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Properties of concrete modified with mineral additives

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HIGHLIGHTS

- Mineral additives are among the most promising of concrete components in the development of new building materials.
- Replacement of cement with mineral additives can be increased concrete density, compressive strength, freeze-thaw resistance.
- Mineral additives can be used for modification of cementations systems.

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ABSTRACT

Concrete is the most widely used building material that is obtained by curing the mixture prepared from coarse and fine aggregates, cement and water. The properties of concrete depend on the quality and properties of the aggregates, w/c ratio, the uniformity of compression of the mix. Compressive strength of concrete is one of the most important properties. The present paper analyses the effect of mineral additive content on the properties of concrete. Materials used for the test: Portland cement CEM I 42.5 R, 0/4 fraction sand, 4/16 fraction gravel, mineral additive, polycarboxylatether based superplasticizer and tap water. Concrete mixes of 9 compositions were made by adding 0%, 2.5%, 5%, 7.5% and 10% of mineral additives by weight of cement. The tests revealed that the addition of mineral additives up to 10% increases the compressive strength of concrete. According to the test findings the compressive strength of hardened cement paste containing 10% of mineral additives increased 0.99% compared to the control mix. After 7 and 28 days of curing the ultrasonic pulse velocity in specimens with mineral additives increased 2.6% and 4.1% respectively. With the increase of mineral additives content up to 10%, water absorption of concrete reduces and the predicted freeze-thaw resistance increases.

1. Introduction

Different additives are used to control technological properties of concrete mixes as well as physical and mechanical properties of hardened concrete. It is important to investigate the effect of these additives on the physical and mechanical properties of concrete in order to achieve the effective performance of concrete and the required properties and durability of hardened concrete.

Mineral additives of concrete are dispersive natural and technical materials (mainly inorganic and non-water-soluble as opposed to chemical additives) described by the particle size less than 0.16 mm (as opposed to aggregates). With mineral additives added to the concrete mix the strength of concrete with the same or higher w/c ratio increases [1].

Mineral additives (zeolites, SiO_2 micro dust etc.) are some of the most prospective components of concrete in the development of new building materials such as high performance concretes, special concretes absorbing heavy metals or suppressing radioactive radiation. These additives modify and accelerate Portland cement hydration process, change its physical characteristics and mechanical behaviour. There a number of studies investigating the use of silica fume, coal, zeolites and ash as concrete supplements (pozzolanic additives) [2,3]. Zeolites contain a high content of SiO_2 and Al_2O_3. Silica dioxide and ash, like other pozzolanic materials, can increase concrete strength through the reaction of $Ca(OH)_2$ with pozzolans. Zeolites, like other pozzolanic materials, give higher strength to concrete compared to cement. Zeolites, however, also induce the occurrence of undesirable products such as alkalis and other complex compounds [4–6].

Researchers have found that zeolites of different modifications act as pozzolanic additives in concretes, during cement hydration increase CSH and CAH gel phases, which increase the resistance of Portland cement compositions to acids and sulphate corrosion and increase its durability [7].

Both natural zeolites of almost 50 types (clinoptilolite, mordenite, philipsite, ernonite, chabazite, vermiculite etc.) and artificial

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zeolites synthesized for special purposes (A, X, Y, L, ZSM-5 etc.) are widely used [8].

The use of natural zeolites as pozzolanic materials in construction dates back 3000 years, to the Greek and Roman periods when zeolites occurred as altered volcanic ash, tuff, and trass were used with lime in mortars and concretes for construction. The Romans used Neapolitan Yellow Tuff near Pozzuoli, Italy in construction of aqueducts, public buildings, and highways. The lime zeolite combination showed excellent cementitious property. Natural zeolite tuffs have been used for many years for cement pozzolans in Serbia, Germany, Italy, Bulgaria, China, and Russia [9,10].

The main building materials with zeolite production takes place in the following directions: binders, concrete, autoclaved lime products [11]. Synthetic zeolites can be used as adsorbents or conventional water softening agents, detergents [12,13].

