often determine the possibility of achieving the required buildability of the structure. Shanmuhasundaram and Praveenkumar [23] conducted a study to determine the mechanical properties of fresh cementitious composites modified with various powders. They noted [23] that, depending on the type of additive, the composite can sometimes significantly change the dynamics of compressive strength gain (accelerate or decelerate), which is particularly important in 3D printed concrete. Yu et al. [24] determined compressive stress-strain relationship curves for printable fly ash-modified cementitious composites, noting that differences in material behavior are evident both in the shape of the graph (different angle of the stress-strain line) and in the failure mode. Xie et al. [25] prepared a computational model that allows for the calculation of the effect of the rheological properties of a cementitious mixture with supplementary cementitious materials (SCM) on the mechanical properties of the composite. They [25] concluded that the type of used SCM influences the rheological properties of the composite, which can be modified depending on its quantity. Bos et al. [26] conducted a study to correlate the rheological and mechanical properties of cementitious composites with a particular focus on the buildability of a 3D printed composite. They observed [26] that it is possible to create a mixture with the desired rheological properties, which will allow increase the buildability of the structure. It should also be emphasized that constant attempts to reduce the environmental impact of cement composites used in additive manufacturing have made it necessary to strictly control the stress-strain correlation and rheolog**ical** properties.

Mixtures used for concrete 3D printing require special rheological properties, which usually leads to the use of high amounts of cement (sometimes even more than 1000 kg/m^3) [3,7]. To reduce the environmental footprint of these mixtures, several approaches have been proposed: the use of mineral additives [8,27,28], the search for alternative binders [29,30], improving the packing density of the mixture [31–33], or the use of chemical admixtures [15,34]. Bhattacherjee et al. [35] comprehensively reviewed materials that

Table 1
Comparison of literature results.

Authors	Year of publication	Rheological test	Scope of the paper	Main findings
Xu et al. [14]	2022	Rheometer	The use of FA-GGBFS in cement-based 3D printing materials, focusing on its rheology.	When increasing the amount of FA/GGBFS the apparent viscosity and shear stress to decrease and then increase. FA has a stronger and more noticeable effect than GGBFS.
Long et al. [12]	2019	Rheometer	Micro-crystalline cellulose (MCC) was evaluated in composites for 3D-printing.	As the MCC content in cement-based composites increases, their plastic viscosity, yield stress, and thixotropy rise gradually.
Souza et al. [15]	2022	Viscotester (Shear Growth Test)	The impact of chemical admixtures, including setting retarders and accelerators, on the rheological properties.	The small (0.5 % by weight of cement) admixture of the accelerator makes it possible to achieve significantly higher buildability (number of layers laid) due to its effect on the shear stress of the mix.
Zhao et al. [16]	2022	Rheometer with four-blade Vane rotator	The study investigates how silica fume (SF) affects the rheology of 3D printed magnesium potassium phosphate cement (MKPC).	The static yield stress of MKPC with 15 % SF increase twice. Also, the shear stress increased, highlighting SF's role.
Ducoulombier et al. [17]	2021	The slug test	A new rheological method for evaluating the yield stress of printable materials at the nozzle exit.	The method is a simple tool for determining the rheological properties of a mixture used in 3D printing. Requires additional testing for measurement quality.
Roussel et al. [11]	2022	Comparison of different methods	Description of the effectiveness of using different methods to determine the rheological properties of cement mixtures.	The slug test is a simple and reliable inline method for measuring yield stress at the nozzle. Penetration tests effectively track yield stress changes over time, while uniaxial compression tests assess elastic modulus but are destructive and need separate strain measurements.

can be successfully used to reduce the cement content in 3D printed concrete, indicating that alternative binders are a significant substitute for cement. One material that allows to replace part of the cement in the mixture is granite powder waste (GP). However, it has been reported that GP cannot be used as high-volume substitution of cement in its natural form. Gupta and Vyas [36] described results of partial cement replacement with using of granite powder: it lead to minor improvements of mechanical properties of the composites, but did result in decreased porosity and improved frost resistance. Rojo-Lopez et al. [37] observed, that, compared to other supplementary cementitious materials, GP does not lead to significant improvement of mechanical properties of cementitious composites. Therefore, functionalized GP is increasingly being used to reduce the amount of cement in the mixture [38–40].

Herein, we used two methods of functionalization of granite powder, mechanical and chemical. Then, we investigated the impact of treated granite powder on the properties of fresh cementitious mixture used in additive manufacturing. For this purpose, we used the Slug test and the Vane test, in addition allowing us to compare these methods and indicate their limitations. We described innovative methods of functionalization of granite powder and correlated them with the properties of the fresh mixture, filling a significant research gap and striving to reduce the environmental footprint of printable concrete mixtures.

2. Materials and methods

We prepared seven test series of cementitious pastes modified with three types of granite powder: 1 – natural granite powder (NGP), 2 - sieved granite powder (SGP) and 3 – carbonated granite powder (CGP). Details of the composition of the mixtures are shown in Table 2. The mixtures were designed to be used in the additive manufacturing of cementitious composites. Cement CEM I 42.5R (Odra, Poland), siliceous fly ash (FA), (PGE, Poland), natural granite powder (NGP) from the granite rock cutting process (Strzegom, Poland) and tap water were used. To improve the viscosity of cementitious mixes used in additive manufacturing, we used the viscosity modifier - Sika Latex (Sika, Poland) in an amount of 40 g/l (a fixed amount for all series, determined in preliminary studies). Superplasticizer Duruflow (Atlas, Poland) in an amount of 11.6 g/l (a fixed amount for all series, determined in preliminary studies) was used to reduce the amount of water. A detailed scheme of the tests is presented in Fig. 1.

2.1. Functionalization of GP

To improve the properties of granite powder, two functionalization methods were used: 1 - sieving and 2 - direct aqueous carbonation (Fig. 2).

The extracted natural granite powder (NGP) (which originated as a waste product of the granite rock cutting process) was dried at 105 °C to a solid mass. 5 kg of NGP was used. Then, it was divided into two parts - the first was left as for use in the GP0 test series and the second was sieved through a 0.063 mm sieve. The material prepared in this way was divided into two parts - the first was used in the study as SGP (sieved granite powder), while the second was subjected to a direct aqueous carbonation procedure (carbonated granite powder - CGP). For aqueous carbonation process, the powder was poured into a pre-prepared glass container that had been adapted for this procedure. Carbonation was carried out in an aqueous medium of 0.1 mol sodium hydroxide, into which a mixture of two technical gases - carbon dioxide (CO_2) and nitrogen (N_2) - was introduced under constant control for 60 min. The gas flow rate was 8 l/h and 4 l/h, respectively. The reaction took place at 23 °C (± 0.3 °C). Efforts were made to keep the pH constant at around 11 (-). After completing the process, the mixture was filtered through a laboratory filter, and then the filtered CGP was dried at a temperature of 105 °C until constant weight was obtained. The NGP, SGP and CGP prepared in this way were characterized and then used to prepare cement mixtures.

2.2. Physical and chemical properties of powders

To characterize the powders, three methods were used: 1 – particle size distribution, 2 - bulk density, 3 - chemical composition.

Particle size distribution was determined based on the standard PN-EN 1015-1:2000. The prepared powder samples were weighed (m_c) and then sifted through a set of standard sieves with measurement of mass of samples on each sieve ($Sm_{1,x1..n}$). As a result, the percentage mass content of residues on individual sieves (d_x) was plotted based on Eq (1).

$$d_x = \frac{m_c - \sum m_{1,x_{1...n}}}{m_c} * 100\% \ (\%) \tag{1}$$

Bulk density (ρ) was determined based on the PN-EN 1097-3:2000 standard. The prepared powder samples were carefully poured into a prepared glass container (m_1) of known volume (v_f), and then the filled container was weighed (m_2). The density was determined

Table 2
Compositions of research series.

