

T. Markiv*, O. Huniak, Kh. Sobol
Lviv Polytechnic National University,
Department of automobile roads,
* Department of building production

OPTIMIZATION OF CONCRETE COMPOSITION WITH ADDITION OF ZEOLITIC TUFF

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In this article concrete mixture composition with the additives of zeolitic tuff and superplasticizer was optimized by the method of mathematical planning of experiment. The research reveals that use of optimal amount of zeolitic tuff results in increasing strength of concrete at later age of hardening and does not influence significantly the water absorption, porosity and freezing temperature of the liquid phase of fresh frozen concrete mixture.

Key words: concrete, zeolitic tuff, superplasticizer, chemical admixture

Методом математичного планування експерименту оптимізовано склад бетонної суміші з добавкою цеолітового туфу та суперпластифікатора. Дослідження показали, що використання оптимальної кількості цеолітових туфів призводить до зростання міцності у пізніші терміни тверднення і несуттєво впливає на водопоглинання, пористість і температуру замерзання рідкої фази свіжозамороженої бетонної суміші.

Ключові слова: бетон, цеолітовий туф, суперпластифікатор, хімічна добавка

Introduction

Zeolitic tuffs are widely used as an additive in constructions since ancient times, especially as a supplementary cementitious material for concrete production. In most cases, natural zeolites possess proper pozzolanic activity and their use as partial replacement of Portland cement leads to enhancement of concrete composite durability. However, due to the various types, structures and purities of natural zeolites, the obtained results are not expected to be similar in all experiments [1-3]. The replacement of cement by zeolite reduces slump and increases water demand of fresh concrete. This requires using of superplasticizer to compensate workability decrease of fresh concrete and strength of hardened concrete [4, 6]. From the practical point of view, optimization of the amount of zeolite and superplasticizer in concrete allows to obtain the best solution providing designed properties for the concretes. That is why computational materials science can be validly used when it comes to search for optimal technological parameters and compositions of materials with required complex of properties. Furthermore it is expedient to use it when solution can't be found directly in physical experiment or off the computer technology and without too much time and financial recourses spent. The means of computational materials science based on experimental-statistical models can substantially help in solving the problems of optimization of concrete compositions with mineral additives and chemical admixtures [7].

Analytical research

Natural zeolite, which involves crystalline aluminosilicates composed of a three dimensional arrangement of silicon-oxygen (SiO_4) and aluminum-oxygen (AlO_4) tetrahedra, is widely used in some regions of the world as a mineral additive. Clinoptilolite, heulandite, analcime, chabazite and mordenite are the most common types of natural zeolite minerals on the earth. It is known that they show considerable pozzolanic activity despite their distinct crystalline structure [4, 5]. Uzal et al. [8, 9] reported that the clinoptilolite zeolite possesses a lime reactivity which is comparable to silica fume and higher than that of fly ash, and they also concluded that the high reactivity of the clinoptilolite is attributed to its specific surface area which depends on grinding method and its durations well as its reactive SiO_2 content. Zeolitic

tuffs have a lot of small pores and channels with large specific surface area of 35–45 m²/g (internal and external) and ability to absorb and lose water up to 30% of its weight. Large quantities of reactive SiO₂ and Al₂O₃ in zeolitic tuff, which react with Ca(OH)₂ to form further calcium hydrosilicate and calcium hydroaluminosilicate, are responsible for pozzolanic activity of this mineral additive [2, 4]. These result in growth of compressive strength of concrete incorporating zeolite and enhances durability of conventional concrete by reducing concrete permeability and especially improves resistance to alkali-aggregate reaction [8, 10].

Materials and methods. A clinoptilolite type of natural zeolitic tuff from Sokyrnytsia, Zakarpattia region of Ukraine and commercially available Portland cement PC I-500 (Heidelberg cement, Dniprodzerzhynsk, Ukraine), superplasticizer (sikaplast 520) and air-entraining agent (Sikanol A) were used in this study.

The chemical composition and mineralogical compounds of the Portland cement and the natural zeolite used in this study are presented in table 1. It should be noted, that specific surface of zeolitic tuff was 500 m²/kg.

Table 1

Chemical composition and mineralogical compounds of Portland cement and natural zeolite

Components of concrete	Oxides content, wt. %									Mineralogical composition, wt. %			
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	insoluble residue	C ₂ S	C ₃ S	C ₃ A	C ₄ AF
Cement	22,04	4,85	3,59	65,10	1,44	0,49	-	-	1,24	19,0	59,0	6,8	10,9
Zeolite	79,63	14,59	0,76	3,86	-	-	0,44	0,72	-	-	-	-	-

Physical and mechanical properties of the Portland cement are presented in table 2.