The use of zeolite additives in cement structures is broadly described in scientific literature. According to Yun-Sheng, Chen-Lin, zeolite added at 15% to the cement mix increases the early-age strength of concrete. Hydration time is reduced with the use of zeolites [14].

Turkish researchers made tests with 5, 10, 20 and 40% of zeolite added to concrete mixes. The compressive strength was measured after 1, 2, 7 and 28 days of curing. The results showed that after 24 h of curing the compressive strength of concrete with zeolite additive was higher compared to control specimens. The same trend was observed after 2 and 7 days of curing [15].

Researchers Ahmadi and Shekarchi studied the effect of zeolite on mechanical characteristics and durability of concrete, compared to other cement additives. The tests showed that although the reaction of zeolite with portlandite was different than that of SiO_2 micro dust, zeolite had good pozzolanic activity. Besides, the researchers found that compressive strength, water absorption, oxygen permeability, chloride penetration and electric resistance characteristics of concrete with different content of zeolite were similar or even better than the same characteristics of the mix prepared with silica fume [16].

Canpolat and co-authors studied the characteristics of concrete where zeolite was used as an active mineral additives. 5–35% of cement was replaced by zeolite. The test results revealed that the highest compressive strength after 28 days of curing was achieved when 20% of zeolite was added. According to the tests, the optimal limit of fly ash used together with zeolite was 10–25% of zeolite and 5% of fly ash [17].

Latvian researchers have tested the compressive strength of regular concrete modified with aluminosilicate additives. The compressive strength of concrete was tested after 7, 28 and 155 days of curing. After 7 days concrete specimens with pozzolanic admixture had 15.2% higher compressive strength compared to the control specimen, after 28 days of curing in water the compressive strength increased more than fourfold, namely 26.38%. Later, the specimens were cured for 127 days in air at 20 °C. After 155 days of curing the compressive strength of specimens without the additive was 61.1 MPa, whereas the compressive strength of specimens with the additive was 67.4 MPa [18].

Researchers have also studied the properties of concrete modified with catalysts used in the oil industry. Stonys with co-authors have found that the compressive strength of concrete modified with 5% of catalyst increases 25%. Paya with co-authors also used the catalyst waste added at 20% to concrete mixes; the compressive strength of concrete was higher compared to control specimens [19,20]. Aleknavičius and Antanovič according that catalysts waste (zeolite) can be used for fire-resistant cement materials [4].

According to Yun-Sheng and co-authors, the compressive strength of concrete with 10% catalyst admixture increases 7–11% after 3–28 days of curing. The compressive strength of mortars containing 10% of catalyst additive increases 8–18% [14].

Chinese researchers Gai-Fei, Qiang and co-authors investigated the effect of silica fume and fly ash on the freeze-thaw resistance (durability) and porosity of concrete. The test results showed that the addition of pozzolanic additives to the concrete mix resulted in increased pore volume and the average pore size, thus better freeze-thaw resistance of concrete [21].

The aim of the study presented in this article was to determine the effect of mineral on the alumosilicate bares additives on the properties of hardened concrete and its durability.

2. Materials and research methods

Portland cement of type CEM I 42.5 R complying with EN 197-1:2001 requirements. Portland cement characteristics are presented in Table 1. Chemical composition of the cement, natural zeolite is presented in Table 2.

0/4 fraction sand complying with EN 12620:2003 requirements was used as the fine aggregate. 4/16 fraction gravel complying with EN 12620:2003 requirements was used as the coarse aggregate. Physical characteristics of the sand and gravel are presented in Table 3.

High quality polycarboxylatether based superplasticizer was used to improve the properties of concrete. This superplasticizer accelerates the initial setting and provides the early-age strength to concrete. It is used in the manufacturing of high-performance concretes. Clean water without harmful impurities that have a negative effect on the setting of concrete, namely potable water complying with EN 1008:2003, was used to prepare the concrete mix. Natural zeolite clinoptilolite $(Na,K,Ca)_{2\text{-}3}\,Al_3(Al,Si)_2Si_{13}O_{36}12H_2O$ is a microporous aluminosilicate hydrate of alkali metals or alkaline-earth metals. Clinoptilolite is used to absorb different materials from gas and solutions due to its unique properties: resistance to high temperatures, aggressive media, ionizing radiation, alkaline-earth metals and some heavy metals. It is also successfully used in the production of molecular sieves dues to its unique crystalline structure.

