CONTACT HARDENING BINDERS USING ROCK CRUSHING WASTE

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ABSTRACT

This article is devoted to the production of pressed materials based on mechanically activated granite. The ability of granite after mechanical activation in the presence of sulphate activator to form a contact hardening binder - sulphopetrocement is studied. The influence of mechanical and sulphate activation factors, pressing parameters and hardening conditions on the binder properties has been studied.

Keywords: contact hardening binder, granite powders, sulphopetrocement. mechanical activation, phosphogypsum.

INTRODUCTION

To date, classifications of mineral binders have been proposed according to a number of basic features: production methods, hardening conditions, chemical and physicochemical processes occurring during hardening and other [1]. Contact hardening binders are included in the group of geopolymers. The founder of geopolymer technology is the French scientist Joseph Davidovits [2], who proposed a new material obtained by dissolving natural and artificial aluminosilicates in an alkaline medium, followed by condensation and the formation of a three-dimensional frame structure. As mineral components to produce geopolymers, aluminosilicate materials of both natural (rocks) and technogenic origin (slags, ash, microsilica and other production wastes) are used [3 - 8].

A significant contribution to the development of the theory of contact hardening binders was made by V. Glukhovsky and his scientific school. As a result of research at the Kiev Engineering and Construction Institute, he proposed two groups of substances that can serve to obtain contact hardening binders [9]: anhydrous substances of unstable structure activated by alkalis (blast furnace and electrothermophosphorus slags, highly basic fuel ash) and silicate substances in the form of natural hydroaluminosilicates, coal preparation waste, asbestos production and other industries.

In accordance with the results of studies by V. Glukhovsky, P. Krivenko and R. Runova [10 - 12], the main principle to produce contact hardening binders is to obtain, with minimal energy consumption, a dispersed substance in an amorphous or unstable crystalline state. In addition to the composition and degree of instability of the structure of the starting materials, the properties of contact hardening binders are determined by the degree of convergence of dispersed particles during forming.

One of the directions for obtaining contact hardening binders, concretes and mortars based on them is the use of rock crushing wastes as raw materials. The practice of construction work has shown that several natural stone materials such as marble, granite, dunite, chrysotile, etc., after their fine grinding in the presence of moisture, acquire the ability to be cemented [13, 14]. It has been observed, for example, that because of abrasion of crushed stone laid in a road, the resulting dust and stone chips eventually harden to form a hard road surface.

The first attempt to obtain building materials based on moistened powders of some rocks, mainly of metamorphic origin, was made by V.N. Young [15]. He conducted tests on pressed samples of cemented rocks and showed the possibility of achieving a strength of 10 - 15 MPa. V.N. Young explained the effect obtained by the processes of surface hydration of grains of the initial rocks.

In our work, the main results of which are presented in this article, we show the possibility of obtaining and significantly improving the properties of pressed materials from rock crushing waste using mechanical and chemical activation of dispersed powders.

EXPERIMENTAL

The main studies were carried out with the use of granite crushing waste from three Ukrainian deposits. Chemical and mineral compositions of the studied granite samples are given in Table 1 and Table 2, physical properties - in Table 3.

Samples were presented in the form of screenings crushed granite when receiving crushed stone. The fineness modulus of the studied granite screenings was in the range of 3.1 - 3.5. As a chemical hardening activator, phosphogypsum, a waste product formed during the production of phosphoric acid by the dihydrate method, was used. The used phosphogypsum was formed at the Rivne JSC "Azot" (Ukraine) and contains $CaSO_4$ - 94 %, phosphates according to P_2O_5 - 2.3 %, fluorides - 0.4 %.

Grinding and mechanical activation of the binders obtained were carried out in a laboratory ball mill with the measurement of the specific surface by the Blaine's air permeability method [16]. Determination of the strength of binders was carried out on beam specimens 40 ´ 40 ´ 160 mm in accordance with EN 196-1 [17]. Features of the microstructure of artificial stone on contact hardening binders were studied using optical microscopy. The joint influence of technological factors during complex mechanochemical activation was

Table 1. Chemical composition of granites.

