Influence of mineral additives on the rheological and strength properties of fine-grained concrete

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Abstract. The paper considers 4 types of mineral additives for concrete - metakaolin, silica fume, wollastonite and zeolite - and their influence on the rheological properties and strength of fine-grained concrete, in which part of the cement is replaced by a mineral additive. It is shown that the replacement of 5-10% of cement with active mineral additives with a specific surface area 1.5 times or more greater than the specific surface area of cement (metakaolin, silica fume) leads to a decrease in the flowability of the mixture in proportion to the increase in the amount of additive in the system. When replacing 10% of cement with additives, the specific surface of which relative to cement is in the range of 0.88-1.2 (wollastonite, zeolite), on the contrary, increases the flowability of the mixture. The strength of all samples with mineral additives at 28 days of age was greater than that of the control composition. An increase in strength by 1.7-1.76 times is noted for compositions with the replacement of 10% cement with metakaolin, wollastonite or zeolite.

1 Introduction

One of the tasks of modern building materials science is to reduce the proportion of cement material in the composition of concrete. This is primarily due to the high cost of cement, as well as the negative impact on the environment during its production. One way to solve this problem is to use mineral additives of natural or technogenic origin instead of a part of cement, since, depending on the type of additive, cement systems are given properties that improve their structural and mechanical characteristics.

In addition, mineral additives are actively used in compositions for construction 3D printing. Construction by the method of additive technologies, or construction 3D printing, is currently being actively developed, studied and implemented, which is confirmed by a large number of modern scientific articles on this topic. The most common used additives of technogenic origin are fly ash and silica fume, as well as their combined use [1-3]. Metakaolin, which is thermally processed kaolin clay, is also actively used. [4-5]. The problem in the reinforcement of structures arises during the construction of buildings and structures using the construction 3D printing method, since traditional reinforcement cannot be used due to the layer-by-layer laying of the material and the continuity of printing. The introduction of such a mineral additive as wollastonite, the grains of which are needle-

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shaped, contributes to the micro-reinforcement of the mixture and imparting increased flexural strength. A promising mineral additive in concrete for 3D printing is zeolite [6], a mineral that has a whole range of properties to improve the characteristics of fresh and hardened concrete. Materials for construction 3D printing are subject to increased requirements for rheological properties, so it is necessary to know the contribution of each of the additives used to change the flowability of fresh concrete.

Metakaolin is a highly active mineral additive with pozzolanic activity. Metakaolin is obtained by dehydration of enriched kaolin clays, resulting in the formation of active silica and alumina, the chemical formula of metakaolin is Al2O3·2SiO2. Active alumina, which is part of metakaolin, along with silica is able to bind lime and gypsum, so the addition of metakaolin increases the strength of binders such as Portland cement [7]. In addition, the introduction of metakaolin makes it possible to control the formation of ettringite in the early stages of concrete strength development, which makes it possible to reduce cracking and shrinkage deformations. The addition of metakaolin to the concrete mixture increases its homogeneity and cohesion due to the fineness of the filler, the indicators of mortar and water separation are reduced, which makes it possible to reduce the threshold for the minimum consumption of cement in concrete while ensuring the required strength [8].

Silica fume is an ultradispersed active mineral additive obtained by gas cleaning of furnaces in the production of silicon-containing alloys, that is, it is a waste of the metallurgical industry. It consists of spherical particles, the main component of the material is amorphous silicon dioxide. Due to the high specific surface area, which is several times greater than the specific surface area of cement, concretes containing silica fume have a denser and more compact structure. In hardening concrete, silica fume binds calcium hydroxide, compacting the structure of the cement stone with additional volumes of calcium hydrosilicates C–S–H and accelerating the hydration process. [9]. It is known that the addition of silica fume in small amounts contributes to imparting a plasticizing effect to the mixture due to the occurrence of total repulsive forces between its particles at high values of the specific surface [10]. Also, the introduction of microsilica additives into concretes increases the strength properties, frost resistance, water resistance and chemical resistance, and also reduces corrosion and the formation of efflorescence on the surface of the material.