Research series	Cement	FA	NGP	SGP	CGP	Water	Viscosity modifier Sika Latex	Superplasticizer Atlas Duruflow
	(g/l)							
REF	1510	290	0	0	0	370	40	11.6
GP0.20	1208		302	0	0			
GP0.40	906		604	0	0			
GP1.20	1208		0	302	0			
GP1.40	906		0	604	0			
GP2.20	1208		0	0	302			
GP2.40	906		0	0	604			

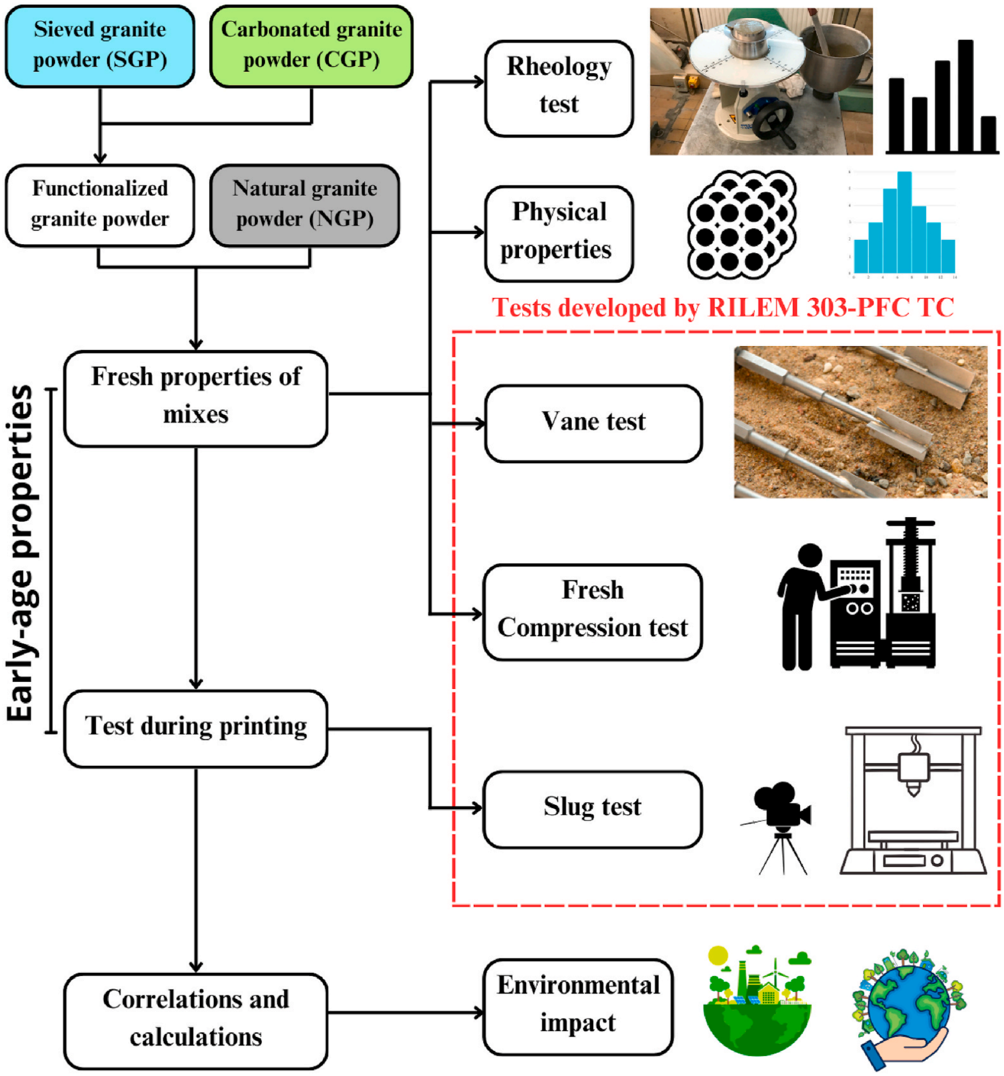

Fig. 1. General plan of the research.

based on Eq (2).

$$\rho = \frac{(m_2 - m_1)}{V_f} \ (\mathrm{kg}/\mathrm{m}^3) \quad (2)$$

The chemical composition of used powders was determined using a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS), and the oxides present in the powders were analyzed. Tables 3 and 4 present results of powders characterization.

2.3. Fresh properties of mixes

Characterization of fresh properties of cementitious mixtures was performed in two stages: 1 - investigation of fresh properties before printing, 2 - analysis of fresh properties during printing. The first stage consists of the following tests: slump flow analysis, fresh compression test [41,42] and Vane test. The second stage relied on the Slug test [17,18].

Slump flow r_m was measured based on the PN-EN 1015-3 standard. A container was placed on the measuring plate and filled with the fresh mixture. Then, the container was removed, and the table was shaken 15 times. The test was performed 5 min after the mixture was mixed. After this, the diameter of the resulting flow was determined based on length measurement in two directions of flow (*a, b*), according to Eq (3).

$$r_m = \frac{(a+b)}{2} (\mathrm{cm}) \quad (3)$$

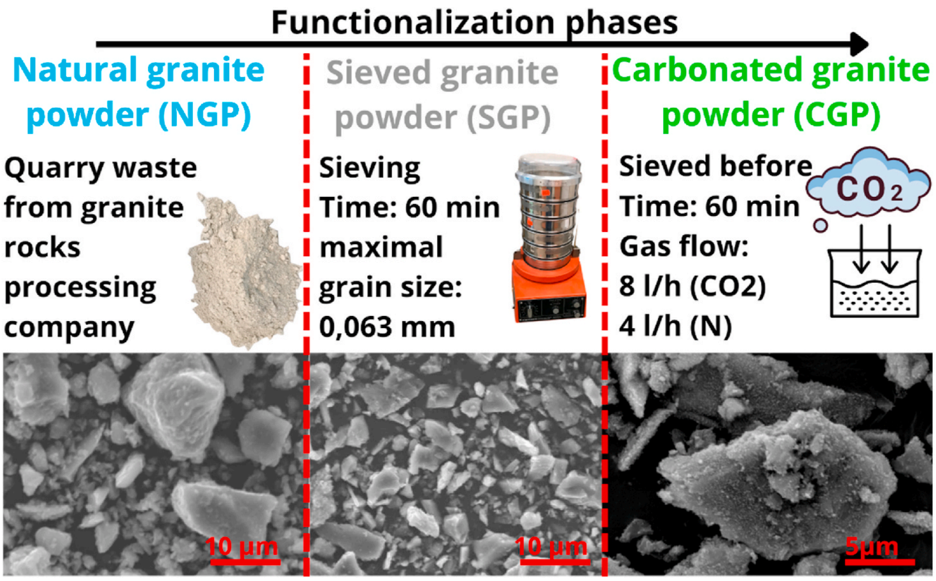

Fig. 2. Methods of functionalization of GP used in this research.

Table 3
Physical properties of used powders.

	Cement	FA	NGP	SGP	CGP
Physical properties					
d_{10} (um)	<20	24	28	<20	
d_{50} (um)	48	39	51	44	
d_{90} (um)	99	96	115	58	
Bulk density (kg/m^3)	1448	1521	1612	1781	1895
Specific surface area (cm^2/g)	3240	4110	2950	3940	4410

Table 4
Chemical properties of used powders.