Additive of concrete (aluminosilicate) is a pozzolanic concrete additive based on amorphous alumo-silicate. It concerns a synthetically manufactured material, not an industrial by-product. Apart from a high uniformity long term availability is also ensured. New generation materials like this aluminosilicate based on special nanocrystallizers have been recently developed. These new materials improve the properties that are crucial for the durability of high-performance concrete. In addition to reducing chloride migration, an exceptional chemical and acid resistance of the high-performance concrete can be achieved with this aluminosilicate. The concrete structure is simultaneously reinforced right down to nano scale, density is improved and compressive and flexural strength as well as abrasion resistance of the high-performance concrete is increased.

Table 1
Portland cement characteristics.

Properties	Portland cement CEM I 42.5 R
Specific surface, cm^2/g	3700
Particle density, kg/m^3	3200
Bulk density, kg/m^3	1200
Standard consistency paste, %	25.4
Initial setting time, min	140
Final setting time, min	190
Compressive strength after 7 days, MPa	28.9
Compressive strength after 28 days, MPa	54.6

Table 2
Chemical composition of the cement and natural zeolite.

Portland cement, %									
SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	SO_3	Na_2O	H_2O	MgO	Other
20.76	6.12	3.37	63.50	1.00	0.8	0.3	–	–	4.45
Natural zeolite, %									
71.50	13.10	0.9	2.10	2.45	–	0.8	8.08	1.07	–

Table 3
Physical properties of gravel and sand.

Aggregates	Fraction	Characteristics	Test results
Gravel	4/16	Particle density, kg/m^3	2300
		Bulk density, kg/m^3	1582
		Water absorption, %	0.59
Sand	0/4	Particle density, kg/m^3	2650
		Bulk density, kg/m^3	1546
		Water absorption, %	1.30

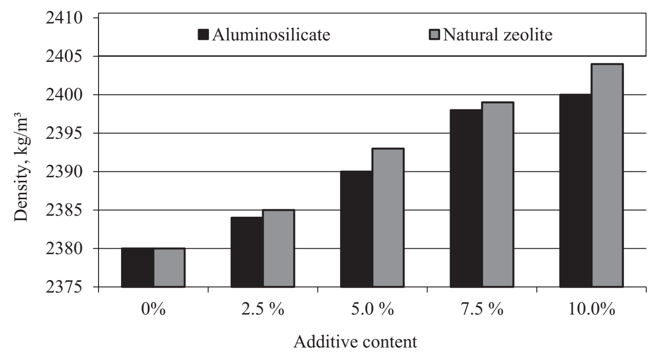

Fig. 1. Relationship between density and mineral additives content.

9 compositions of concrete mixes were manually prepared for the test under laboratory conditions. The compositions differed by mineral additives and their amount in the mix ranging from 0% to 10% by weight of cement. Compositions of cement mixes used to produce 1 m^3 of concrete are presented in Table 4.

Concrete mixes were made in the laboratory while forming the specimens in 100 × 100 × 100 mm metal forms. After 24 h the specimens were taken out from the forms and kept in water of 20 ± 2 °C for 28 days. The compressive strength of concrete cubes was tested according to EN 12390-3:2009 standard after 7, 28 days and 6 months of curing in water. The density of the specimens was measured according to EN 12390-7:2009 standard. Ultrasonic pulse velocity was measured according to EN 12504-4:2004 standard. Water absorbtion was measured after 4 days of soaking using the methods described in scientific literature [22]. Freeze-thaw resistance of concrete depends both on open porosity (the amount of capillary pores), and on closed porosity (air content in the mixture), and quantitatively can be determined by the frost resistance coefficient K_F [23]. Knowing the value of frost resistance coefficient K_F, the freeze-thaw resistance of the conglomerate can be predicted according to the function of conglomerate freeze-thaw resistance and frost resistance coefficient K_F [24].