Wollastonite is a natural calcium silicate with the molecular formula CaSiO3. It is a white powder, mainly consisting of needle-shaped crystals, has a hardness of 4.5-5 on the Mohs scale. One of the main advantages of wollastonite filler is its environmental friendliness, since the mineral does not contain asbestos-forming substances, is not carcinogenic and, accordingly, is classified as safe. When used in construction as a microfiller in concrete compositions, wollastonite has a reinforcing effect due to the acicular structure of the material particles, improves the strength characteristics of hardened concrete [11], reduces concrete shrinkage by covering microcracks and preventing their propagation [12]. Besides, the addition of wollastonite filler gives water resistance to materials using it, and has a biocidal effect.

Zeolites are a large group of minerals of volcanic-sedimentary origin, similar in composition and properties, aqueous calcium and sodium aluminosilicates from a subclass of frame silicates with a glass or pearl luster. They have unique properties, such as: molecular sieve effect, high ion-exchange, sorption and catalytic properties, which appear due to the presence of cavities and channels in the crystal lattice. Zeolites have pozzolanic properties and are among the naturally occurring pozzolans due to their reactive silica (SiO2) and alumina (Al2O3). These compounds, reacting with Portlandite during Portland cement hydration, convert it into C-S-H gels and aluminates, while the microstructure of the hardened cement concrete improves, and the water resistance of concrete increases [13]. Due to the introduction of natural zeolite into the formulation, it is possible to significantly reduce the content of expensive clinker without compromising the properties of cement [14-20]. Also, zeolites are used as a drying filler for building materials, they have the ability to absorb excess moisture in the cement mortar and gradually release it as needed, thereby contributing to the complete hydration of the cement. The addition of zeolite improves the setting of building mixtures and increases their strength [21].

The purpose of this work is to determine the effect of these mineral additives on the rheological properties of fine-grained concrete, as well as to study the strength properties of concrete with the replacement of part of the cement with a mineral additive.

2 Materials and methods

To determine the effect of the introduction of mineral additives on the rheological properties of a fresh mixture and the strength properties of hardened fine-grained concrete, 9 compositions were investigated. The control composition consists of cement, sand and water in a ratio of 1:2.5:0.5. In the following 8 compositions, 5% and 10% of cement were replaced with a mineral additive: MTK5 and MTK10 - replacement of 5% and 10% of cement with metakaolin; SF5 and SF10 - replacement of 5% and 10% of cement with microsilica; Woll5 and Woll10 - replacement of 5% and 10% of cement with wollastonite; Zeo5 and Zeo10 - replacement of 5% and 10% of cement with zeolite. The consumption of materials and the density of the studied compositions are presented in Table 1.

Table 1. Material's consumption.

Material	**Control**	**MTK5**	**MTK 10**	**SF5**	**SF10**	**Woll5**	**Woll 10**	**Zeo5**	**Zeo10**
Cement	1	0.95	0.9	0.95	0.9	0.95	0.9	0.95	0.9
MTK	-	0.05	0.10	-	-	-	-	-	-
SF	-	-	-	0.05	0.10	-	-	-	-
Wollastonite	-	-	-	-	-	0.05	0.10	-	-
Zeolite	-	-	-	-	-	-		0.05	0.10
Sand	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Water	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Density, kg/m3	2135.4	2239.6	2203.1	2213.5	2140.6	2265.6	2239.6	2270.8	2255.2

The main binder: Portland cement "Eurocem 500 Plus" CEM I 42.5 H produced by Peterburgcement LLC, Russia. The chemical and mineralogical composition is presented in Table 2.

Table 2. Chemical and mineralogical composition of cement.

MgO, %	**C_3S, %**	**C_2S, %**	**C_3A, %**	**C_4AF, %**
3.24	55.5	17.4	6.6	11.6

Sand: quartz construction sand, fraction 0-2 mm, fineness modulus 3.3, manufacturer - Klester System, Russia.

Metakaolin (MTK): amorphous aluminum silicate, highly active, white, grade VMK-45 according to TU 5729-097-12615988-2013, manufactured by SINERGO LLC, Chelyabinsk region, Russia. Loss on ignition is 1%, the pH of the aqueous suspension is 6.5. The chemical composition is presented in Table 3.

Table 3. Chemical composition of VMK-45 metakaolin.

Al_2O_3, %	Fe_2O_3, %	SiO_2, %
42.0	0.1	53

Silica fume (SF): waste from the metallurgical industry, produced in Poland.