Symbol of granite	Oxides, % by weight													
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	H_2O	LOI
G-1	66.34	0.40	15.35	0.60	4.98	0.03	1.90	1.91	3.07	3.01	0.09	0.29	0.33	1.20
G-2	72.85	0.30	12.48	1.21	2.46	-	0.20	1.40	2.36	5.47	-	-	-	0.41
G-3	72.97	0.30	13.60	0.97	0.58	-	0.46	1.29	3.91	5.18	0.08	-	0.15	0.60

Note: LOI - loss on ignition.

Table 2. Mineral composition of granites.

Symbol of granite	Minerales, % by weight				
	Plagioclase (albite, oligoclase)	Potassium feldspar (microcline)	Quartz	Mica (biotite)	Others
G-1	32.1	32.3	26.5	5.9	3.2
G-2	31.2	33.8	28.5	3.9	2.6
G-3	24.7	34.5	33.1	3.3	4.4

Table 3. Physical properties of granites.

Symbol of granite	Average density, g cm^{-3}	Density, g cm^{-3}	Total porosity, %	Thermal conductivity, W m^{-1} K^{-1}	Compressive strength R_c, MPa
G-1	2.70	2.77	2.6	2.79	124.5
G-2	2.64	2.68	1.5	3.06	151.3
G-3	2.64	2.69	1.6	3.41	159.6

studied using the methods of mathematical planning of experiments [18], followed by obtaining and analysis of experimental-statistical models.

RESULTS AND DISCUSSION

At the first study stage, the hardening ability of granite powders was determined at various values of moisture and compression pressure. The test results are shown in Fig. 1 and Fig. 2. They show the possibility of achieving, after 7 days, pressed specimens of granite powders (petrocement) with an average specific surface area of 350 $m^2 kg^{-1}$, moisture 7 % and a pressure of 20 MPa, compressive strength up to 1.7 MPa, 50 MPa - up to 4 MPa.

With increasing duration of hardening the intensity of growth of strength of pressed granite specimens' fades. In contrast to strength, the values of water resistance have a steady upward trend, indisputably indicating the occurrence of structure-forming processes. The water resistance is characterized by the water resistance coefficient (WRC). The water resistance coefficient is the ratio of material strength in the water-saturated state to its dry strength. The water

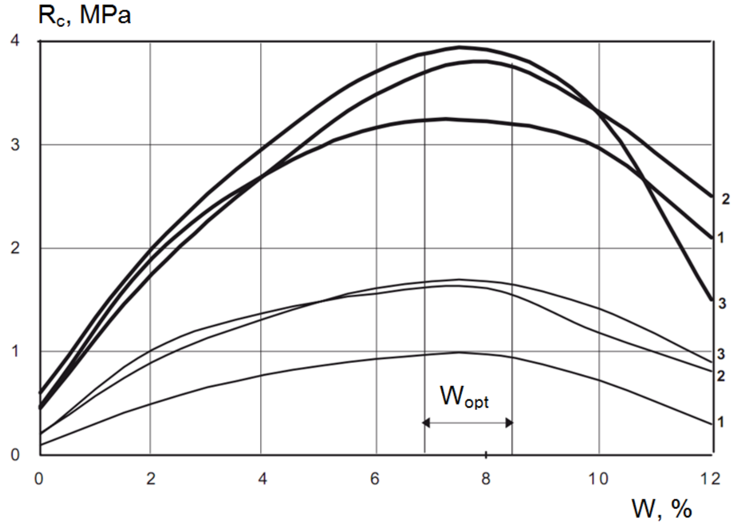


Fig. 1. Effect of powder moisture (W) on compressive strength (Rc) of specimens: 1, 2, 3 - granite numbers, bold lines - compression pressure is 20 MPa, thin lines - compression pressure is 50 MPa.

