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Modified binders on the basis of flotation tailings

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Abstract. The article proposes compositions of efficient modified composite binders on the basis of portland cement and flotation tailings; the new binders attain the ultimate compressive stress that is twice as high as that of the cement stone. At that, use of annually growing volume of flotation tailings in the production of the composite binder is a rational way for recycling this type of waste and allows saving the planet's natural resources.

1. Introduction

Nowadays, composite binders are prioritized over other binders. Use of dispersed mineral aggregates allows unlocking the potential of the binding compounds to a great extent, thus determining physical, mechanical, performance and technical properties of the composite binders, as well as those of the building materials produced on their basis; it allows reducing consumption of expensive binding materials. Creating highly efficient composite binders is based on controlling the production process at all stages: selection of feed materials, development of optimal compositions, application of mechanical activation to the feeds, modification of the composite binders with functional chemical additives and other methods.

2. Materials and methods

The following materials were used in creation of the composite binders: portland cement, grade CEM I 42.5 N, produced by Belgorod Cement Plant OJSC; banded iron formation (BIF) flotation tailings with flotation reagent PA-14 concentration of 250 g/tonne, produced by Mikhailovsky GOK; functional additives. Tailings from flotation of magnetite and hematite fraction of BIF are highly dispersive loose materials ($S_{\text{spec}} = 250 \text{ m}^2/\text{kg}$), with prevailing quartz content (65 – 70%). Inert materials sieve 0.08 residue (more than 50%). Variation in the chemical composition of the flotation tailings is determined from samples taken during one month, %: $\text{SiO}_2 = 65 - 70$; $\text{Fe}_2\text{O}_3 = 16 - 20$; $\text{MgO} = 2.5 - 3.5$; $\text{CaO} = 0.9 - 1.5$; $\text{Al}_2\text{O}_3 = 0.1 - 0.5$; $\text{Na}_2\text{O} = 0.3 - 0.5$; $\text{K}_2\text{O} = 1 - 2.5$; $\text{SO}_3 = 0.1 - 0.2$; $\text{CO}_2 = 0.1 - 0.2$, others 1.1 – 3;

3. Design of a modified composite binder composition

The authors' previous studies in mechanical activation of binders produced from CEM I 42,5 N portland cement and flotation tailings [1-5] revealed efficiency of joint milling of the components in production of binders based on the BIF flotation tailings. Thus, the modified composite binders were produced by the joint milling of portland cement, flotation waste and functional additives.



The modified composite binders were produced by jointly milling the CEM I 42,5 N portland cement (as a binder), BIF hematite fraction flotation tailings < 0.63 mm (as a mineral aggregate) in a ratio of 3/7, together with the chemical additives, for 30 minutes.

The selection of the chemical additives was directed by the objective to obtain maximum useful properties with minimal consumption of the functional additives and the consulted previously studied range of chemical additives used in self-leveling floor dry construction mixes [6-10]. The following additives were selected:

- the latest generation of the Melflux 5581F hyperplasticizer;
- Vinnapas4220L complex additive (leveler, antifoamer, reduces water gain, dispersion agent, increases adhesion, increases workability, prevents aggregate sedimentation, increases wear capacity, provides smoothness and durability of the coating);
- calcium formate (hardening accelerator, anti-freeze additive).

Using the mathematical experiment design method, the authors selected the optimal compositions of the modified composite binders and studied the influence of the binders' components onto their physical and mechanical properties. During the experiment, consumption of additives (as compared to the weight of cement) was held as variable factors: Melflux 5581F – 0.1-0.2%; Vinnapas 4220L – 0.5-0.9%; Calcium formate – 1.5-2%.

The experiment design conditions are shown in Table 1.

Table 1. Experiment design conditions

Name of the factor	Factor's code	Levels of variation			Range	Output data
		-1	0	+1		
melflux 5581F, % wt	X ₁	0.1	0.15	0.2	0.05	melflux 5581F, % wt
vinnapas 4220L, % wt	X ₂	0.5	0.7	0.9	0.2	vinnapas 4220L, % wt
calcium formate, % wt	X ₃	1.5	1.75	2	0.15	calcium formate, % wt

In accordance with the experiment design matrix (Table 2), the authors have calculated 17 compositions of the modified composite binder with variations in functional additives content as per the limits stated in the matrix.

When selecting the optimal composition of the modified composite binder, the following were used as output parameters: average compressive stress limit and average density.

The authors molded 17 series of binder sample with the cement content of 70% and the tailings content of 30%; there were 7 samples sized 30×30×30 cm in each series. The amount of tempering water was taken from a 17 cm cone flow. The samples were hardened under normal conditions during 28 days. The results of physical and mechanical testing of the samples are shown in Table 2.