3. Analysis of test results

Concrete density was measured during the tests and the test results are presented in Fig. 1. The highest density was observed in specimens containing 10% of mineral additives and the lowest density was recorded in specimens without any additives. The increase in density in specimens containing natural zeolite was 0.99% and in specimens containing aluminosilicate additive was 0.83%. The function in Fig. 1 illustrates how densities of concrete increase with higher content of mineral additives.

Compressive strength is the most important characteristics of structural materials. Figs. 2–4 illustrate the compressive strength of concrete after 7, 28 days and 6 months of curing.

After 7 days of curing the lowest compressive strength of 67.30 MPa was recorded in specimens without any mineral additives. In specimens containing 10% of natural zeolite the compressive strength of 77.40 MPa was recorded. It was found that in specimens containing natural zeolite the compressive strength after 7 days of curing increased 15,01%. In specimens with aluminosilicate, after 7 days of curing the highest compressive strength of 72.70 MPa was recorded in specimens containing 10% of aluminosilicate additive. The lowest compressive strength value was recorded in specimens without any mineral additive. It was found that in specimens containing aluminosilicate additive the compressive strength after 7 days of curing increased 8.02%. The analysis of results (Fig. 2) showed that with the increase of mineral additive content the compressive strength of concrete increases after 7 days of curing.

After 28 days of curing the lowest value of compressive strength of concrete of 70.10 MPa was recorded in specimens where no mineral additives were added. The highest value of compressive strength of 79.40 MPa was recorded in specimens where natural zeolite was added at 10%. It was found that with the use of natural zeolite the compressive strength after 28 days of curing increased 13.27%. After 7 days of curing the highest compressive strength of 79.0 MPa was recorded in specimens where 10% aluminosilicate was added. It was found that aluminosilicate additive increased the compressive strength 12.70% after 28 days of curing. The analysis

Table 4
Concrete mix 1 m^3 compositions.

Cement, kg	371	361.7	352.5	343.2	333.9	361.7	352.5	343.2	333.9
Sand – 381 kg in all mixtures									
Gravel – 1158 kg in all mixtures									
Natural zeolite, kg	–	–	–	–	–	9.3	18.6	27.9	37.1
Aluminosilicate, kg	–	9.3	18.6	27.9	37.1				
Admixture content, %	0	2.5	5.0	7.5	10.0	2.5	5.0	7.5	10.0
Water – 130 kg in all mixtures									
Polycarboxylatether based superplasticizer – 1.855 kg in all mixtures									
W/C	0.35	0.36	0.37	0.38	0.39	0.36	0.37	0.38	0.39
In all mixtures concrete slump class – S1									

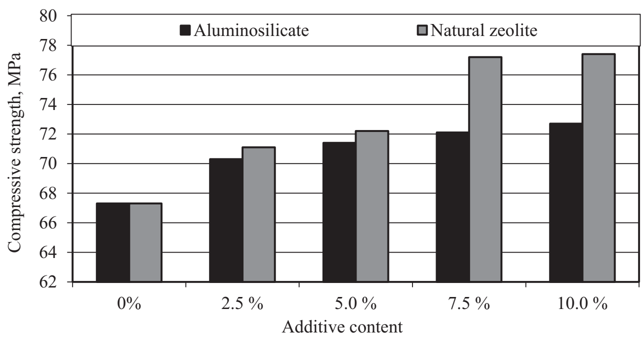

Fig. 2. Relationship between compressive strength and mineral additive content after 7 days of curing.

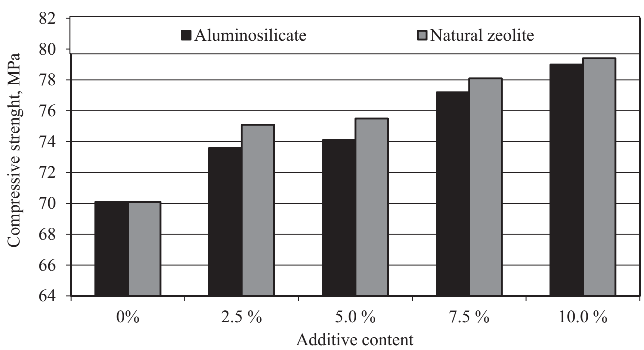

Fig. 3. Relationship between compressive strength and mineral additive content after 28 days of curing.