	Cement	FA	NGP	SGP	CGP
Chemical properties					
chemical compound	wt. (%)				
CaO	67.1	3.5	9.6		11.5
SiO_2	18.0	61.2	62.1		63.1
Al_2O_3	4.7	28.1	17.6		17.5
MgO	1.9	1.6	2.1		2.9
SO_3	3.9	0.4	0.3		0.5
K_2O	1.1	1.2	2.1		1.2
FeO	2.9	2.8	4.2		2.8
Others	0.4	1.2	2.0		0.5

Fresh compression test was performed based on recommendations for members of the RILEM 303-PFC Technical Committee and literature [41,42]. Pipes with a 5 cm in diameter, each 10 cm high, were prepared and then the inside was lined with tape or foil. Into the moulds thus prepared, the cement mixture was laid (in two layers, compacting each layer accordingly). The moulds were then removed from the pipes and the foil carefully removed. The specimens thus prepared were subjected to a compression test in a testing machine. A variable machine load and a machine piston displacement of 42 mm/min (0.5 %/sec) were set. The test rig was adapted to ensure that the horizontal and vertical deformation of the specimen could be measured as a function of load using a camera (iPhone 15 Pro, equipped with a camera with a resolution of 24 MPa (photo) and recording videos in 4K resolution 30 frames/second). The test was performed a minimum of 5 times for each specimen at 5, 15, 30, 45 and 60 min after mixture preparation (time zero was the time of the end of the mixing). The results are presented in Force-Displacement and Stress-Strain correlations. Stress (σ) was calculated as the ratio of force (F) to initial specimen area (A_0) and Strain (ε) as the ratio of displacement (δ) to initial specimen length (L_0) (Eq (4)). The test was terminated if, for each series of cementitious mixtures, a load of 30, 40, 70, and 100 (N) - after a time of 5, 15, 30 and 60 (min) after forming, respectively or displacement equal 30 mm was noted.

$$\sigma = \frac{F}{A_0} \; ; \; \varepsilon = \frac{\delta}{L_0} \tag{4}$$

The Vane test was performed based on recommendations of the RILEM 303-PFC Technical Committee. The study used a 10 × 20 Vane tip and a 0–100 Nm torque wrench with an accuracy of 1 Nm. The cement mixture was placed in a prepared cuboid-shaped container (15 × 15 × 30 cm) and its surface was then leveled. The Vane apparatus was inserted into the mixture so that the top of the tip was recessed approximately 4 cm from the top surface of the mixture. Then the test began and was conducted in such a way that the maximum moment destroying the mixture structure was achieved within 1 min. Time, rotation rate, and maximum torque were recorded. Then, yield stress was determined based on Eq (5). The test was repeated 5 times for each mixture. The test was performed for the mixture at 5 different times after mixing the ingredients – after 5, 15, 30, 45 and 60 min.

$$\tau = \frac{T}{\pi^* d^{2*}\left(\frac{H}{2} + \frac{d}{6}\right)} \ (Pa) \tag{5}$$

2.4. Test during printing

The Slug test was performed based on the recommendations of the RILEM 303-PFC Technical Committee. The study used a 3D printer for cement mixtures, which extrudes the mixture based on air pressure. At 50 cm from the print head, a phone stand equipped with an LED lamp to improve lighting conditions was positioned. The camera was placed about 20 cm lower than the printer head. The research used an iPhone 15 Pro, equipped with a camera with a resolution of 24 MPa (photo) and recording videos in 4K resolution 30 frames/second. The test was performed at a constant temperature of 23 °C and humidity of 75 %. For each mixture, measurements were performed at least 5 times. A head with a diameter of 8 mm (S) was used, which was placed 30 cm above the table. The test was performed for a constant air pressure of 0.2 MPa. An attempt was made to obtain a minimum of 20 slugs/trial. Each slug was weighed (m) and the average dimensions of slugs for each mixture were determined based on the video. The number of slugs (n_{slugs}) was counted, and the volume density of the mixture (ρ) was calculated. A laboratory scale with an accuracy of 0.1 g was placed under the print head, and an empty container (m_{bucket}) was placed on it. After starting the mixture flow, the weight of each slug was measured. Based on Eq. (6), the average slug mass (m_s) was determined and based on Eq. (7) yield stress (τ_c) was calculated. The slugs measured from the test video ($s_{l,m}$) with using graphical program GIMP were compared with the calculated slug value ($s_{l,c}$) based on Eq. (8).

$$m_s = \frac{m - m_{bucket}}{n_{slugs}} \ (g) \tag{6}$$

$$\tau_c = 100^* \frac{m_s}{\sqrt{3}^* S} \ (Pa) \tag{7}$$

$$s_{l,c} = 1000^* \frac{m_s}{\rho^* S} \ (cm) \tag{8}$$

The diagram of the performed test is shown in Fig. 3.

2.5. Environmental impact

To estimate the environmental impact of used functionalization of granite powder grains, we performed a simplified analysis to calculate the associated carbon dioxide emissions. Table 5 shows the specific emissions associated with the components of the cementitious mixtures used in this study, based on a literature analysis [43,44]. In the case of CGP granite powder, emissions were calculated by assuming SGP powder emissions minus CO_2 bound permanently on the granite powder surface (15.72 kg of CO_2 was used to produce 0.1 kg of CGP powder – therefore, a 10 % efficiency of CO_2 deposition on the powder surface was assumed), that calculated

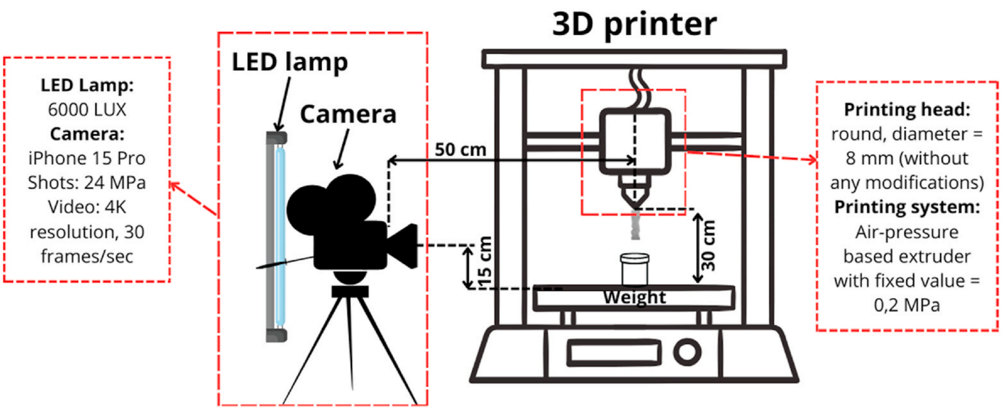

Fig. 3. The Slug test stand used in this research.

Table 5
Emission of carbon dioxide of used powders.

	Cement	FA	NGP	SGP	CGP	Water	Plasticizer
Emission of CO_2 i_{CO2} (kg CO_2/kg)	0.58	0.15	0.086	0.11	−0.146	0.011	0.089

emission of CGP is equal: -0.146 kg CO_2/kg.

Eq. (9) was used to calculate the total emission of CO_2 (TCO_2) associated with the mixture. By multiplying the content of the individual ingredients in the mixture $c_{\text{ingredient}}$ and their specific emissions (i_{CO2}) determined in Table 5. An environmental impact index (*EI*) was then calculated to compare the impact of the different mixture series, which is the ratio of the total emission of CO_2 of the modified series ($TCO_{2,\text{ series}}$) to the total emission of CO_2 of the reference series ($TCO_{2,\text{ ref}}$) (Eq. (10)).

$$TCO_2 = c_{ingredient} \times i_{CO2} \left(kg \frac{CO_2}{l} \right) \tag{9}$$

$$EI_{series} = \frac{TCO_{2,series}}{TCO_{2,ref}} \times 100\% \ (\%) \tag{10}$$

3. Results and discussion

3.1. Fresh properties of mixes

3.1.1. Slump flow

Slump flow of cementitious mixes is an important property allowing basic verification of its viscoelastic properties (Fig. 4). Modification of the mixture with the addition of granite powder led to a decrease of slump flow compared to reference series. However, that the effect of GP addition depends on the type of GP used. NGP led to a change in slump flow from 180 mm to 160 (20 %) and 150 mm (40 %). Mechanical functionalization of granite powder (SGP) led to a greater change in slump flow -20 % of cement replacement with this additive reduced the slump flow to 140 mm, and 40 % even to 130 mm. Chemically functionalized granite powder showed interesting results, as the slump flow increased compared to the SGP-modified mixture by 20 mm (for 20 % and 40 % modification). This may be related to the modification of the surface of the granite powder with calcite forms [45], which led to a change in its roughness and the need for cementitious paste to cover the mixture grains.