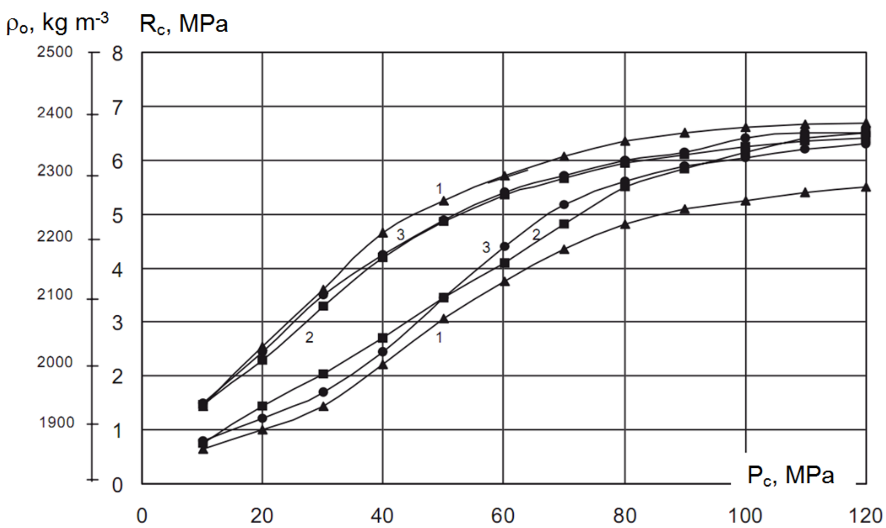


Fig. 2. Dependence of compressive strength (R_c) and average density (ρ_o) of specimens on compression pressure (P_c): 1, 2, 3 - granite numbers, upper lines - density, lower lines - strength.

resistance coefficient of pressed specimens from the studied granites after 6 months exceeds 0.6 (Table 4).

Significant increase in density of specimens is observed with the increase of compression pressure up to 60 - 70 MPa with subsequent stabilization. The increase of compression pressure up to 100 MPa (Fig. 2), leads to the increase of strength of wetted specimens of petrocement at the age of 7 days up to 6 - 6.5 MPa, with corresponding increase of specimens' density.

The obtained results indicate the possibility of dispersed and moistened granite to form an artificial stone as a result of compression. At the same time, the absolute strength values of such stone are not high enough for its wide practical use. From this point of view, to improve the physical and mechanical characteristics and promote the processes of structure formation, we used the effect of sulfate (gypsum) activation of dispersed aluminosilicate rocks [19], by introducing sulfate salt-crystalline hydrate additives into their composition. This effect is manifested in the stimulation of processes of formation of crystallization contacts between particles of aluminosilicates and sulfocrystalline hydrates during hardening of pre-wetted pressed material - sulfopetrocement (SPC).

As can be seen from the data in Table 5, sulfate-activated dispersed granites have significantly higher strength compared with non-activated. Already with the introduction of only 2.5 % of the sulfate additive strength increases on average by 3 times. For all types of granite, it can be concluded that a sharp increase in strength is observed when the additive content is increased up to 20 %, after which its effect decreases.

The microphotographs (Fig. 3) show the characteristic microstructures of sulfopetrocement specimens based on granite, made by pressing. The maximum water resistance of the SPC specimens, as can be seen from Table 6, is achieved with a sulfate additive content of about 5 %.

The most evident growth of the strength of SPC specimens is observed with an increase in the compression pressure (P_c) in the range of 40-80 MPa (Fig. 4a). Average density (r_o) naturally decreases with the increase of phosphogypsum content (Fig. 4b), while the dependence r_o on P_c acquires a rectilinear character. In contrast to the strength, water resistance of SPC characterized by WRC depends less significantly on the compression pressure at the values more than 40 MPa (Fig. 4c).