Table 2

Physical and mechanical properties of the Portland cement

Specific surface, m ² /kg	Residue on sieve 008, %	Water demand, %	Setting time, min		Compressive strength, MPa	
			initial	final	2 days	28 days
431	0,2	29,5	160	210	25,4	52,1

In addition to natural zeolite and Portland cement, fine (0-5 mm) and coarse (5–20 mm) aggregates meeting the requirements of Ukrainian standard were used in this investigation.

Physico-mechanical tests of cements and concretes were carried out under known common procedures.

The purpose and objectives of the study. Aim of the work is to optimize amount of zeolitic tuff and superplasticizer in concrete and study its properties.

Experimental research. For optimization of zeolite and superplasticizer content in concrete, method of statistical mathematical processing of the results - the method of orthogonal central composite design was used. Optimization of the amount of zeolitic tuff, as a substitute of cement in concrete, opens the way for direct formation of phase composition of hydration products which contribute to increase of the compressive strength.

Results of the investigations as well as the concrete mixture proportions are presented in Table 3. Research studies have shown that no segregation or bleeding was observed in the fresh concretes. As shown in Table 3, in general, the strength of concrete depends on the content of zeolite and superplasticizer. It should also be noticed, that at dosage of superplasticizer about 1 wt.%, the strength of concrete in all terms of curing is declined. However, the percentage of strength reduction was generally decreased over time, which can be related to the pozzolanic activity of natural zeolite.

Planning matrix and results of the complete two factor experiment

No.	Planningmatrix		Content of concrete components, kg/m ³		Compressive strength (MPa)		
	Superplasticizer (x ₁)	Zeolite (x ₂)	Portland cement	Natural zeolite	3 days	7 days	28 days
1	0,7	4	326,4	13,6	32,2	40,4	55,8
2	1,0	4	312,8	13,6	24,7	32,7	46,9
3	0,7	8	326,4	27,2	33,3	38,3	57,9
4	1,0	8	312,8	27,2	19,9	28,2	44,4
5	1,0	0	312,8	0	21,4	32,7	47,1
6	0,7	0	326,4	0	26,2	36,1	47,8
7	0,4	8	340,0	27,2	25,5	32,1	46,2
8	0,4	4	340,0	13,6	29,7	36,7	56,8
9	0,4	0	340,0	0	28,9	37,9	50,5

By means of experimental statistical modeling method in given interval of change of a quantitative ratio of zeolite (0; 4; 8 wt. %) and superplasticizer Sikaplast (0,4; 0,7; 1,0 wt.%) in concrete, by mathematical processing there were received regressive equations of compressive strength of concrete. Based on experimental data, regression equations in coded variables that characterize the effect of the studied factors on the strength of concrete were obtained:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2$$

$$Y_3 = 34,40 - 0,36X_1 + 0,83X_2 - 3,50 X_1^2 - 10,00 X_2^2 - 0,57 X_1 X_2$$

$$Y_7 = 39,85 - 0,95X_1 - 1,41X_2 - 2,58 X_1^2 - 5,18X_2^2 - 0,67 X_1 X_2$$

$$Y_{28} = 61,33 + 1,49X_1 + 0,31X_2 - 10,21 X_1^2 - 6,74X_2^2 - 0,13 X_1 X_2$$

Analysis of the regression coefficients indicates a positive combined effect of zeolite and superplasticizer on concrete strength at all ages, as it is evidenced by positive signs in corresponding regression coefficients. Analysis of the obtained mathematical dependences and their graphical interpretation (fig. 1) allow determining optimal amount of zeolite and chemical admixture (SikaPlast 520), which are respectively 4 wt. % of zeolite and 0.7 wt.% of sikaplast 520 after 7 day sharding, but after 28 days the area of optimal compositions shifted towards growth of zeolite (8 wt.%) and optimum content of superplasticizer remained unchanged (0.7 wt.%).