3.1.2. Vane test

The lowest yield stress results were obtained for the reference mixture (Fig. 5). This is also correlated with the previously described highest fluidity of this mixture. For the REF mixture, an increase in the yield stress value was recorded with time, which confirms the known course of changes in the viscoelastic properties of cementitious composites [46], which occurs with the hydration of cement in the mixture. Modification of the mixture with the addition of NGP leads to an increase in its yield stress, which increases with the increase in the percentage of cement replacement. This is related to the higher water demand known from the literature [47], which is usually caused by the larger specific surface of GP grains compared to cement. Furthermore, the change to a finer grain size (SGP) led to a further increase in the yield stress of the mixture, which was predictable because this mixture was less fluid than the REF mixture. Interesting results were again obtained for CGP-modified mixtures, as they showed viscoelastic properties (yield stress) similar to those of the NGP-modified mixture. There is a significant impact of chemical functionalization of GP on the fresh properties of the mixture. It should be stressed that, according to Ducoulombier et al. [17], the Slug test has limitations, because if the cementitious mixture exceeds the shear stress limit (related to the progress of cement hydration), then the test may indicate significant differences in the results obtained, or lead to it being impossible to perform - because the mixture will start to set, preventing it from being extruded through the printer head. In the Slug test, additional forces act on the mixture (e.g., frictional resistance against the printer tank walls, discharge pressure) which makes this test more sensitive to factors unrelated to the mixture properties compared to the Vane test.

3.1.3. Fresh compression test

Modifying the material composition of the mixes using the replacement of cement with granite powder allowed the effect of the mix on the load to be altered (Fig. 6). In addition, depending on the type of modifier used, different results were obtained - NGP allowed lower necessary forces to induce the same deformation compared to the reference series. A different effect is observed for SGP and CGP

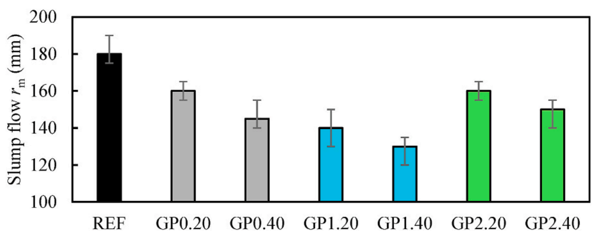

Fig. 4. Slump flow of the tested mixes.

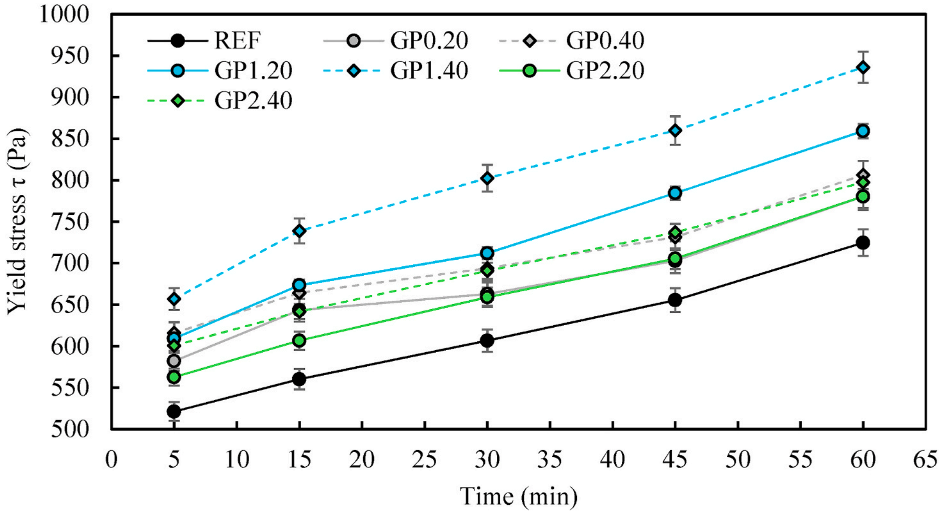

Fig. 5. Results of the Vane test.

powder, where a higher value of compressive force had to be used to produce the same deformation. It can therefore be hypothesized that the sieved powder accelerates the setting of the cement mix, which has a positive effect on its compression behavior. The highest value of force required for strain was recorded for the series modified with CGP powder (GP2.20 and GP2.40).

Analyzing the changes in the force-displacement correlation over time, it can be seen that the course of the graphs changes with time. In the initial period after mixing (after 5 and 15 min), the results obtained for the different test series are not significantly different and it is difficult to estimate the apparent inflection point of the graph. After a longer period (30 and 60 min), much greater differences are observed between the results. A visible inflection point in the graph can be distinguished, after which the displacement increases disproportionately to the increase in force. In addition, differences between the results for the individual test series became apparent. Higher forces were obtained for SGP and CGP powders at lower deformation, indicating a faster setting process than for the other test series. Liu et al. [41] similarly noted that the way the cement mix is modified with different additives has a significant effect on the behavior of the mix during fresh compressive testing. They [41] noted that finer additives than cement to increase the necessary force to achieve the same deformation than the reference series, while the use of additives that accelerate cement setting lead to increase of maximal compressive stress in this test even 8 times. Voigt et al. [42] observed that different material compositions of cementitious composites affect the stiffness of the composite over time, which has a significant impact on its behavior (compressive stress – strain relation), especially in the initial period after placing the mixture. This is extremely important in the additive manufacturing of cementitious composites because it ensures the required buildability of the printed structure.

3.2. Test during printing – The Slug test

The Slug test results allow for a comprehensive analysis of the viscoelastic properties of cementitious mixes. However, the results reported are significantly different than those obtained using the Vane method. The yield stress calculated by the Slug test method is much lower than that determined by the Vane apparatus. Nevertheless, similar variations were demonstrated depending on the mixture composition. However, the observed changes in the calculated yield stress values (Fig. 7a) are not as significant as those described for Fig. 5, which may affect the accuracy of this method. It should also be noted that the calculated yield stress using the Slug test method allows for the conclusion that the CGP modified mixture has properties more similar to the REF series than to the NGP modified series. There is also a smaller difference between the modification of 20 and 40 % of cement content than described in point 3.2. The number of slugs obtained for the study over time (Fig. 7b) confirms the calculated viscoelastic properties. This is because a more fluid mixture has a greater tendency to produce smaller, higher frequency slugs. It seems that modifying the mixture using CGP allows for obtaining much better viscoelastic properties than NGP or SGP (more similar properties to the reference series, which would confirm the possibility of adding CGP to the mixture without affecting its building properties in the additive manufacturing process) (see Fig. 8).

3.3. Relationships between different properties

Interesting results were obtained by comparing the calculated length of slug and the measured length of slug (Fig. 6). Comparing these two methods, it can be seen that the convergence of the results is relatively good within the first 30 min of mixing the mixture components. Significant differences are observed in the next 30 min of the test, which differ up to three times (red frame on Fig. 6). This can be explained by the applicability of the Slug test method for calculating the length of slug only within a certain range of the viscoelastic properties of mixes. Additionally, it appears that measuring the length of slugs based on photos is a more accurate method because it better reflects the correlation of the test run and the print parameter. The method of calculating the length of slug is also correlated with the printing process itself - its parameters and the machine used in the study, so more comparative research on these