All the above studies were conducted with SPC obtained by grinding granite and sulfate additive together. When mixing separately milled granite and dried phosphogypsum (PG) with subsequent pressing the results were much worse. During the joint grinding of granite and sulfate additive there are processes of mechanical activation. Increased chemical activity of mechanoactivated components of sulfopetrocement contributes to an increase in the probability of chemical interaction between them both at the stage of grinding and in the pressed moistened material. Thermodynamic analysis indicates a high probability formation of sulfoaluminosilicates of the $9CaO \times 4SiO_2 \times Al_2O_3 \times 7SO_3 \times 80H_2O$ type, discovered by Lafuma [20], as well as silica gel, potassium (sodium) sulfate, etc. in pressed specimens.

To establish the joint effect of the duration of mechanochemical activation, compression pressure, and PG content on the strength of the SPC, experiments were implemented algorithmized in accordance with a typical three-level plan for three factors [18]. The experimental planning conditions are given in Table 7, the planning matrix, and experimental data in Table 8. Activation of SPC was carried out at the previously established optimum cylpeps-ball mill feed with an average weighted ball diameter of 20 mm, the ratio of the mass of the grinding bodies to the material equal to 7, granite No. 3 was used.

Table 4. Kinetics of change in water resistance of petrocement over time.

No. of granite according to table 1	Water resistance coefficient (WRC) at age, days				
	3	7	28	90	180
1	0.15	0.22	0.31	0.45	0.62
2	-	0.30	0.36	0.55	0.73
3	0.12	0.28	0.33	0.61	0.76

Table 5. Dependence of SPC strength on phosphogypsum additive content.

No. of granite according to table 1	Phosphogypsum content, %	Compressive strength, MPa at age			
	0	2.9	3.5	4.8	4.9
	2.5	8.8	11.2	14.3	14.5
	5	9.7	14.2	24.5	25.8
1	10	10.9	18.5	30.7	31.6
	20	12.1	18.7	35.5	36.8
	30	15.8	22.1	39.4	40.3
	50	17.5	34.2	48.2	49.1
	0	3.6	4.7	6.0	6.1
	2.5	9.6	14.7	17.1	16.9
	5	11.8	17.6	26.7	27.5
2	10	13.9	21.8	32.9	34.4
	20	14.0	21.5	38.2	40.3
	30	16.2	22.7	40.5	41.2
	50	18.3	36.3	48.4	50.2
	0	3.4	4.6	5.9	6.2
	2.5	8.7	12.2	15.5	15.8
	5	11.2	16.3	26.0	26.5
3	10	13.8	22.1	32.5	34.9
	20	14.6	22.9	38.0	40.7
	30	16.3	23.8	40.3	41.5
	50	18.8	35.9	48.7	50.9
-	100	17.7	27.8	40.9	44.1

Note: compression pressure is 100 MPa.

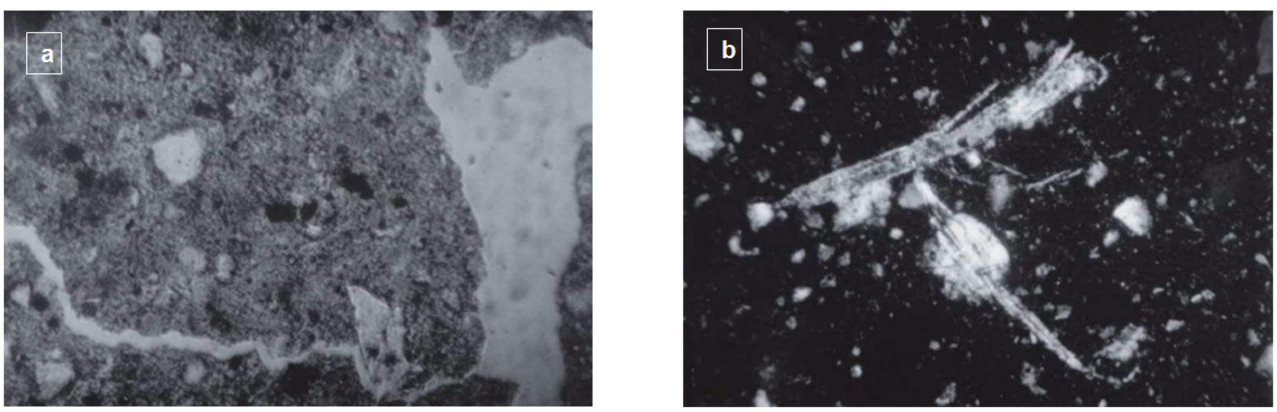


Fig. 3. Microscopic images (x270) of pressed sulfopetrocement specimens with phosphogypsum content, wt. %: (a) - 10, (b) - 20.

