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Production of dry building mixes using waste of the mining and metallurgical complex of Kazakhstan

Abstract. A serious ecological issue not only in Kazakhstan, but also in the world is deposits of waste from the mining and metallurgical complex, the amount of which exceeds the production volume. The article provides information about the possibility of using waste from the mining and metallurgical complex – shungite materials (shungite ore, concentrate, and “tails” after enrichment) obtained by multi-stage flotation enrichment as a filler in the production of tile adhesives. The chemical composition of shungite materials has been studied by the method of X-ray phase elemental analysis. By the method of experimental selection based on the manufacturer of concrete additives and dry building mixes, the optimal amount of shungite material added to the resulting formulations was determined without deterioration of the physical and mechanical properties of the samples (adhesive strength, open time, sliding, distribution) relative to standard analogs. It is established that the obtained tile adhesives fully comply with the standards, are environmentally safe, the adhesive strength after twenty-eight days is 1.03 N/mm^2, and allow to reduce cement consumption in the production of tile adhesives by 30%, which significantly affects the reduction of the cost of the products. Experiments with shungite concentrate (carbon content 55.4%) obtained by multi-stage flotation enrichment as a black pigment for grout production based on the Ceresit CE33 Graphite/Grey trademark showed high physical and mechanical properties compared to standard samples.
Keywords: dry building mixes, shungite, flotation enrichment, tails, concentrate, cement, tile adhesive, grout.

Introduction

Dry building mixes (DBM) production usually uses sand or pulverized quartz, limestone flour, powdered chalk and cement, and various additives, most of which are environmentally harmful materials. Modern DBM manufacturers use many different additives in their formulations, which often leads to significant emissions of CO_2 and secondary liquid waste [1].

An important additive to cement in the production of DBM is fly ash. It is formed at thermal power plants after coal burning and captured using electric filters. Fly ash in construction significantly increases economic attractiveness and keeps high standards of the obtained products [2].

Since two thousand twenty three, the European Union introduces a carbon tax on products produced with the help of “dirty” energy, which also includes thermal power plants powered by coal [3]. Therefore, the study of the possibility of using shungite rocks of East Kazakhstan and waste during their processing as a filler and additives in the production of DBM is the subject of this study.

In the works of Ryzhov A.S., shungite was used in the production of DBM and concrete coatings. [4-5]. In the work of Zagoruiko T.V. shungite was used as a heat-resistant filler [6]. Replacing the base materials of the DBM with waste from polymetallurgical production – shungite rocks will improve the ecological issues of the region while reducing the economic costs of DBM production. The products of the enrichment of shungite are concentrate, which can be used for the production of various sorbents and catalysts, and waste after enrichment – "tails", which have not found practical application in the further processing cycle and remain in dumps.

Shungite rocks are waste products of the mining and metallurgical complex with unique composition, properties, and structure of natural formations. The chemical composition of shungite is unstable: on average it contains 10-50% of carbon and 50-90% of mineral part [7]. Currently, shungite deposits are known in Russia (Karelia) and Kazakhstan (Bakyrchik, Koksu).

In the work of Glebashev S.G., in shungite ore of the Bakyrchik gold deposit found impurities of platinoids and other rare metals [8]. Accordingly, it can be considered industrially promising along with the Zazhoginsky shungite deposit in Karelia, where precious metals are contained in the ores [9]. The basis of the mineral part is quartzite and various aluminosilicates, which makes it possible to consider shungite rocks as a promising carbon-mineral raw material in the production of DBM. The combination, at the same time, of such valuable properties as chemical resistance, heat resistance, electrical conductivity, and low thermal conductivity allows using a silicate as a universal filler, which provides for replacing several modifying additives in the composition of DBM.

Work of Mizernaya M. proved that East Kazakhstan shungite additives can be used as a notable filler and as a pigment with anticorrosive properties in DBM production [10]. Stroganov V. found that adding of shungite filler in composition increases the level of adhesion to concrete up to 3.0 MPa and resistance to aggressive environments [11]. In the work of Estemesova A.S., shungite dispersed additives contributes to the production of concrete and mortar with high features [12].