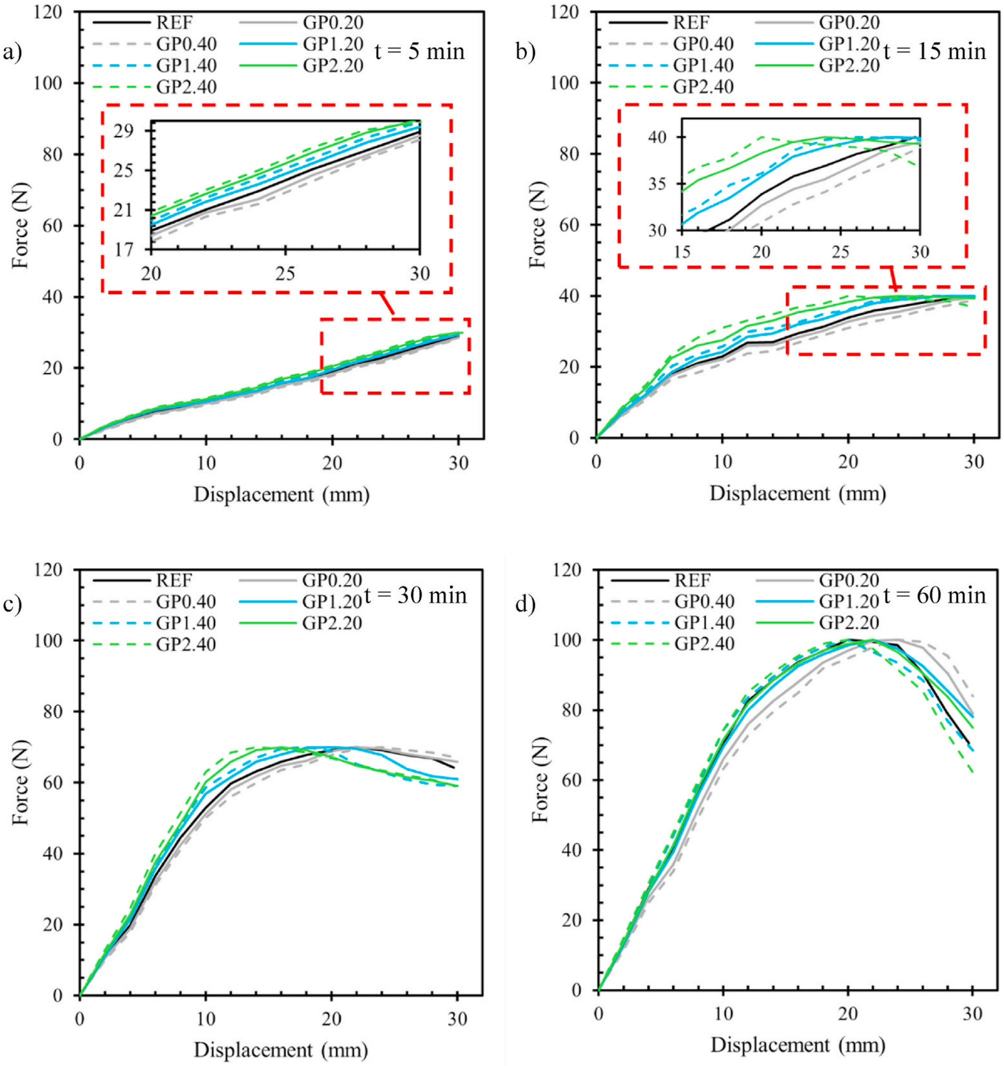

Fig. 6. Force – displacement correlations based on fresh compression test after mixing: a) 5 min, b) 15 min, c) 30 min, d) 60 min.

two methods of determining the length of slug should be performed.

The analysis of the behavior of the composite in a short time (in particular the stress-strain relationship) was performed in Fig. 9. The results obtained after 5, 15, 30 and 60 min were compared on separate graphs for mixtures in which 20 % of the cement was replaced (Fig. 9a) and 40 % cement (Fig. 9b). It is visible that in the case of mixtures with a lower cement replacement, less variable test results were obtained than for the series with a higher cement replacement. This may be related to the greater heterogeneity of the composite.

Fig. 10 shows the correlation between the obtained maximum compressive stress and the yield stress (Fig. 10a - vane test) and calculated yield stress (Fig. 10b - the Slug test). It can be noticed that extremely different results were obtained, which additionally indicates that both research methods (the Slug test and the vane test) lead to the determination of the correct yield stress variability, but the obtained value cannot be compared with each other. It is also noted that as the yield stress value increases, the maximum compressive stress also increases, which is related to the changes inside the composite structure, which becomes harder as a result of the cement hydration process.

3.4. Environmental impact

The use of functionalization methods of granite powder allows to optimize the impact of this material on the environment (Fig. 11a and b). The use of 20 % and 40 % NGP to replace cement allowed for a reduction of 15 % or 32 % of CO_2 emission, respectively. Slightly worse results were recorded with the use of SGP (13 % and 30 % reduction in emission compared to the REF series), however, the positive effect of this type of powder on early-age properties of cementitious composites should be taken into account. The highest reduction in the emissivity of the cement mixture is possible when using CGP, which allows for its reduction by 24 % and 48 %.

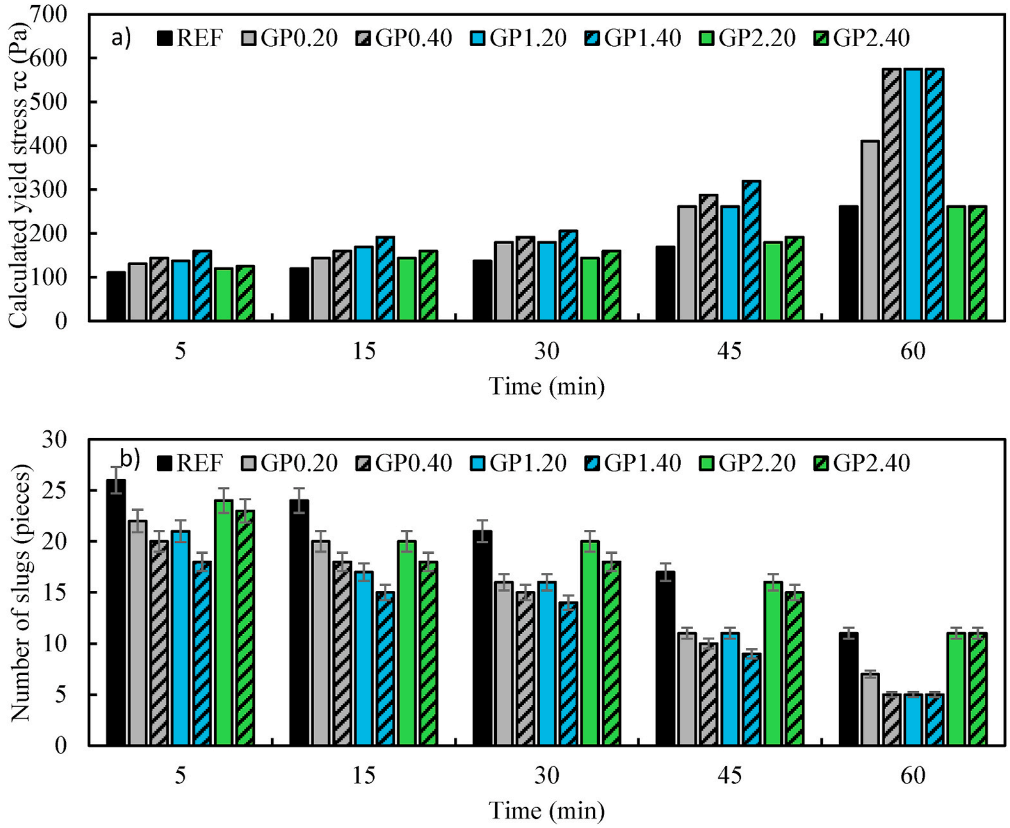

Fig. 7. Results of the Slug test: a) calculated yield stress, b) number of slugs in correlations to time.

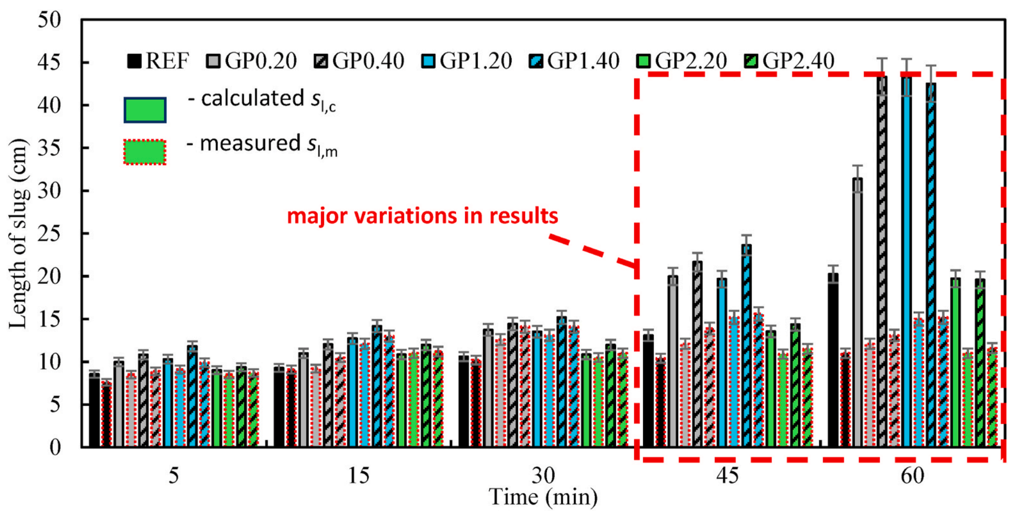

Fig. 8. Results of the Slug test – correlations between calculated and measured slugs length.