Table 6. Kinetics of change in water resistance of SPC with PG additive over time.

No. of granite according to table 1	Phospho-gypsum content, %	WRC at age, days				
		3	7	28	90	180
	2.5	-	0.20	0.32	0.45	0.54
	5	-	0.32	0.40	0.50	0.58
1	10	-	0.18	0.22	0.37	0.46
	20	-	-	0.17	0.21	0.27
	50	-	-	-	0.19	0.20
	2.5	0.15	0.23	0.37	0.48	0.56
	5	0.26	0.35	0.43	0.51	0.60
2	10	-	0.18	0.25	0.42	0.49
	20	-	-	0.22	0.24	0.28
	50	-	-	-	0.20	0.25
	2.5	-	0.21	0.36	0.49	0.64
	5	0.20	0.32	0.48	0.55	0.62
3	10	-	0.17	0.28	0.44	0.51
	20	-	-	0.21	0.25	0.31
	50	-	-	-	0.20	0.24

Note: compression pressure is 100 MPa.

As a result of experimental data processing by methods of mathematical statistics [12], quadratic regression equations in coded variables (Eqs. 1 - 3) characterizing the influence of the studied factors on the strength of pressed specimens of SPC, respectively, after 1, 7 and 28 days of air-dry hardening ($R_{c.1}$, $R_{c.7}$, $R_{c.28}$) were obtained.

$$R_{c.1}=8.61+1.40X_1+4.18X_2+4.58X_3-1.07X_1^2+1.73X_2^2-1.97X_3^2+0.95X_1X_3+2.35X_2X_3 \quad (1)$$

$$R_{c.7}=18.40+2.81X_1+6.73X_2+8.77X_3-1.42X_1^2-0.68X_2^2-5.92X_3^2+1.73X_1X_2+2.05X_1X_3+4.03X_2X_3 \quad (2)$$

$$R_{c.28}=20.06+2.88X_1+6.91X_2+9.12X_3-1.48X_1^2-0.56X_2^2-6.98X_3^2+1.72X_1X_2+2.12X_1X_3+4.0X_2X_3 \quad (3)$$

The analysis of the obtained regression equations shows that the linear effects of the influence of factors X_2 and X_3 on the strength of SPC are close to each other in magnitude and significantly (several times) exceed the influence of factor X_1. With the increase in the duration of specimens' hardening there is an increase in the influence of factor X_3 in comparison with X_2, which is noticeable by the difference in the value of the quadratic effects (at the age of 28 days for X_3 it is 12 times higher than for X_2).

The nature of the influence of factor X_1 (Fig. 5a) on the output parameter indicates that a certain increase in the strength value occurs when X_1 changes in the range -1...0, i.e. 1...2 h. Moving X_1 to the upper level (t = 3 hours) gives a lower increase in strength.

The most significant effect of the influence of the PG additive content is observed when X_3 increases in the section from -1 to 0.4 (Fig. 5c). At a compression pressure of 60 MPa and an activation time of 2 h (X_1 = X_2 = 0), the strength at the age of 7 days in this section increases almost linearly from 4 to 21 MPa, that is, more than five times. A further increase in X_3 does not cause a significant increase in strength, which corresponds to the previous results of the study. The character of the influence of compression pressure (Fig. 5b) is practically linear over most of the range of variation for both SPC and pure granite. When analyzing Eqs. 1 - 3, the presence of a significant interaction effect of factors X_2 and X_3, which considerably exceeds the other two interaction coefficients, draws attention. This indicates that the effect of PG content in SPC depends on the value of compression pressure.

