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Evaluation of the possibility to use powders of polymineral silica-containing sands as a hydrophobizing coating

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ABSTRACT: Introduction. An important performance characteristic of many building materials is one related to water. Therefore, hydrophobization of the surface of the material is an important task, which at the current level is solved by applying special means. It has been found that it is possible to impart water repellent properties to the surface by using polydisperse mineral materials capable of forming a rough surface. Fine powder from polymineral sand is proposed to be used as a hydrophobisate. The revealed functional relationship between the specific surface and the value of the average particle diameter of the powders, having a linear character, allows assessing their morphological structure and predicting the powder's ability to form a rough layer that enhances the water repellent properties of the surface. **Methods and Materials.** Four deposits of polymineral construction sands are selected as raw materials. The samples were washed and dried. Then their size modulus and true density were determined. To obtain finely dispersed powders, the raw material was ground by dry dispersion. Particle dimensional characteristics were determined by photon-correlation spectroscopy. The visual characteristic of the shape and size of the particles is determined on a laser analyzer. The specific surface area of highly dispersed rock systems was determined by gas sorption, according to BET theory. Measurement of the edge stationary wetting angle was carried out by applying a drop of distilled water to the powder surface. **Results and Discussion.** The dimensional characteristics of the obtained fractions showed that with a milling time (30 min) for the sands of all deposits, the average particle size (*d*) is 360±45 nm. At the same time, the sands of the Kenitsy and Nekhtskoye deposits have the highest values of specific surface area (S_{sp}). The functional relationship between the S_{sp} of the powders tested and 1/*d* was determined. The resulting linear dependencies were characterized by mathematical expressions of the form $S_{sp} = (a/d)+b$, *a* where reflects the rate of change in the specific surface value as the average particle diameter of the samples changes; *b* – is the regression line shift associated with the asymmetric shape of the particles and the non-uniformity (roughness) of the surface. It has been found that as the value of b increases, the degree of inhomogeneity of the surface formed by these particles also increases. Determination of the edge wetting angle of the surface of the powders under study showed that as the grinding time increased, the wetting angle (surface hydrophobicity) increased. So, for the surface of the fine powder of the Nekhtskoye deposit, the wetting edge angle reaches a value (114°) close in magnitude to superhydrophobicity (120°). **Conclusion.** The experiments showed the validity of the proposed working hypothesis related to the possible assessment of surface hydrophobicity by the experimentally determined dependence of $S_{sp} = f(1/d)$. This technique can be used to select mineral powders whose fine systems are capable of hydrophobizing (if necessary hydrophilizing) the surface of the material.

KEY WORDS: polymineral sands, average particle size, specific surface, hydrophobization, edge wetting angle, surface roughness, assessment of hydrophobicity.

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INTRODUCTION

It is known that an important operational characteristic of many building materials (concrete, wood, mineral wool, etc.) is their relation to water. Hydrophilicity of the surface of such systems leads to a number of negative consequences, especially when used at alternating temperatures [1, 2]. Therefore, hydrophobization of the surface of the material is an important task, which at the current level is solved by applying special means (waterproofing mixtures, protective films, impregnations) [3–7]. However, a significant disadvantage of such hydrophobization remains the poor resistance of coatings to environmental temperature differences, oxidative degradation, low environmental friendliness and high cost [8–10].

Recently, a new direction in the creation of protective coatings for materials of various nature has been developed, associated with the use of an emulsion with the content of nano- and microparticles [5], dry mixtures [11], fluorocarbon coatings [12], etc. However, studies show that it is possible to impart (or enhance) water repellent properties to the surface by using polydisperse mineral materials capable of producing a certain (necessary) surface roughness [13–14]. For example, some natural surfaces are characterized by the manifestation of superhydrophobicity, one of the reasons for which is its roughness ("lotus effect") [13–15].

As hydrophobizing agents of material surface we successfully tested fine powder from polymineral sand, obtained by method of mechanical dispersion [13].

The dominant characteristics of the powder used to impart water repellent properties to the surface are the morphology and particle size (the polydispersity index may not be high) and its specific surface area. At the same time, it is necessary to take into account the fact of the relationship of these characteristics. So, if the particles have a shape close to spherical and exhibit the properties of elastic bodies, the ratio [14, 15] is true:

$$d = 6/(\rho_{real} \cdot S_{sp}), \qquad (1)$$

where d – is the average linear particle size, m; ρ_{real} – powder density, kg/m^3; S_{sp} – specific surface area, m^2/kg.

It follows that the larger the difference between the calculated particle dimension parameter of expression (1) and their experimental value, the morphological structure of the components of the disperse systems will be different from simple spherical symmetry, and, therefore, the more effective, from the point of view of roughness, they are able to form a protective surface composition [16].

A practical solution to the problem of selecting rational powder polymineral systems (sands) can be an experimentally determined functional relationship $S_{sp} = f(1/d)$, based on equation (1), which should be linear in nature. Based on the working hypothesis, the coefficients of these linear equations will make it possible to evaluate the difference in the shape of the powder particles from the spherical one, and, therefore, predict the ability of the powder to form a rough layer on the surface of the material with water repellent properties.