Due to the peculiarities of the material composition and structure, shungite powders easily bind to polymers of different polarities and form strong bonds with the binding components of the DBM [13]. In addition, due to the presence of carbon in the composition, shungite concentrates have a rich black color, which makes it possible to replace expensive black pigments based on iron oxides in the production of DBM for decorative and outdoor work.

Materials and methods

Crushing and grinding. The shungite ore of the Bakyrchik deposit was crushed on a laboratory jaw crusher SD-6 by Vibrotekhnik (Russia), after which it was further ground on a planetary mill Pulverisette 6 by Fritsch (Germany). After samples were screened on a laboratory sieve to the sizes of 140 µm and 71 µm (Figure 1).

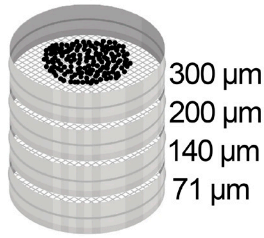

Figure 1 – Screening process of shungite ore

Flotation enrichment. Flotation enrichment of shungite ore was carried out according to a well-known technique on a laboratory flotation machine with a chamber volume of 3.0 liters [14]. Flotation experiments were carried out in the reagent mode adopted at the enrichment plant, using the following reagents: kerosene – 1134 g/t, Flotol B – 1260 g/t. The duration of the main and control flotation is 10 minutes. To increase the carbon content in the concentrate carried out three stages of re-flotation (Figure 2). The resulting products of flotation enrichment of shungite waste tested in the production laboratory of Master Builders Solutions Central Asia LLP (Almaty, Kazakhstan), a manufacturer of concrete additives and dry building mixes.

In the research work part of the cement in the composition of industrial C1T classification tile adhesive was replaced by the objects of research: shungite ore, concentrate, and "tails" after enrichment, fractions of which are 71 µm and 140 µm. The glue solutions were made on a mortar mixer by Testing (Germany). Adhesive strength, open time, sliding, and distribution of the obtained tile adhesive samples was tested. Testing samples was store under normal conditions according to the requirements of EN 1348 standard for three, seven, and twenty-eight days in the Osworld climate chamber (India) [15].

Determination of adhesive strength. The adhesive strength was determined by EN 1348 standard [15]. A layer of mortar was applied to the concrete slab and smoothed with a notched trowel at an angle of 60°. After 5 minutes, unglazed tiles with a flat matte surface were glued and pressed with a load of 2 kg for 30 seconds. After three, seven, and twenty-eight days of storage, a metal washer (50x50 mm) was glued to the tile or the material with epoxy glue, and the adhesion strength of the materials to the substrate was determined using a DYNA Proceg laboratory adhesive meter (Switzerland). Adhesion test results for each storage condition are reported in newtons per square millimeter (N/mm^2).