For technological interpretation of the equation of regression (Eq. 2) the two-dimensional section of a surface of the response (Fig. 6), received at the solution of the equation concerning two variables (X_2 and X_3) and the set values of response function, at fixing of factor X_1 on zero level is constructed. The cross-section shows a group of curves of equal strength showing the influence of factors X_2 and X_3 when X_1 is fixed. Isolines characterize the possible ratio of factors, at which the same strength is provided.

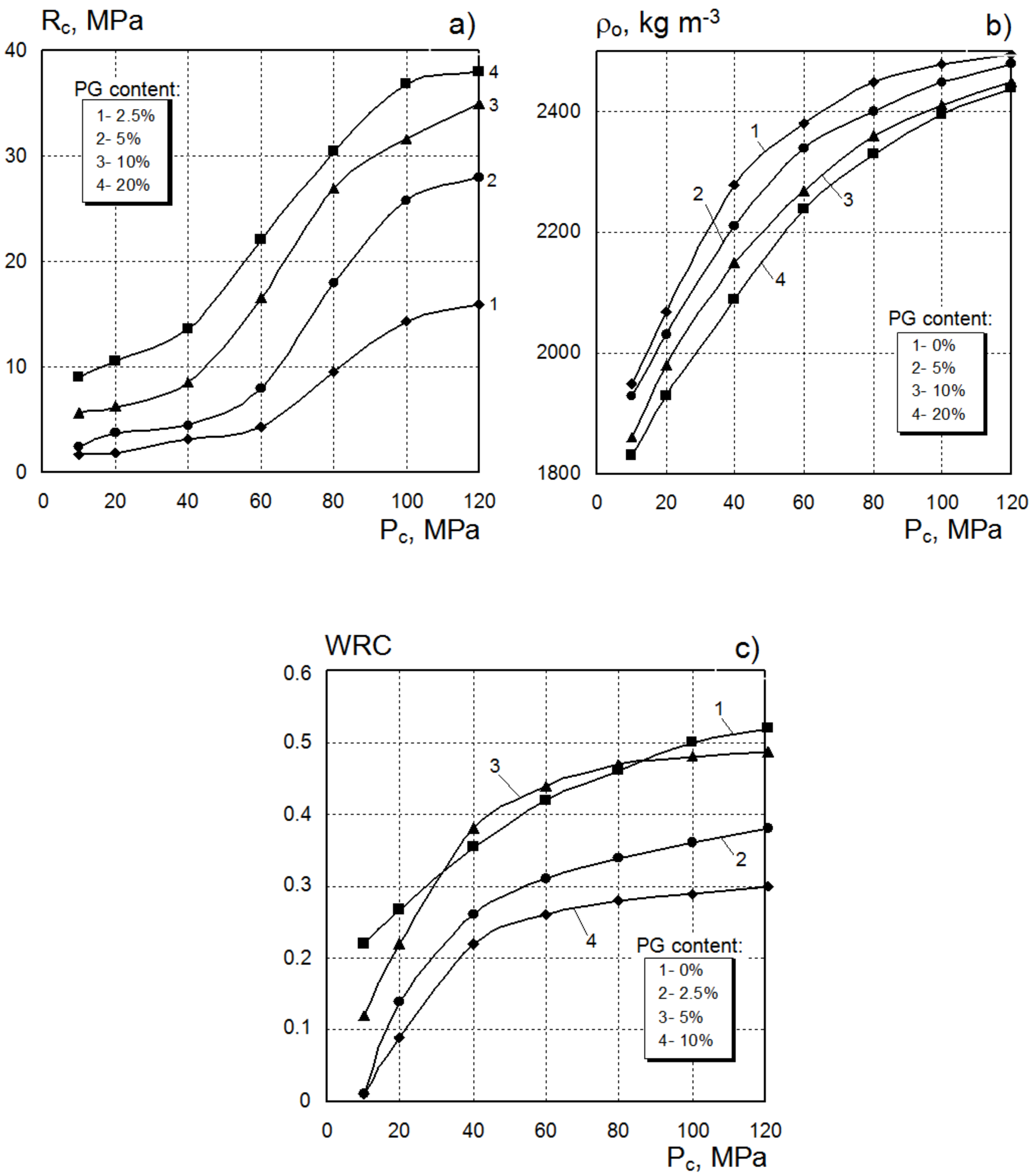


Fig. 4. Dependencies of compressive strength (a), average density (b) and water resistance coefficient (c) on compression pressure (used granite No.3).

Table 7. Experiment planning conditions.

Factors		Variation levels			Variation interval
Code	Natural	-1	0	+1	