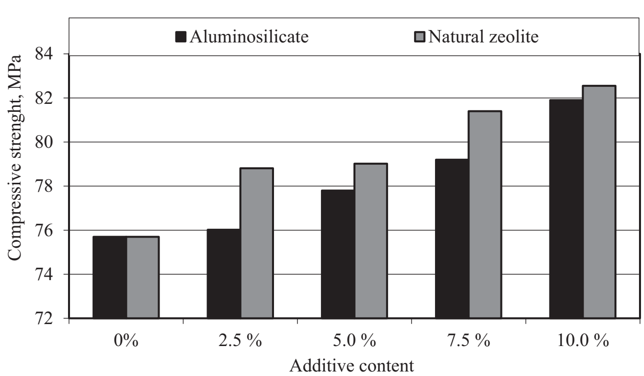

Fig. 4. Relationship between compressive strength and mineral additive content after 6 months of curing.

of results (Fig. 3) revealed that with higher content of mineral additives in the mix the compressive strength of concrete after 28 days of curing increases.

After 6 months of curing the lowest value of compressive strength of concrete of 70.70 MPa was recorded in specimens where no mineral additives were added. Meanwhile, the highest compressive strength value of 82.55 MPa was recorded in specimens where natural zeolite was added at 10%. It was found that with the use of natural zeolite the compressive strength after 6 months of curing increased 9.05%. The tests of specimens with aluminosilicate additive revealed that the highest compressive strength of 81.90 MPa was reached in specimens containing 10% of mineral additive. Specimens without the mineral additive had the lowest strength value. It was found that aluminosilicate additive increased the compressive strength 8.19% after 6 months of curing. The analysis of results (Fig. 4) revealed that higher content of mineral additives increase the compressive strength of concrete after 6 months of curing.

Ultrasonic pulse velocity was measured (Figs. 5 and 6) in concrete specimens after 7 and 28 days of curing. After 7 days of curing the ultrasonic pulse velocity in concrete (Fig. 5) was the lowest (4609 m/s) when no mineral additives were used. Meanwhile, the highest ultrasonic pulse velocity value of 4730 m/s was obtained when 10% of natural zeolite was used. It was found that with the use of natural zeolite the ultrasonic pulse velocity in concrete increased 2.6% after 7 days of curing. In specimens with aluminosilicate additive the highest ultrasonic pulse velocity of 4699 m/s was recorded in specimens with 10% of this mineral additive after 7 days of curing. Specimens without the mineral additive had the lowest ultrasonic pulse velocity value. It was found that after 7 days of curing the ultrasonic pulse velocity in specimens with aluminosilicate additive increased 1.9%. The analysis of results (Fig. 5) revealed that after 7 days of curing the ultrasonic pulse velocity in concrete increases with higher content of mineral additive.

After 28 days of curing the ultrasonic pulse velocity in concrete (Fig. 6) was the lowest (4734 m/s) when no mineral additives were used. Meanwhile, the highest ultrasonic pulse velocity value of 4930 m/s was obtained when 10% of natural zeolite was used. It was found that with the use of natural zeolite the ultrasonic pulse velocity in concrete increased 4.1% after 28 days of curing. In specimens with aluminosilicate additive the highest ultrasonic pulse velocity of 4902 m/s was recorded in specimens with 10% of this mineral additive after 28 days of curing. Specimens without the mineral additive had the lowest ultrasonic pulse velocity value. It was found that after 28 days of curing the ultrasonic pulse velocity in specimens with aluminosilicate additive increased 3.5%. The