Table 2. Experiment design matrix

Point no.	Factor Variation			Physical and mechanical properties	
	X ₁	X ₂	X ₃	Average density Y ₁ , kg/m ³	Breaking compressive strength Y ₂ , MPa
1	0.2	0.9	2	2812	108.6
2	0.2	0.9	1.5	2801	105.3
3	0.2	0.5	2	2809	108.6
4	0.2	0.5	1.5	2785	100
5	0.1	0.9	2	2798	101
6	0.1	0.9	1.5	2756	99
7	0.1	0.5	2	2775	98.7

8	0.1	0.5	1.5	2696	97,
9	0.2	0.7	1.75	2803	106.8
10	0.1	0.7	1.75	2699	97.2
11	0.15	0.9	1.75	2786	100.5
12	0.15	0.5	1.75	2742	98
13	0.15	0.7	2	2810	108.6
14	0.15	0.7	1.5	2695	97
15	0.15	0.7	1.75	2792	98.9
16	0.15	0.7	1.75	2800	99
17	0.15	0.7	1.75	2786	98.4

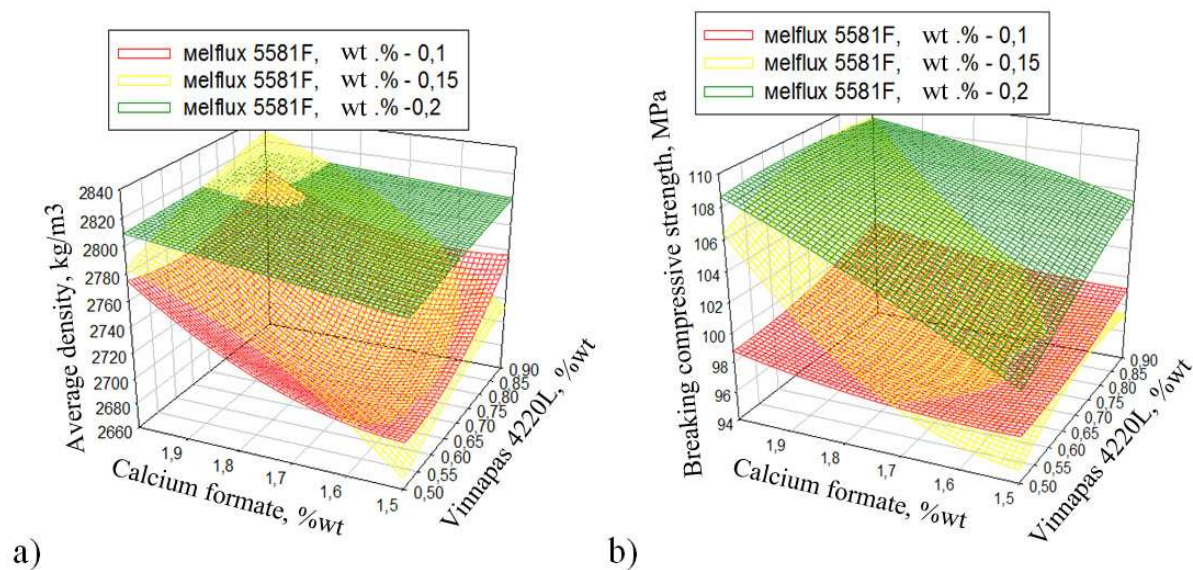


Figure 1. A nomograph showing the functional additives influencing: a - the average density of the composites; b – the average strength of the composites

Statistical treatment of the data resulted in mathematical models, which characterize the changes in physical and mechanical properties of the composites. The obtained regression equation for the average density is:

$$Y_1 = 2777.5 + 28.6 \cdot x_1 + 14.6 \cdot x_2 + 27.1 \cdot x_3 - 5.6988x_1^2 + 7.3012x_2^2 - 4.199x_3^2 - 8 \cdot x_1 \cdot x_2 - 10.75 \cdot x_1 \cdot x_3 - 6.25 \cdot x_2 \cdot x_3$$

The complex concept of influence that the content levels of Melflux 5581F, Vinnapas 4220 L and calcium formate exert on the density of the composites may be obtained from a nomograph build with the SigmaPlot 10.0 software, which shows the complex influence of the functional additives on the average density of the composites (Figure 1).

The obtained regression equation for the average strength is:

$$Y_2 = 99.99 + 3.79 \cdot x_1 + 1.191 \cdot x_2 + 2.69 \cdot x_3 + 1.4476x_1^2 - 1.2624x_2^2 + 2.3226x_3^2 + 0.1200 \cdot x_1 \cdot x_2 - 0.6200 \cdot x_2 \cdot x_3$$

The complex concept of influence that the content levels of Melflux 5581F, Vinnapas 4220 L and calcium formate exert on the breaking compressive strength of the composites may be obtained from a nomograph, which shows the complex influence of the functional additives on the average strength of the composites (Figure 1).

While analyzing the results of the composite binder composition optimization with the functional additives, it is worth noting that the highest values of strength and density were provided by the maximum ratios of the additives in the experiment (compound no.1), and by the maximum amount of Melflux 5581F and calcium formate in combination with the medium amount of Vinnapas 4220 L. Thus, to avoid excessive consumption of Vinnapas 4220 L, the following optimal composition of the composite binder was approved:

1. binder - CEM I 42,5 N portland cement, 70%;
2. mineral aggregate - flotation tailings, 30%;
3. additives: Melflux 5581F hyperplasticizer, 0.2%wt of the weight of cement; Vinnapas 4220L complex additive, 0.5%wt of the weight of cement; calcium formate complex additive, 2%wt of the weight of cement.

4. Conclusion

The results of the studies allowed modifying the composition of the composite binder produced on the basis of flotation tailings and cement with the functional additives. The optimal composition of the modified composite binder was determined: cement -70%; flotation tailings – 30%; additives, as %wt of the weight of cement: Melflux 5581F - 0.2%, Vinnapas 4220L - 0.5%, calcium formate - 2%. The designed composition allows saving 30% of energy-intensive cement. The breaking compressive strength of the composite is 2 times higher than that of the cement stone.

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