X_1	Grinding duration τ, hrs	1	2	3	1
X_2	Compression pressure P_c, MPa	20	60	100	40
X_3	PG content, %	0	15	30	15

Table 8. Planning matrix and experimental values of SPC strength.

No	Coded factors values			Natural values			Compressive strength, MPa		
	X_1	X_2	X_3	τ, hrs	P_c, MPa	PG, %	$R_{c.1}$	$R_{c.7}$	$R_{c.28}$
1	+1	+1	+1	3	100	30	21.6	37.9	38.8
2	+1	+1	-1	3	100	0	4.8	6.3	6.4
3	+1	-1	+1	3	20	30	7.3	12.7	13.6
4	+1	-1	-1	3	20	0	1.3	1.4	1.4
5	-1	+1	+1	1	100	30	14.5	22.7	23.4
6	-1	+1	-1	1	100	0	2.9	3.5	3.7
7	-1	-1	+1	1	20	30	4.8	8.6	9.3
8	-1	-1	-1	1	20	0	1.2	1.3	1.4
9	+1	0	0	3	60	15	8.7	19.6	21.4
10	-1	0	0	1	60	15	6.3	13.7	15.0
11	0	+1	0	2	100	15	16.6	29.2	31.5
12	0	-1	0	2	20	15	4.0	8.3	9.0
13	0	0	+1	2	60	30	10.5	21.3	22.2
14	0	0	-1	2	60	0	2.7	3.0	3.2
15	0	0	0	2	60	15	8.8	18.8	20.0
16	0	0	0	2	60	15	8.1	19.0	21.1
17	0	0	0	2	60	15	9.0	18.5	20.4