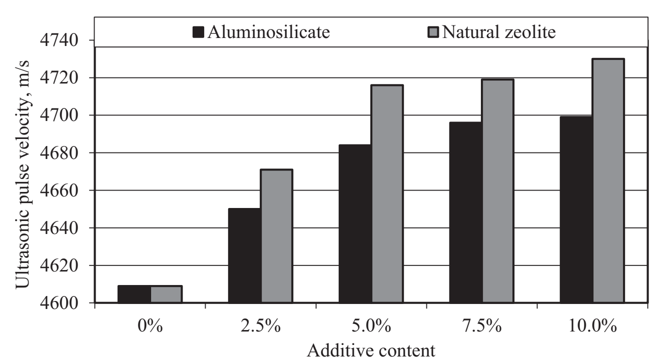

Fig. 5. Relationship between the ultrasonic pulse velocity and mineral additive content after 7 days of curing.

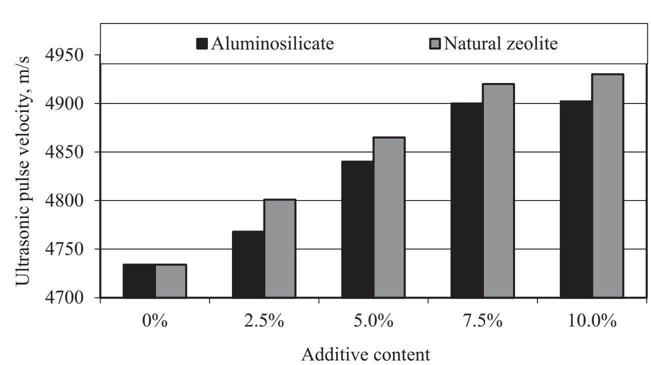

Fig. 6. Relationship between the ultrasonic pulse velocity and mineral additive content after 28 days of curing.

analysis of results (Fig. 6) revealed that after 28 days of curing the ultrasonic pulse velocity in concrete increases with higher content of mineral additives.

Ultrasonic pulse velocity in concrete specimens was also tested after 6 months of curing. According to the obtained results the highest ultrasonic pulse velocity value was 4945 m/s in specimens where 10% of natural zeolite was added. The lowest value of 4758 m/s was recorded in specimens without any additive. It was found that in specimens with natural zeolite the ultrasonic pulse velocity increased 3.8% after 6 months of curing. In the case of aluminosilicate additive, after 6 months of curing the highest ultrasonic pulse velocity was 4938 m/s in specimens containing 10% of mineral additive. The lowest value of ultrasonic pulse velocity was recorded in specimens without any additive. It was found that in specimens with aluminosilicate additive the ultrasonic pulse velocity increased 3.6% after 6 months of curing. The analysis of results (Fig. 7) revealed that after 6 months of curing the ultrasonic pulse velocity in concrete increases with higher content of mineral additives.

Water absorption of the specimens was tested (Fig. 8). The obtained results showed that the lowest value 0.88% is obtained in specimens containing 10% of natural zeolite. The highest absorption value of 3.21% was recorded in specimens without any additive. It was found that the absorption decreased 3.64 times when natural zeolite was used. In the case of aluminosilicate the lowest absorption of 1.38% was recorded in specimens with 10% of mineral additive. The highest absorption value was recorded in specimens without any zeolite additive. It was found that in specimens with aluminosilicate additive the absorption decreased 2.33 times. The analysis of results showed (Fig. 8) that water absorption of concrete reduces with higher content of mineral additives.

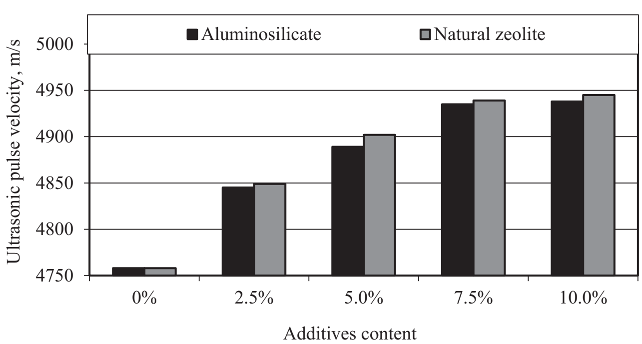

Fig. 7. Relationship between the ultrasonic pulse velocity and mineral additive content after 6 months of curing.