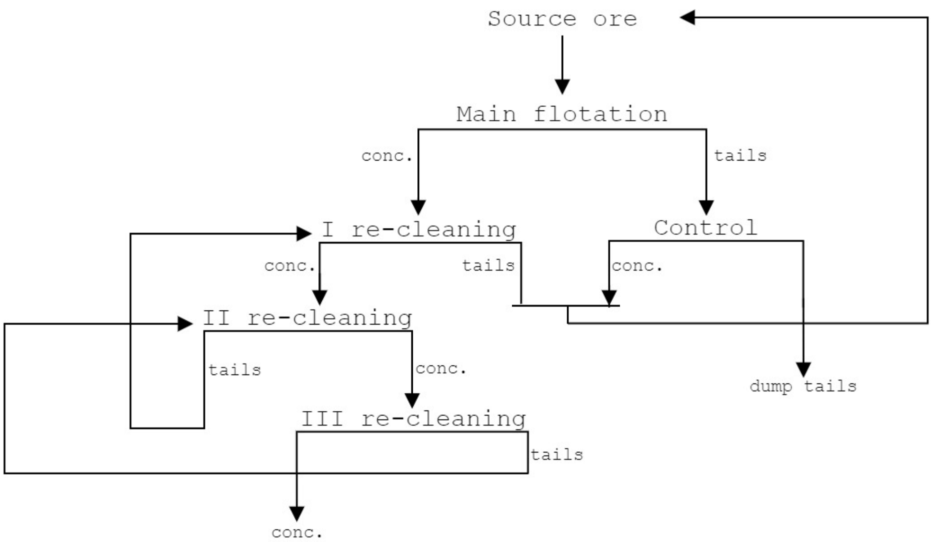

Figure 2 – Technological scheme of flotation enrichment of shungite ore

Definition of open time. Open time (adjustment time) was determined by EN 1346 standard [16]. A layer of mortar was applied to the concrete slab and smoothed with a notched trowel at an angle of 60 °. After 5, 10, and 20 minutes, glazed porous earthenware ceramic tiles were glued and pressed with a load of 2 kg for 30 seconds. After three, seven, and twenty-eight days of storage under normal conditions, a metal washer (50x50 mm) was glued to the tile or the material with epoxy glue, and the adhesion strength of the materials to the base was determined. The results of the open time are indicated in minutes.

Definition of sliding. Sliding was determined by EN 1308 standard [17]. A steel ruler was fixed to the concrete slab, then a protective tape glued under the ruler. Next, a layer of solution was applied under the protective tape, smoothed with a notched trowel perpendicular to the steel ruler. After removing the protective tape 25 mm two supports were installed to the ruler. Then a ceramic tile (100x100 mm) was applied to the support and pressed with a 5 kg load for 30 seconds. Distance between ruler and tile measured with a caliper at three points. 20 minutes later, measures were repeated at the same points. The difference in caliper is equal to the sliding of the tile in millimeters.

Definition of distribution. The distribution was determined by the internal methodology of Master Builders Solutions Central Asia LLP (Almaty, Kazakhstan) – Internal methods of testing. A layer of mortar was applied to the concrete slab and smoothed with a notched trowel at an angle of 60°. Next, a transparent glass (100x100 mm) was applied and pressed with a weight of 5 kg. Then the distribution of the solution over the entire surface of the glass was determined as a percentage (%).

Results and discussion

Flotation enrichment. Flotation enrichment is one of the most widely used methods of mineral enrichment, used to increase the carbon content in concentrates and mineral oxides in "tails" [13].

Flotation enrichment of shungite ore showed the following results: the carbon content in concentrate is 55.40 %, in "tails" is 9.89 %.

Table 1 – Results of flotation enrichment

Name	Carbon content, %
Shungite ore	10.23
Concentrate	55.40
Tails	9.89

Analisys of the result of X-ray spectroscopy (XRS) showed an increasing of a mineral part in “tails” – calcium, silicon, iron, magnesium oxides, etc., which affect the hardness, adhesive strength, and better setting of DBM (Table 2).

Production of tile adhesives. Based on the results of the experiments carried out in the production laboratory of Master Builders Solutions Central Asia LLP (Almaty, Kazakhstan), found the optimal ratios of the components added to the standard formulation of C1T classification tile adhesive with the addition of shungite materials (shungite ore, concentrate and “tails” after enrichment). Part of the cement in the standard formulation for tile adhesive was replaced by the objects of study: shungite ore, concentrate and “tails” after enrichment, the fractions of which are 71 μm and 140 μm. The resulting formulations with shungite materials are presented in Table 3.

Table 2 – Results of X-ray spectral analysis

Name	Content, %										
	C	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
Shungite ore	10.23	1.77	1.31	21.13	49.44	0.22	3.42	2.47	3.06	0.20	6.75
Tails	9.89	1.93	1.49	20.51	51.15	<0.01	3.30	2.66	1.31	0.15	7.61

Table 3 – Formulations of the obtained samples with shungite enrichment products

Name	Component content, g						
	C1T	C1T + tails 140 μm	C1T + tails 71 μm	C1T + shungite 140 μm	C1T + shungite 71 μm	C1T + conc-t 140 μm	C1T + conc-t 71 μm
Cement M400	300-400	200-300	200-300	200-300	200-300	200-300	200-300
Sand dunes	600-700	700-800	700-800	700-800	700-800	700-800	700-800
Cellulose ether	2-4	2-4	2-4	2-4	2-4	2-4	2-4
Tails 140 μm	–	4.5	–	–	–	–	–
Tails 71 μm	–	–	4.5	–	–	–	–
Shungite 140 μm	–	–	–	4.5	–	–	–
Shungite 71 μm	–	–	–	–	4.5	–	–
Conc-t 140 μm	–	–	–	–	–	4.5	–
Conc-t 71 μm	–	–	–	–	–	–	4.5

Significant changes in the results for the determination of physico-mechanical properties were shown by formulations with “tails”. The values of the adhesive strength of the resulting formulation after twenty-eight days are higher than that of the standard analogue of tile adhesive by 10 %, which can be explained by the increased content of the mineral component in the “tails”, which provides better adhesion to the surface. The size of the materials has a slight difference in results. The test results of the obtained formulations of tile adhesive with “tails” are presented in Table 4.