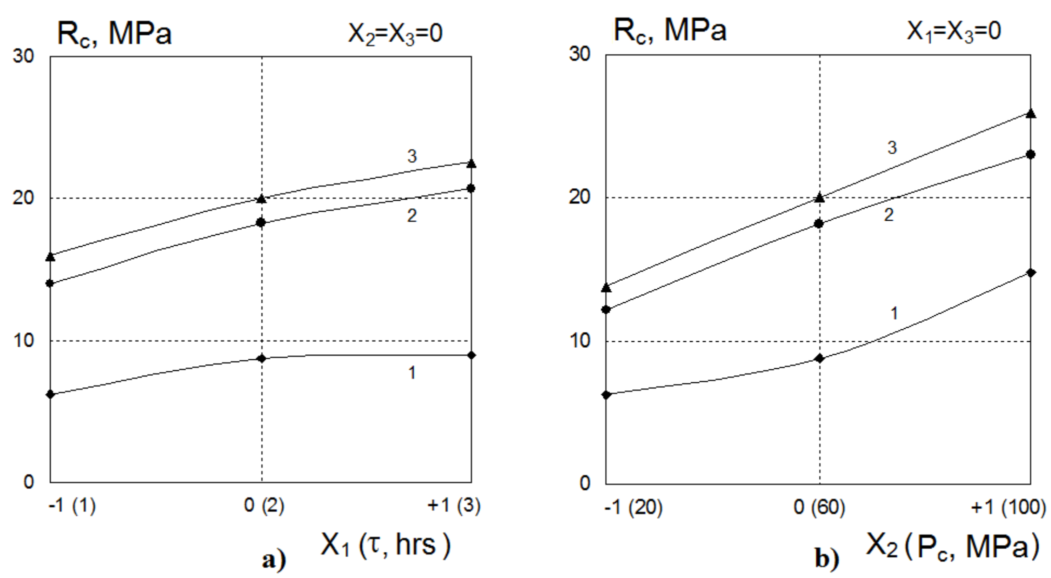
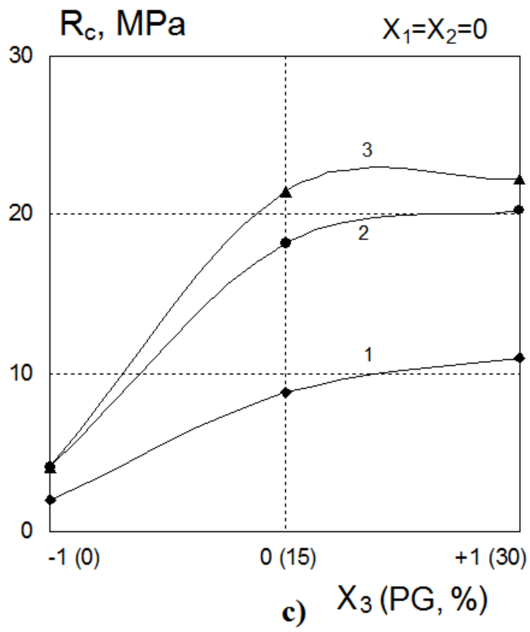


Fig. 5. Influence of the investigated planning factors on the strength of SPC: (a) grinding duration, (b) compression pressure, (c) phosphogypsum content; 1 - strength at the age of 1 day, 2 - strength at the age of 7 days, 3 - strength at the age of 28 days.



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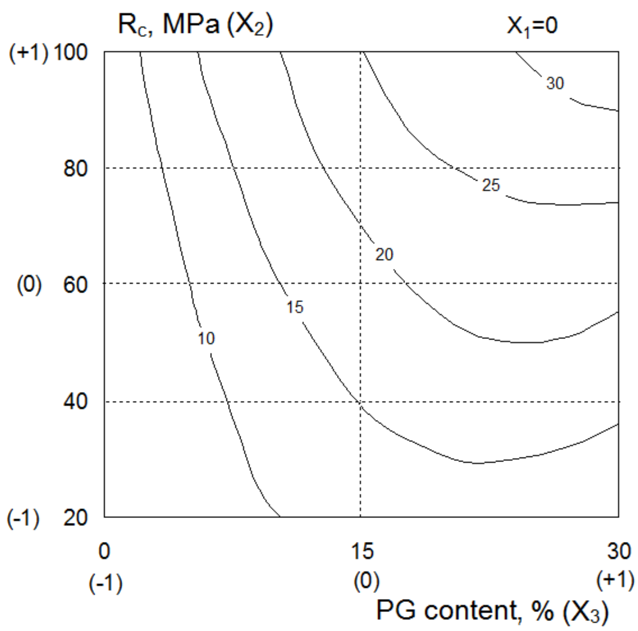

Fig. 6. Compressive strength isolines (MPa) of SPC specimens (grinding duration is 2 h).

CONCLUSIONS

Hardening parameters of granite powders, the kinetics of their strength gain, and water resistance were established. The effectiveness of sulfate activation of hardening of pressed granite powders with the addition of phosphogypsum, and its impact on the strength and microstructure of artificial stone has been shown. The conditions for achieving increased water resistance of artificial stone based on sulfate-activated pressed granite powders (sulfopetrocement) are considered. Using the methodology of mathematical planning of experiment the mathematical models of sulfopetrocement strength at different ages have been obtained. The influence of the main technological factors on the efficiency of complex mechanical-chemical activation of contact hardening binders based on granite-crushing wastes has been established.

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