To compare the environmental impact results obtained with those from the literature, we prepared Table 6.

The need to assess the environmental impact of waste powders used as partial replacements for cement in composites has been recognized by many researchers. Kumar et al. [48] used SF and FA to replace up to 65 % of the cement in a composite, reducing the environmental impact by up to 31 %. Oliveira et al. [49] replaced up to 25 % of cement with waste concrete powder, resulting in a 27 % reduction in environmental impact. Singh et al. [50] achieved a 78 % reduction in environmental impact by using MP. Patel et al. [51] used WFG to replace 20 % of cement, cutting environmental impact by 20 %. Kim et al. [52] replaced up to 70 % of the cement with the

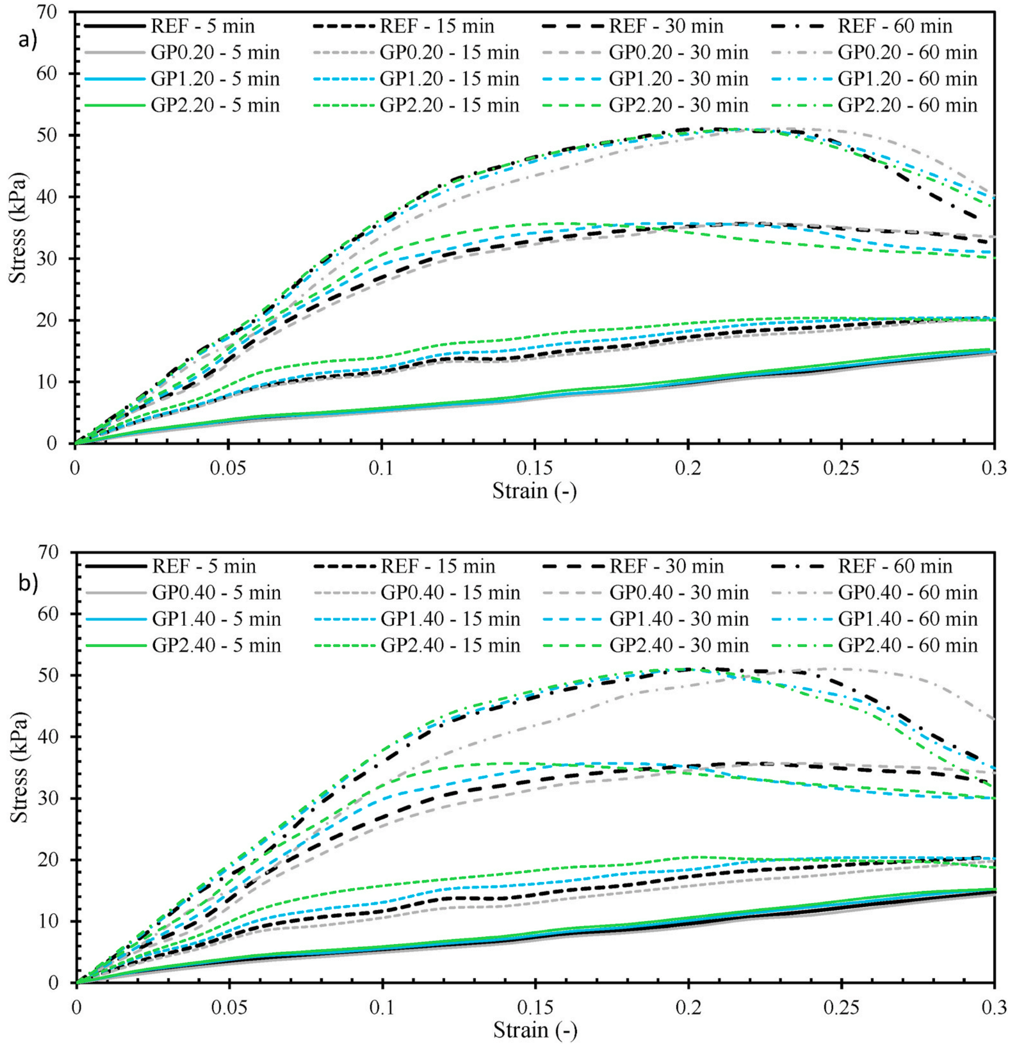

Fig. 9. Stress – strain correlations based on fresh compression test: a) series with 20 % cement replacement, b) series with 40 % cement replacement.

SW additive, achieving a significant 69 % reduction in environmental impact. Compared to the literature, these results are among the more significant reductions in environmental impact. Particularly notable are the positive outcomes for carbonated meal, highlighting the effectiveness of this method for the functionalization of waste powders.

4. Conclusions

In the research, we verified the possibility of using functionalized granite powder on the rheological properties of a cementitious mixtures in additive manufacturing. We determined the impact of NGP, SGP and CGP on the variability of yield stress over time and compared it to the REF mixture. Implementation of two different yield stress testing methods, leaded us to indicate their advantages and disadvantages. The fresh compressive strength test allowed us to determine the effect of NGP, SGP and CGP on the dynamics of the increment of mechanical properties over the time. We also examined the environmental impact of cementitious mixes modified with the addition of NGP, SGP and CGP, indicating the optimal series in this respect - GP2.40. We drew the following conclusions:

1. The main finding of this research is that functionalization of granite powder allows modification of the viscoelastic properties of 3D printable mixtures.
2. Direct aqueous carbonation of granite powder is optimal as it enables up to 40 % cement replacement without significantly affecting yield stress and improves compressive strength. Preliminary tests have shown positive results in print tests compared to the reference series.
3. The Slug test and the Vane test effectively determine the rheological properties of cementitious composites for additive manufacturing. The yield strength from the Slug test is accurate only within the first 30 min after mixing and shows significant differences afterward.

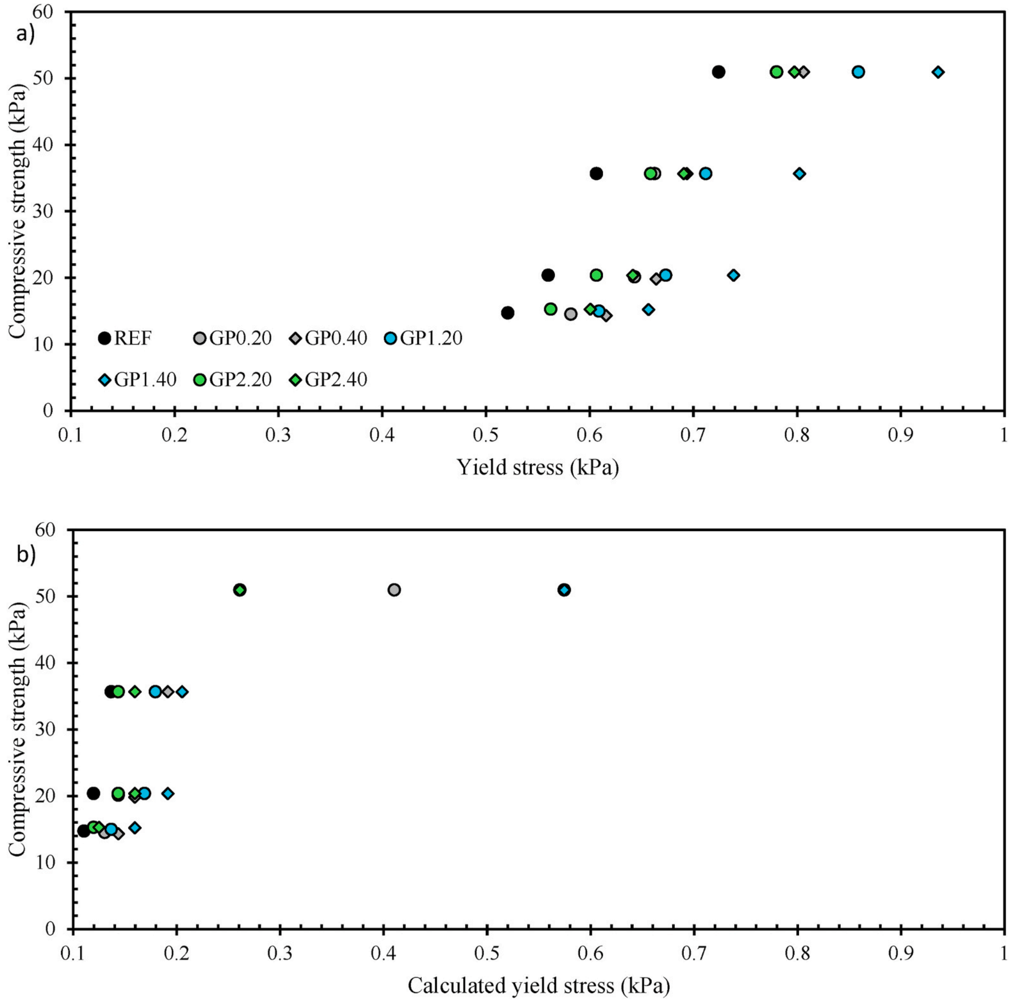

Fig. 10. Correlations between: a) compressive strength – yield stress, b) compressive strength – calculated yield stress.