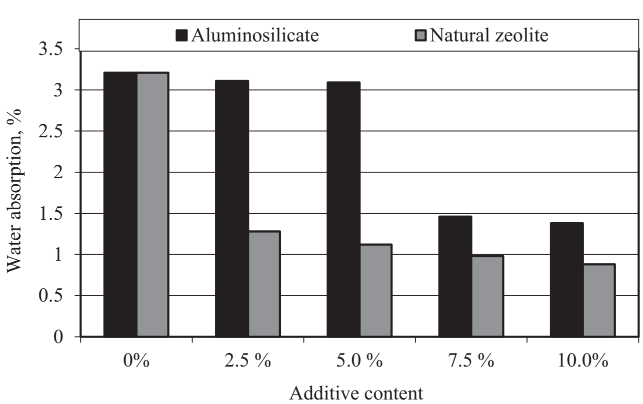

Fig. 8. Relationship between the absorption and mineral additive content in concrete.

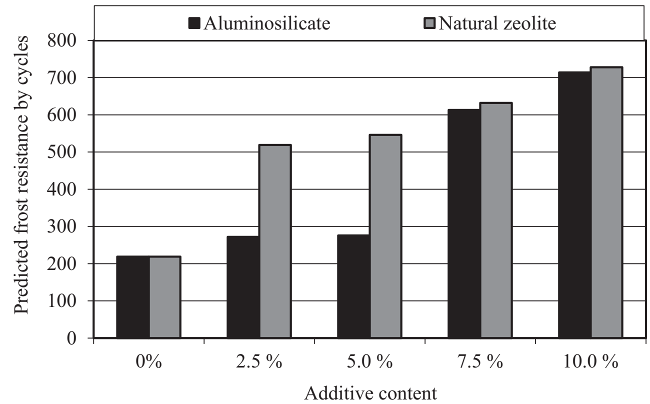

Fig. 9. Relationship between the predicted freeze-thaw resistance in cycles and mineral additive content.

Freeze-thaw resistance of concrete in cycles was predicted according to frost resistance coefficient K_F. The relationship between the predicted freeze-thaw resistance in cycles and the content of mineral additives is presented in Fig. 9. The obtained results showed that the highest freeze-thaw resistance value 728 was obtained in specimens containing 10% of natural zeolite. The lowest freeze-thaw resistance value 219 was recorded in specimens without the additive. It was found that with natural zeolite the predicted freeze-thaw resistance increased 3.32 times. The highest predicted freeze-thaw resistance of specimens with aluminosilicate was 714 cycles when 10% of mineral additive was added. It was found that with the use of aluminosilicate additive the predicted freeze-thaw resistance increased 3.26 times. The analysis of results (Fig. 9) showed that freeze-thaw resistance and durability of concrete increases with higher content of mineral additives.

4. Conclusions

1. The tests have shown that with the increase of mineral additive content up to 10% the compressive strength of concrete after 7, 28 days and 6 months of curing increased up to 15.01%, 13.27%, 9.05% respectively.
2. It was found that by adding 10% of mineral additives into concrete mix the density of hardened concrete increased 0.99% compared to the control specimens, ultrasonic pulse velocity after 7 and 28 days of curing increased 2.6% ir 4.1% respectively.
3. It was found that natural zeolite added to the concrete mix reduced water absorption of hardened concrete 3.64 times, whereas aluminosilicate additive caused water absorption to reduce 2.33 times. The analysis of results revealed that water absorption of concrete diminishes with higher content of mineral additives.
4. The tests have shown that in specimens containing natural zeolite the predicted freeze-thaw resistance in cycles increased 3.32 times and in specimens containing aluminosilicate additive the predicted freeze-thaw resistance increased 3.26 times. The analysis of results showed that the predicted freeze-thaw resistance in cycles increases with higher content of mineral additives.

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