The results of determining the physical and mechanical properties of formulations with shungite ore showed values corresponding to the standard analogue of tile adhesive. The adhesive strength of the obtained and standard formulations after twenty-eight days is less than 1 %. The test results of the obtained formulations of tile adhesive with shungite ore are presented in Table 5.

Minimal values of physical and mechanical properties were shown by formulations with shungite concentrate, which can be explained by a high carbon content (55.40 %), which negatively affects the adhesion of tile adhesive to the surface. The values of the adhesive strength of the obtained formulation in relation to the standard analogue after twenty-eight days are 9 % lower. The test results of the obtained formulations of tile adhesive with shungite concentrate are presented in Table 6.

Table 4 – Test results of tile adhesive formulations with «tails»

Name		C1T	C1T + tails 140 µm	C1T + tails 71 µm
Adhesive strength, N/mm^2	3 days	0.45	0.76	0.76
	7 days	0.68	0.94	0.95
	28 days	0.92	1.03	1.03
Open time, at least 20 minutes		20	20	20
Sliding, no more than 0.5 mm		0	0	0
Distribution, more than 90 %		90	90	90

Table 5 – Test results of tile adhesive formulations with shungite ore

Name		C1T	C1T + shungite 140 µm	C1T + shungite 71 µm
Adhesive strength, N/mm^2	3 days	0.45	0.39	0.4
	7 days	0.68	0.85	0.86
	28 days	0.92	0.91	0.91
Open time, at least 20 minutes		20	20	20
Sliding, no more than 0.5 mm		0	0	0
Distribution, more than 90 %		90	90	90

Table 6 – Test results of tile adhesive formulations with shungite concentrate

Name		C1T	C1T + conc-t 140 µm	C1T + conc-t 71 µm
Adhesive strength, N/mm^2	3 days	0.45	0.55	0.55
	7 days	0.68	0.7	0.72
	28 days	0.92	0.84	0.84
Open time, at least 20 minutes		20	20	20
Sliding, no more than 0.5 mm		0	0	0
Distribution, more than 90 %		90	90	90

According to the research results, it was found that high results obtained with the addition of shungite materials to the tile adhesive formulation in an amount of 4.5 g, because the addition of more filler contributed to a strong thickening of the solution, which is explained by the high specific surface area of shungite. Thus, the optimal amount of filler makes it possible to reduce the consumption of added cement in the tile adhesive formulation by up to 30 %, without compromising the physical and mechanical properties and showing comparable results relative to standard analogues.

A significant result was obtained for the C1T formulation with 140 µm "tails". The adhesive strength is 1.03 N/mm^2, the open time is 20 minutes, no tile sliding, and the distribution of the solution over the surface is 90 %. Optimal formulation of tile adhesive using shungite materials is presented in Table 7.

Table 7 – Optimal formulation of tile adhesive using shungite materials

Name	Amount, g
Cement M400	200-300
Sand dunes	700-800
Cellulose ether	3.0
Shungite materials	4.5

The analysis of the conducted studies showed that the obtained tile adhesives have high adhesive strength in comparison with industrial analogues, fully comply with all the requirements for tile adhesives and are environmentally safe according to the EN 12004 standard [17].

Production of grout. Also, in the production laboratory of Master Builders Solutions Central Asia LLP (Almaty, Kazakhstan) were carried out experiments with using of 71 µm shungite concentrate as a black pigment in the production of grouts based on Ceresit CE33 in an amount of 1% (Figure 3).

According to the results of the experiments, the obtained solutions have the following physical and mechanical parameters (Table 8).