Wollastonite (Woll): fractionated microwollastonite according to TU 5777-006-40705684-2003, product brand: MIVOLL 30-96, manufacturer: CJSC Geokom, Kaluga region, Russia. It is a fine dry friable powder of white color, with an average particle diameter of 26.7 microns, a maximum diameter of 92.7 microns, the ratio of particle length to diameter is 4:1. The loss on ignition is 1.3%, the mass fraction of water-soluble substances is 0.4%, pH 9.8. The chemical composition of the wollastonite filler is presented in Table 4.

Table 4. Chemical composition of the MIWOLL 30-96 additive.

CaO, %	MgO, %	SiO_2, %	Fe_2O_3, %	Al_2O_{3}, %
44.3	0.7	51.1	0.27	0.35

Zeolite (Zeo): natural volcanic zeolite according to TU 08.11.12-003-00327325428-2019, manufacturer "Zakarpatsky zeolite plant", Sokirnitskoye deposit, Ukraine. It is a light gray granules with a size of 0-0.5 mm. Porosity 38-48%, Mohs hardness 3.5-4, pH 6.8-7.2, water adsorption capacity 34-38%. Mineral and chemical composition are presented in Table 5.

Table 5. Zeolite properties.

Mineral composition, %									
Clinoptilolite	**X-ray Amorphous phase**	**Quartz**	**Plagioclase**	**Dolomite**	**Hydromica**				
75	8	9	3	1	4				
Chemical composition, mass fraction,%									
SiO_2	**Al_2O_3**	**CaO**	**K_2O**	**Fe_2O_3**	**MgO**	**Na_2O**	**TiO_2**	**MnO**	**P_2O_5**
71.4	11.9	1.26	3.02	1.14	0.45	2.086	0.16	0.034	0.02

For cement and mineral additives, the values of the specific surface area were determined by the air permeability method on an instrument of the Blaine type.

As a rheological test of a fresh mixture, standard methods for determining the flowability and density of mixtures were adopted:

- determination of the cone spread diameter on a shaking table according to GOST 310.4-81 [22];

- determination of the flowability of the concrete mixture by the depth of penetration of the steel cone according to GOST 5802-86 [23];

- determination of the immersion depth of the pestle of the Vicat apparatus according to GOST 310.3-76 [24].

To determine the compressive strength at the age of 7 and 28 days, samples-cubes with dimensions of 20x20x20 mm were made from each composition. Samples were kept at a temperature of 20 ± 2 °C and relative humidity of 90-95% for 7 and 28 days, and then tested for compressive strength using a ToniNORM testing machine with a modification of ToniPRAX.

3 Results and discussion

The results of determining the specific surface of cement and mineral additives are presented in Table 6.

Table 6. Specific surface area of powder materials.

Cement	Metakaolin	Silica fume	Wollastonite	Zeolite
2719.07 cm^2/g	4116.84 cm^2/g	44435.92 cm^2/g	2387.62 cm^2/g	3278.62 cm^2/g

Silica fume has the highest specific surface area among all the studied additives, the value of the specific surface area is 16.3 times higher than that of cement. The values of the specific surface of metakaolin and zeolite are higher than those of cement, by 1.5 and 1.2 times, respectively; the specific surface of wollastonite turned out to be 0.88 times less than the value for cement.

The results of determining the rheological characteristics of the control composition and compositions with mineral additives are presented in Table 7.

Table 7. Rheological characteristics of mixtures

	Control	MTK5	MTK 10	SF5	SF10	Woll5	Woll 10	Zeo5	Zeo10
Flow table test, mm	165.2	126	128.7	115.4	108.9	138.6	162.1	140.6	173.1
Cone penetration test, mm	43	25	20	17	15	32	39	41	39
Vicat depth, mm	12	15	4	0	1	10	21	4	19

According to the results presented in Table 7, there is a significant decrease in the flowabolity of the mixture when metakaolin and silica fume are added, and the flowability decreases in proportion to the increase in the content of the additive. This is due to the increased water consumption of these additives due to the high specific surface area. The values of the rheological characteristics of mixtures containing metakaolin MTK5 and MTK10 are less than those of the control composition, but according to the cone flow diameter spreading, they do not differ significantly for compositions with 5% and 10% additives. Silica fume, being the most finely dispersed additive among those studied, reduces the flowability of the mixture more than other additives. The replacement of 10% cement with wollastonite and zeolite additives (Woll10, Zeo10), on the contrary, leads to an increase in the flowability of the mixture, while the values for additives in the amount of 5% (Woll5, Zeo5) leads to a decrease in the flowability of mixtures.