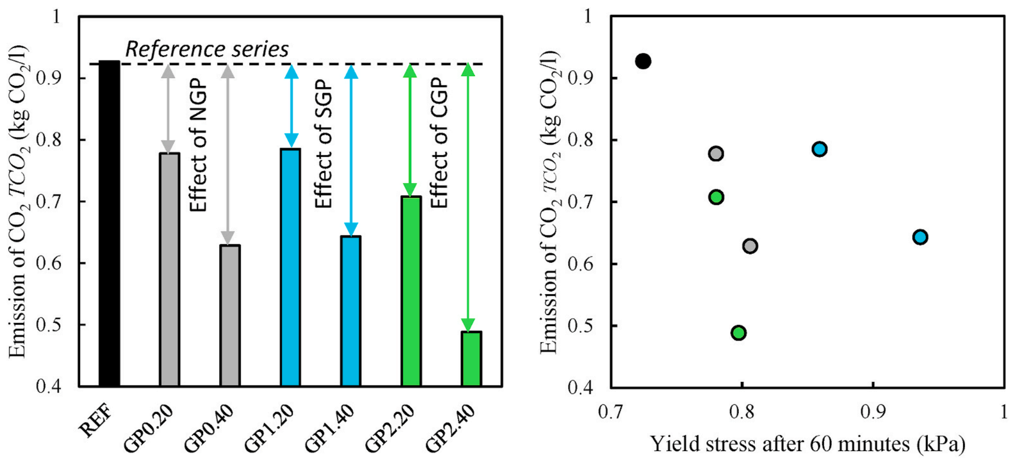

Fig. 11. Results of environmental impact analysis a) total emission of research series b) correlation between emission of CO_2 and yield stress after 60 min for mixes.

Table 6
Literature results of environmental impact comparison.

Reference	Cement replacement and used powder	Environmental impact *EI* (%)
This research	GP: 20 %, 40 %	84 %, 68 %
	GP1: 20 %, 40 %	85 %, 69 %
	GP2: 20 %, 40 %	76 %, 53 %
Kumar et al. [48]	Silica fume (SF) + Fly ash (FA): 50 %, 55 %, 60 %, 65 %	83 %, 78 %, 73 %, 69 %
Oliveira et al. [49]	Concrete powder (CP): 7 %, 15 %, 25 %	94 %, 86 %, 73 %
Singh et al. [50]	Marble powder (MP): 15 %, 25 %	88 %, 78 %
Patel et al. [51]	Waste fine glass (WFG): 5 %, 10 %, 15 %, 20 %	94 %, 89 %, 85 %, 80 %
Kim et al. [52]	Slag waste (SW): 30 %, 70 %	71 %, 31 %

4. Chemical functionalization results in greater stiffness of the mixture at early age. Mechanical functionalization also affects the dynamic of stiffness increase, but to a lesser extent than chemical functionalization. Non-functionalized granite powder does not show this positive effect compared to the REF series.
5. Direct carbonation of granite powder process allows to achieve significantly lower (even 48 %) emission of CO_2 connected with cementitious composites and develop desired for 3D printing process properties of composites.

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CRediT authorship contribution statement

Adrian Chajec: Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Branko Šavija:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Adrian Chajec reports financial support was provided by National Science Centre, Poland under project PRELUDIUM 22 (2023/49/N/ST8/01800). If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] J. Zhang, J. Wang, S. Dong, X. Yu, B. Han, A review of the current progress and application of 3D printed concrete, Compos. Appl. Sci. Manuf. 125 (2019).
[2] M.A.G. Calle, M. Salmi, L.M. Mazzariol, M. Alves, P. Kujala, Additive manufacturing of miniature marine structures for crashworthiness verification: scaling technique and experimental tests, Mar. Struct. 72 (2020).
[3] S.H. Chu, L.G. Li, A.K.H. Kwan, Development of extrudable high strength fiber reinforced concrete incorporating nano calcium carbonate, Addit. Manuf. 37 (2021).
[4] W. Zhu, S. Zhu, W. Li, Y. Zhang, W. Chen, J. Zhang, et al., A study on the printability of manufactured sand concrete, Construct. Build. Mater. 409 (2023).
[5] Y. Zhang, Y. Zhang, L. Yang, G. Liu, H. Du, Evaluation of aggregates, fibers and voids distribution in 3D printed concrete, J. Sustain. Cement-Base Mater. 12 (2023).
[6] A. Das, Y. Song, S. Mantellato, T. Wangler, D.A. Lange, R.J. Flatt, Effect of processing on the air void system of 3D printed concrete, Cement Concr. Res. 156 (2022).
[7] T. Wangler, N. Roussel, F.P. Bos, T.A.M. Salet, R.J. Flatt, Digital concrete: a review, Cement Concr. Res. 123 (2019).
[8] P. Sikora, S.Y. Chung, M. Liard, D. Lootens, T. Dorn, P.H. Kamm, et al., The effects of nanosilica on the fresh and hardened properties of 3D printable mortars, Construct. Build. Mater. 281 (2021).
[9] B. Major, M. Nabiałek, M. Sroka, M. WęGlowski, Abdullah MM. Al Bakri, Structure and Properties of Modern Engineering Materials, 71, Bulletin of the Polish Academy of Sciences: Technical Sciences, 2023.
[10] D. Siang Ng, S.C. Paul, V. Anggraini, S.Y. Kong, T.S. Qureshi, C.R. Rodriguez, et al., Influence of SiO2, TiO2 and Fe2O3 nanoparticles on the properties of fly ash blended cement mortars, Construct. Build. Mater. 258 (2020).
[11] R. Nicolas, B. Richard, D. Nicolas, I. Irina, K.J. Temitope, L. Dirk, et al., Assessing the fresh properties of printable cement-based materials: high potential tests for quality control, Cement Concr. Res. 158 (2022).
[12] W.J. Long, J.L. Tao, C. Lin, Y cun Gu, L. Mei, H.B. Duan, et al., Rheology and buildability of sustainable cement-based composites containing micro-crystalline cellulose for 3D-printing, J. Clean. Prod. 239 (2019).
[13] G. De Schutter, K. Lesage, V. Mechtcherine, V.N. Nerella, G. Habert, I. Agusti-Juan, Vision of 3D printing with concrete — technical, economic and environmental potentials, Cement Concr. Res. (2018) 112.
[14] Z. Xu, D. Zhang, H. Li, X. Sun, K. Zhao, Y. Wang, Effect of FA and GGBFS on compressive strength, rheology, and printing properties of cement-based 3D printing material, Construct. Build. Mater. 339 (2022).
[15] M. Tramontin Souza, I. Maia Ferreira, E. Guzi de Moraes, L. Senff, S. Arcaro, J.R. Castro Pessôa, et al., Role of chemical admixtures on 3D printed Portland cement: assessing rheology and buildability, Construct. Build. Mater. 314 (2022).