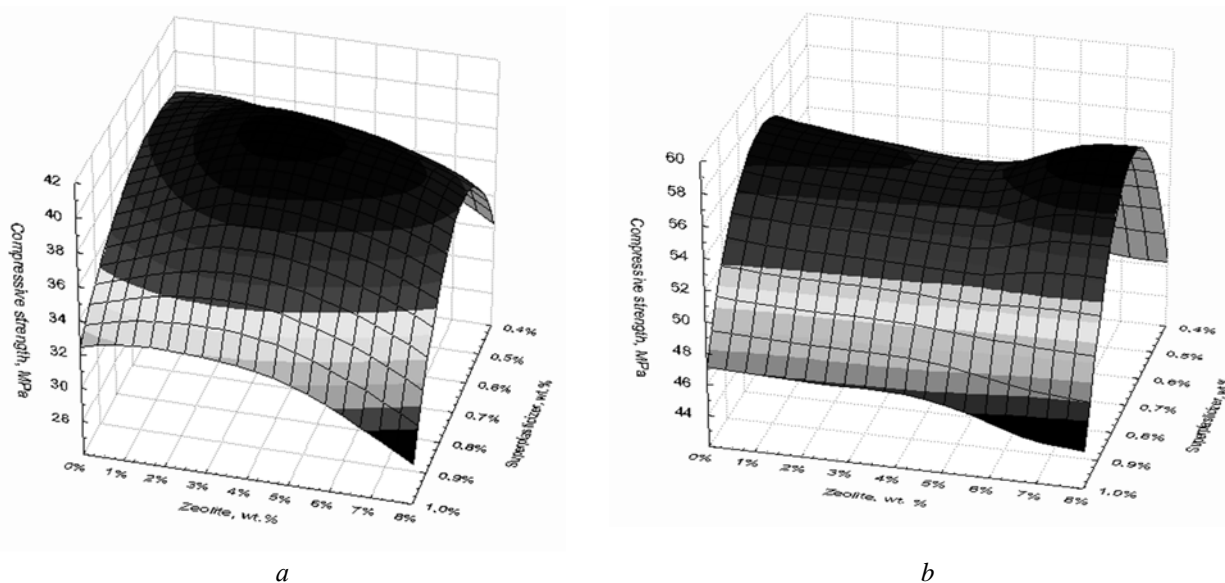


Fig. 1. The response surfaces of concrete strength after 7 (a) and 28 (b) days of cure

Important parameters that affect the durability of concrete are water absorption and porosity. Research showed that with the increase of zeolite content in the concrete water absorption (fig. 2, a, b) and porosity (fig. 3, a, b) increased about 6-10 %. At the same time, increasing the content of superplasticizer in concrete leads to compaction of the fresh concrete and reduction of water absorption and porosity about 10-14%.

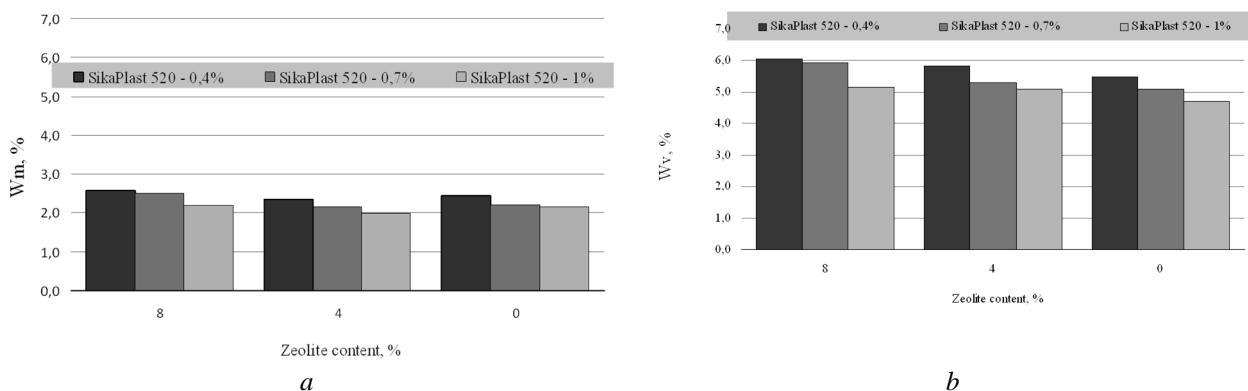


Fig. 2. Water absorption of concretes with different amount of zeolite and plasticizer by weight (a) and by volume (b)

Total porosity of concretes incorporating 8 wt.% of zeolite is higher in comparison with concrete without zeolite. Results shown, that volume of closed pores is lower than opened ones, which can influence expansion deformations and the freezing temperature of the liquid phase of fresh concrete mixture.