The results of tests for compressive strength of samples aged 7 and 28 days are presented graphically in Figure 1.

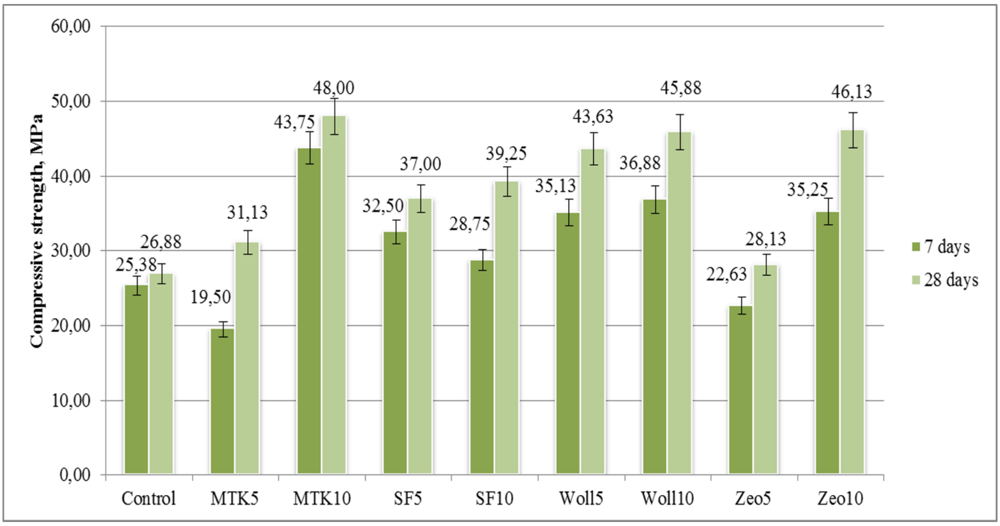

Fig. 1. 7 and 28 days compressive strength of samples.

At 7 days of age, the greatest increase in strength is observed in the composition with 10% metakaolin - the strength is 72.4% higher compared to the control composition. At the same time, the composition with 5% metakaolin showed a drop in strength by 23%. Compositions with the replacement of 5% and 10% of cement with silica fume showed an increase in strength by 28% and 13.3%, respectively. Compositions containing wollastonite showed an increase in strength in proportion to the percentage of addition of the additive. Thus, the strength of samples Woll5 and Woll10 is higher than the strength of the control composition by 39% and 45.3%, respectively. Zeo5 mixture - 10.8% strength reduction; Zeo10 - 38.9% strength increasing.

At 28 days of age, all samples with the replacement of part of the cement with mineral additives showed an increase in strength compared to the control composition. The greatest increase in strength relative to the control composition by 78.6% was achieved by 10% replacement of cement with metakaolin (MTK10 composition), however, the replacement of 5% binder with an additive (MTK5 composition) provided an increase of only 15.8%. The smallest increase in strength of 4.7% was typical for 5% replacement of cement with zeolite (composition Zeo5), but an increase in the content of the additive to 10% (composition Zeo10) increased the strength of concrete almost 2 times. The introduction of 5% and 10% of silica fume (compositions SF5, SF10) provided an increase in strength from 26.88 MPa to 37 MPa (an increase of 37.6%) and 39.25 MPa (an increase of 46%), respectively. In the framework of this work, the wollastonite filler had the most effective effect, since in a small dosage it provided an increase in compressive strength by 1.6 times.

4 Conclusion

In this work, such mineral additives in concrete as metakaolin, silica fume, wollastonite and zeolite were investigated. Additives were introduced into the cement-sand system in the amount of 5% and 10% by weight of cement with its replacement. The influence of these additives on the rheological properties of fresh mixtures, as well as on the strength properties of hardened fine-grained concrete at the age of 7 and 28 days, was investigated.

It is shown that the replacement of 5-10% of cement with active mineral additives with a specific surface area 1.5 times or more greater than the specific surface area of cement (metakaolin, silica fume) leads to a decrease in the flowability of the mixture in proportion to the increase in the amount of additive in the system. When replacing 10% of cement with additives, the specific surface of which relative to cement is in the range of 0.88-1.2 (wollastonite, zeolite), on the contrary, increases the flowability of the mixture.

The strength of all samples with mineral additives at 28 days of age was greater than that of the control composition. An increase in strength by 1.7-1.76 times is noted for compositions with the replacement of 10% cement with metakaolin, wollastonite or zeolite.