[16] Z. Zhao, M. Chen, Y. Jin, L. Lu, L. Li, Rheology control towards 3D printed magnesium potassium phosphate cement composites, Compos. B Eng. (2022) 239.
[17] N. Ducoulombier, R. Mesnil, P. Carneau, L. Demont, H. Bessaies-Bey, J.F. Caron, et al., The "Slugs-test" for extrusion-based additive manufacturing: protocol, analysis and practical limits, Cement Concr. Compos. 121 (2021).
[18] N. Ducoulombier, P. Carneau, R. Mesnil, L. Demont, J.F. Caron, N. Roussel, "The slug test": inline assessment of yield stress for extrusion-based, in: Additive Manufacturing, 28, RILEM Bookseries, 2020.
[19] J.J. Assaad, J. Harb, Y. Maalouf, Effect of vane configuration on yield stress measurements of cement pastes, J. Non-Newtonian Fluid Mech. 230 (2016).
[20] A.W. Saak, H.M. Jennings, S.P. Shah, The influence of wall slip on yield stress and viscoelastic measurements of cement paste, Cement Concr. Res. 31 (2001).
[21] S. Czarnecki, M. Hadzima-Nyarko, A. Chajec, Ł. Sadowski, Design of a machine learning model for the precise manufacturing of green cementitious composites modified with waste granite powder, Sci. Rep. 12 (1 2022) (2022) 12.
[22] A. Chajec, A. Chowaniec, A. Królicka, Ł. Sadowski, A. Żak, M. Piechowka-Mielnik, et al., Engineering of green cementitious composites modified with siliceous fly ash: understanding the importance of curing conditions, Construct. Build. Mater. 313 (2021).
[23] N. Shanmugasundaram, S. Praveenkumar, Influence of supplementary cementitious materials, curing conditions and mixing ratios on fresh and mechanical properties of engineered cementitious composites – a review, Construct. Build. Mater. 309 (2021).
[24] K. Yu, W. McGee, T.Y. Ng, H. Zhu, V.C. Li, 3D-printable engineered cementitious composites (3DP-ECC): fresh and hardened properties, Cement Concr. Res. 143 (2021).
[25] T. Xie, M.S. Mohamad Ali, M. Elchalakani, P. Visintin, Modelling fresh and hardened properties of self-compacting concrete containing supplementary cementitious materials using reactive moduli, Construct. Build. Mater. 272 (2021).
[26] F.P. Bos, P.J. Kruger, S.S. Lucas, van Zijl GPAG, Juxtaposing fresh material characterisation methods for buildability assessment of 3D printable cementitious mortars, Cement Concr. Compos. 120 (2021).
[27] L.A. Vergara, H.A. Colorado, Additive manufacturing of Portland cement pastes with additions of kaolin, superplastificant and calcium carbonate, Construct. Build. Mater. 248 (2020).
[28] B. Melugiri-Shankaramurthy, Y. Sargam, X. Zhang, W. Sun, K. Wang, H. Qin, Evaluation of cement paste containing recycled stainless steel powder for sustainable additive manufacturing, Construct. Build. Mater. 227 (2019).
[29] S.H. Bong, H. Du, Sustainable additive manufacturing of concrete with low-carbon materials, Sustain. Concr. Mater. Struct. (2024) 317–341, chapter 11.
[30] S.M.E. Sepasgozar, A. Shi, L. Yang, S. Shirowzhan, D.J. Edwards, Additive manufacturing applications for industry 4.0: a systematic critical review, Buildings 10 (2020), 231 2020;10.
[31] K. Kondepudi, K.V.L. Subramaniam, B. Nematollahi, S.H. Bong, J. Sanjayan, Study of particle packing and paste rheology in alkali activated mixtures to meet the rheology demands of 3D Concrete Printing, Cement Concr. Compos. 131 (2022).
[32] V. Mechtcherine, F.P. Bos, A. Perrot, W.R.L. da Silva, V.N. Nerella, S. Fataei, et al., Extrusion-based additive manufacturing with cement-based materials – production steps, processes, and their underlying physics: a review, Cement Concr. Res. 132 (2020).
[33] W.J. Long, C. Lin, J.L. Tao, T.H. Ye, Y. Fang, Printability and particle packing of 3D-printable limestone calcined clay cement composites, Construct. Build. Mater. 282 (2021).
[34] L. Shao, Z. liu, Q. Liu, H. Wang, C. Wang, W. Wang, et al., A new strategy to enhance 3D printability of cement-based materials: in-situ polymerization, Addit. Manuf. 89 (2024).
[35] S. Bhattacherjee, A.S. Basavaraj, A.V. Rahul, M. Santhanam, R. Gettu, B. Panda, et al., Sustainable materials for 3D concrete printing, Cement Concr. Compos. 122 (2021).
[36] L.K. Gupta, A.K. Vyas, Impact on mechanical properties of cement sand mortar containing waste granite powder, Construct. Build. Mater. 191 (2018).
[37] G. Rojo-López, S. Nunes, B. González-Fonteboa, F. Martínez-Abella, Quaternary blends of portland cement, metakaolin, biomass ash and granite powder for production of self-compacting concrete, J. Clean. Prod. 266 (2020).
[38] X. Gao, B. Yuan, Q.L.L. Yu, H.J.H.J.H. Brouwers, Characterization and application of municipal solid waste incineration (MSWI) bottom ash and waste granite powder in alkali activated slag, J. Clean. Prod. 164 (2017).
[39] X. Hao, Q. Zhu, D. Li, B. Zhang, W. Wang, A. Wang, Utilization of granite tailings: dry alkaline thermal activation and novel applications as cementitious materials, J. Build. Eng. 88 (2024).
[40] M.S. Savadkoohi, M. Reisi, Environmental protection based sustainable development by utilization of granite waste in Reactive Powder Concrete, J. Clean. Prod. 266 (2020).
[41] Z. Liu, M. Li, T.K.N. Quah, T.N. Wong, M.J. Tan, Comprehensive investigations on the relationship between the 3D concrete printing failure criterion and properties of fresh-state cementitious materials, Addit. Manuf. 76 (2023).
[42] T. Voigt, T. Malonn, S.P. Shah, Green and early age compressive strength of extruded cement mortar monitored with compression tests and ultrasonic techniques, Cement Concr. Res. 36 (2006).
[43] M.E. Boesch, S. Hellweg, Identifying improvement potentials in cement production with life cycle assessment, Environ. Sci. Technol. 44 (2010).
[44] Z.A. Rid, S.N.R. Shah, M.J. Memon, A.A. Jhatial, M.A. Keerio, W.I. Goh, Evaluation of combined utilization of marble dust powder and fly ash on the properties and sustainability of high-strength concrete, Environ. Sci. Pollut. Control Ser. 29 (2022).
[45] M. Zajac, J. Skocek, M Ben Haha, J. Deja, CO2 mineralization methods in cement and concrete industry, Energies 15 (2022) 3597, 2022;15.
[46] M. Sonebi, A. Abdalqader, T. Fayyad, A. Perrot, Y. Bai, Optimisation of rheological parameters, induced bleeding, permeability and mechanical properties of supersulfated cement grouts, Construct. Build. Mater. 262 (2020).
[47] A. Stempkowska, T. Gawenda, A. Chajec, Ł. Sadowski, Effect of granite powder grain size and grinding time of the properties of cementitious composites, Materials 15 (2022).
[48] B. Ganesh Kumar, M. Muthu, A. Chajec, Ł. Sadowski, V. Govindaraj, The effect of silica fume on the washout resistance of environmentally friendly underwater concrete with a high-volume of siliceous fly ash, Construct. Build. Mater. 327 (2022).
[49] D. Ruth Bola Oliveira, G. Leite, E. Possan, J. Marques Filho, Concrete powder waste as a substitution for Portland cement for environment-friendly cement production, Construct. Build. Mater. 397 (2023).
[50] M. Singh, K. Choudhary, A. Srivastava, K. Singh Sangwan, D. Bhunia, A study on environmental and economic impacts of using waste marble powder in concrete, J. Build. Eng. 13 (2017).
[51] D. Patel, R. Shrivastava, R.P. Tiwari, R.K. Yadav, Properties of cement mortar in substitution with waste fine glass powder and environmental impact study, J. Build. Eng. 27 (2020).
[52] Y. Kim, A. Hanif, M. Usman, M.J. Munir, S.M.S. Kazmi, S. Kim, Slag waste incorporation in high early strength concrete as cement replacement: environmental impact and influence on hydration & durability attributes, J. Clean. Prod. 172 (2018).