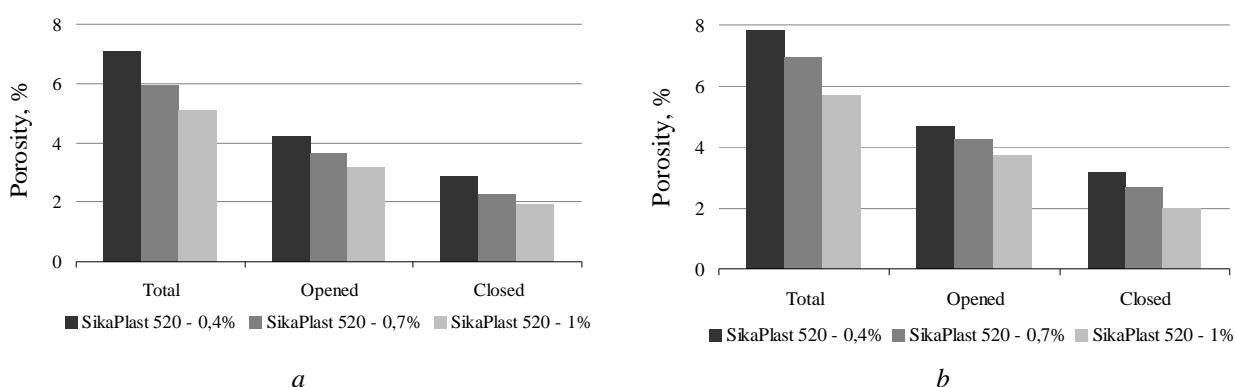


Fig. 3. Porosity of concrete without (a) and containing 8% (b) of zeolitic tuff

According to mathematical processing of the compressive strength results, the area of optimal compositions was shifted towards growth of cement replacement in concrete by zeolite about 8 wt.% and was not maximum. Jana [11] found that incorporating in concretes 0, 10, 20, 30, and 40 percent of zeolite by mass of total cementitious materials, namely 10 percent cement replacement level by zeolite, showed strength benefit compared to the control mixture, that is why further research of concrete incorporating 10 wt.% of zeolite was carried out .

Expansion deformations and the freezing temperature of the liquid phase of fresh frozen fine-grained fresh concrete incorporating 10 wt.% of zeolite was researched. As shown in fig. 4, replacement 10 wt.% of cement by natural zeolite has almost no effect on the freezing point of water in comparison with the composition without additive, but after thawing residual expansion deformations decrease from 15,24 to 12,62 mm/m.

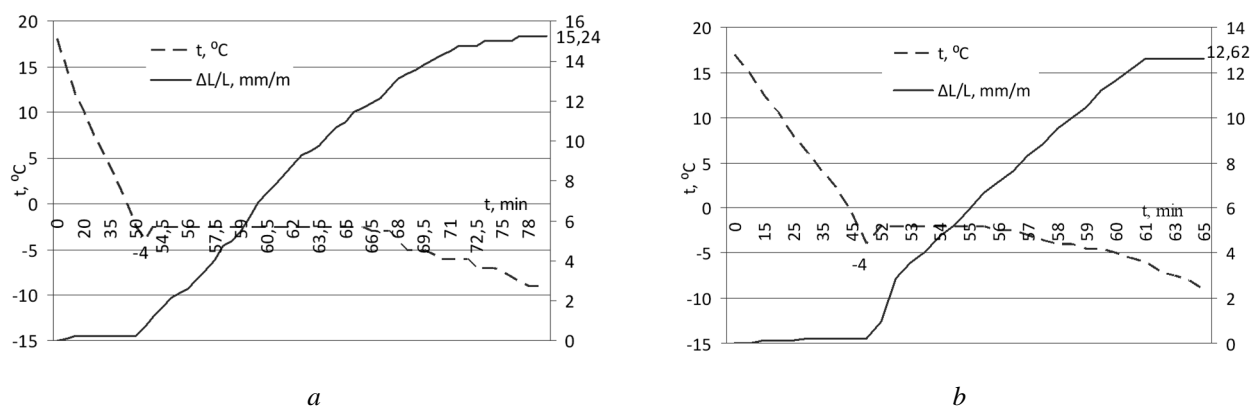


Fig. 4. Expansion deformations and the freezing temperature of the liquid phase of fresh frozen fine-grained fresh concrete mixture (C:S=1:2, fluidity=160 mm)

Conclusions. According to carried out researches, complex incorporation and optimization in concrete zeolitic tuff and chemical modifiers allows to improve technological properties of fresh concrete mixtures and increase the strength of hardened concretes in later ages. This behavior is related to the pozzolanic activity of natural zeolite. Water absorption and porosity of concretes incorporating zeolitic tuff increased about 6-10%. Usage of zeolitic tuff in concretes does not influence the freezing temperature of the liquid phase of fresh frozen concrete mixture, but after thawing residual expansion deformations decrease about 17%.

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