Based on the results obtained, it can be concluded that the use of these mineral additives is promising, since their introduction makes it possible to obtain concrete with a reduced content of the main binder without losing the required strength. Knowing the values of the specific surface of the mineral additive and the principle of its action, it is possible to control the rheological characteristics of the mixtures through the amount of the introduced additive. The data obtained in the work will be used in further studies of mineral additives, including for mathematical modeling of hydration processes in cement systems.

References

1. T. T. Le, S. A. Austin, S. Lim, R. A. Buswell, A. G. F. Gibb, T. Thorpe, Mater. Struct. **45**, 1221–1232 (2012)
2. A.V. Rahul, M. Santhanam, H. Meena, Z. Ghani, Const. and Build. Mater. **227**, 116710 (2019)
3. G. Ji, J. Xiao, P. Zhi, Yu-C. Wu, N. Han, Const. and Build. Mater., **325**, 126740 (2022)
4. V. Saruhan, M. Keskinateş, K. T. Felekoğlu, B. Felekoğlu, J. of Build. Eng. **54**, 104636 (2022)
5. Y. Chen, S. C. Figueiredo, Z. Li, Z. Chang, K. Jansen, O. Çopuroğlu, E. Schlangen, Cem. and Conc. Res. **132**, 106040 (2020)
6. A. Puzatova, M. Dmitrieva, V. Leitsin, A. Panfilova, M.Shinyaeva, Lecture Notes in Civil Engineering **282**, 291-298 (2022)
7. I. N. Shirinzade, E. H. Bashirov, I. D. Kurbanova, Stroitel'nye Materialy, **1–2**, 79–81 (2019) (In Russian)
8. L. I. Dvorkin, V. V. Zhitkovskiy, O. L. Dvorkin, A. R. Razumovskiy, Tekhnologii betonov, **9-10 (110-111)**, 21-24 (2015) (In Russian)
9. A. I. Politaeva, N. I. Eliseeva, G. I. Yakovlev, G. N. Pervushin, J. Havránek, O. Yu Mikhailova, Stroitel'nye Materialy, **2**, 49-55 (2015) (In Russian)
10. E. Velichko, Yu. Shumilina, Vestnik MGSU, **15**, 235-243 (2020) (In Russian)
11. G. I. Berdov, L. V. Il'ina, Sukhiye stroitel'nyye smesi, **6**, 40-42 (2017) (In Russian)
12. N. A. Nair, V. Sairam, J. of Clean. Prod. **283**, 124665 (2021)
13. N. N. Morozova, Kh. A. Kays, Vestnik Kazanskogo tekhnologicheskogo universiteta. **10(19)**, 64-68 (2016) (In Russian)
14. P. Rahul, D. P. Ravella, P.V. Chandra Sekhara Rao, Mat. Today: Proc. **60(1)**, 502-507 (2022)
15. X. Zheng, J. Zhang, X. Ding, H. Chu, J. Zhang, Const. and Build. Mater. **288**, 123062 (2021)
16. F. Dabbaghi, A. Sadeghi-Nik, N. Ali Libre, S. Nasrollahpour, Structures, **34**, 2617-2627 (2021)
17. M. Das, S. K. Adhikary, Z. Rudzionis, Mat. Today: Proc. **61(2)**, 237-242 (2022)

18. G. Sai Teja, D. P. Ravella, P. V. Chandra Sekhara Rao, Mat. Today: Proc. **43(2)**, 2355-2360 (2021)
19. P.V. Madhuri, B. Kameswara Rao, A. Chaitanya, Mat. Today: Proc. **47(15)**, 5369-5378 (2021)
20. A. Erfanimanesh, M.K. Sharbatdar, J. of Build. Eng. **32**, 101781 (2020)
21. B. D. Toturbiev, Trudy Instituta geologii Dagestanskogo nauchnogo tsentra RAN, **58**, 47-51 (2012) (In Russian)
22. GOST 310.4-81 Cements. Methods of bending and compression strength determination (Izdatelstvo standartov, Moscow, 1981) (In Russian)
23. GOST 5802-86 Mortars. Test methods (Standartinform, Moscow, 1986) (In Russian)
24. GOST 310.3–76 Cements. Methods for determination of standard consistency, times of setting and soundness (Izdatelstvo standartov, Moscow, 1976) (In Russian)