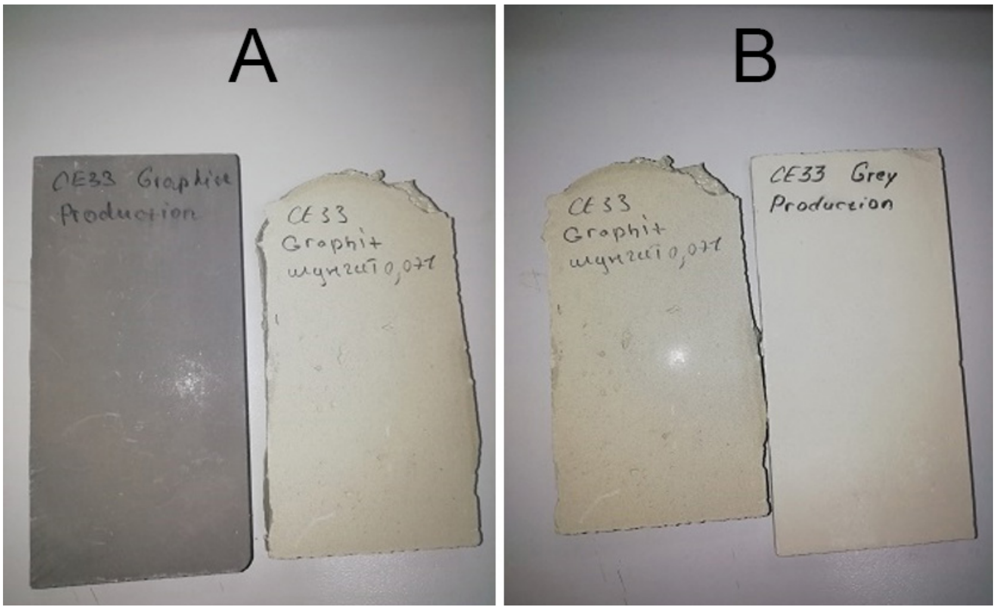

Figure 3 – Grout with shungite concentrate and industrial analogues.
Note: A – Ceresit CE33 Graphit, B – Ceresit CE33 Grey

Table 8 – Physical and mechanical properties of grout based on Ceresit CE33

Name	Description
Solution performance	After adding a water (W = 0.28), the solution is easily mixed, does not clump, plastic and thick homogeneous mass
Spreading	The solution is easy to spread and does not stick to the tool. After drying, the surface of the wedge is without cracks, there is no crack formation at the seams
Color	In dry form, and after adding a water, the grout has a gray color with a yellow tint

An increase in the amount of added shungite concentrate of more than 1 % significantly affects the solution performance: excessive thickening occurs, water consumption increases. However, the obtained grout samples based on Ceresit CE33 fully correspond to industrial analogues.

Conclusion

It has been established that in the shungite ore of the Bakyrchik deposit, the carbon content is 10.23 %. Was carried out a multi-stage flotation enrichment to increase the carbon content, a result of which it was possible to increase the carbon content in the schungite concentrate to 55.40 %, and in the "tails" after enrichment – 9.89 %. As a result of X-ray spectral analysis of shungite materials, it was found that after flotation enrichment in the "tails" the content of the mineral part increases, which positively affects the performance properties of the resulting tile adhesive formulations.

Shungite materials (shungite ore, concentrate and "tails" after enrichment) were used as a filler in the formulation of C1T classification tile adhesives. The conducted studies have shown the possibility of increasing the arsenal of fillers for tile adhesives by partially replacing cement and reducing its consumption in the formulation by up to 30 %, which is one of the most important issues in the production of cement mortar. At the same time, the physical and mechanical properties of the obtained samples of tile adhesives increase relative to standard industrial analogues: the adhesive strength is 1.03 N/mm^2, the open time is 20 minutes, no sliding of the tile, the distribution of the solution over the surface is 90 %.

The results obtained confirmed the effectiveness of the use of shungite materials, in particular, "tails" in the formulation of tile adhesives and the feasibility of continuing research to study them as alternative fillers in the production of dry mortar.

An analysis of the results of testing samples with shungite concentrate showed the minimum values, and its production is a laborious process. Therefore, the solution to use the concentrate can be using as a black pigment in the production of grouts based on Ceresit CE33. The resulting samples have high physical and mechanical values that be up to the standards of industrial analogues.

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