Thus, **the object of the present work** was to determine the functional dependence of the type of $S_{sp} = f(1/d)$ for powder materials obtained from polymineral sands of various deposits, and to experimentally evaluate the hydrophobicity of the surface formed by these powders.

METHODS AND MATERIALS

Four deposits of polymineral construction sands were chosen as raw materials for the study: the "Krasnoflotsky-Zapad" and "Kenitsy" deposits (Arkhangelsk region), the "Khromtsovskoye" deposit (the village of Khromtsovo, Ivanovo region) and the "Nekhtskoye" deposits (the village of Teterinskoye, Nerekhtsky district). The last two deposits are located in the Ivanovo region.

Before starting the experiments, the sand was washed and dried to a constant weight at 105°C. Sands size modulus and their true density (by picnometric method) were determined according to GOST 8735-88.

To obtain finely dispersed rock powders, samples, raw material, were ground to finely dispersed state by dry dispersion in a "Retsch PM100" planetary ball mill using a carbidwolfram grinding headset. The optimal dispersion conditions were selected by test to obtain a reproducible particle size with a satisfactory polydispersity of the fractions obtained.

Dimensional characteristic frequency determiner Nano Series Zeta Potential and Submicron Particle Size Analyzers ("DelsaNano") methodical photon-correlation spectroscopy. Visual characteristic of forms and dimensional frequencies of opredelena na lazernom analizatore razmera chastits "Lasentec D600" i S400E s system video microscopy of "PVM V819".

The specific surface area of highly dispersed rock systems was determined by gas sorption, according to BET theory, on the analyzer "Autosorb-iQ-MP".

The measurement of the edge angle of wetting the surface with water was carried out on an Easy Drop unit at a temperature of 25±1°C. The obtained fine powder was applied as a thin layer on a substrate having a polymer base with a surface adhesive based on synthetic rubber. The layer was then uniformly compacted by applying a slide thereon.

To determine the wetting edge angle, a drop of distilled water was applied to the formed powder surface and the steady wetting angle was measured.

RESULTS AND DISCUSSION

The sands of the selected deposits do not differ significantly in modulus of size (M_k) and true density (ρ_{real}) (Table 1).

To obtain fine samples of rocks, the following grinding times were used: 5, 10, 20 and 30 minutes. The results of analysis of the dimensional characteristics of finely dispersed samples after mechanical grinding showed that good reproducibility of the results was achieved under

Table 1
Main characteristics of rocks

Sand deposit	Designation	Mk	Fineness	ρ_{real}, kg/m^3
Krasnoflotsky-West	S1	1.70	small	2710
Kenitsa	S2	2.21	average	2640
Hromtsovskoye	S3	2.18	average	2500
Nekhtskoye	S4	2.43	average	2600

selected grinding modes. The average particle size characteristics of the obtained powders are shown in Table 2.

The obtained data showed that the selected mode parameters of grinding make it possible to obtain highly dispersed systems of analysed samples of polymineral sands with comparable values of dimensional characteristics. For example, analysis of the obtained fractions with the longest grinding time showed that for all deposits the average particle size is 360±45 nm.

During the experiments, the specific surface area (S_{sp}) was determined for each obtained fine fraction (Table 3).

The data presented in Table 3 showed that the highest Ssp values for the time regime of 30 minutes are typical of the sands of the “Kenitsa” and “Nekhtskoye” deposits.

The difference in specific surface values, with almost equal values of dispersion of the analyzed samples, is explained by the difference in the densities of the materials, the structure of the crystal lattice, porosity and possible morphology of the surface (in addition, possible differences in the composition of minerals should be taken into account).

According to the working hypothesis, the functional relationship between the specific surface of the powders tested and the inverse value of their average particle size was determined (Figure 1).

The resulting linear dependencies were characterized by mathematical expressions of the form:

$$S_{sp} = (a/d)+b, \qquad (2)$$

where *a* – is a straight angle reflecting the rate of change of the specific surface value as the average diameter (linear size) of the sample particles changes; *b* – is the offset of the regression line.

The physical meaning of coefficient *b*, in our opinion, is associated with the asymmetric shape of the particles (deviation from the shape of the sphere). This fact makes it possible to assume that the value of this coefficient char-

Table 2
Particle sizes of finely dispersed rock samples

Sand deposit	Average particle size (nm) at different grinding times			
	5 min	10 min	20 min	30 min
S1	754±6	643±9	446±3	388±7
S2	672±4	559±5	406±3	329±4
S3	687±5	550±3	467±1	342±2
S4	604±6	511±4	389±2	314±1

Table 3
Specific surface area of highly dispersed rock samples

Sand deposit	Specific surface area (m^2/kg) at different grinding times			
	5 min	10 min	20 min	30 min
S1	8241±17	10 140±23	15 302±15	22 231±20
S2	7819±13	9920±19	18 670±12	28 603±18
S3	9101±11	10 893±13	16 384±11	23 187±14
S4	7783±18	8870±17	20 854±15	31 543±16

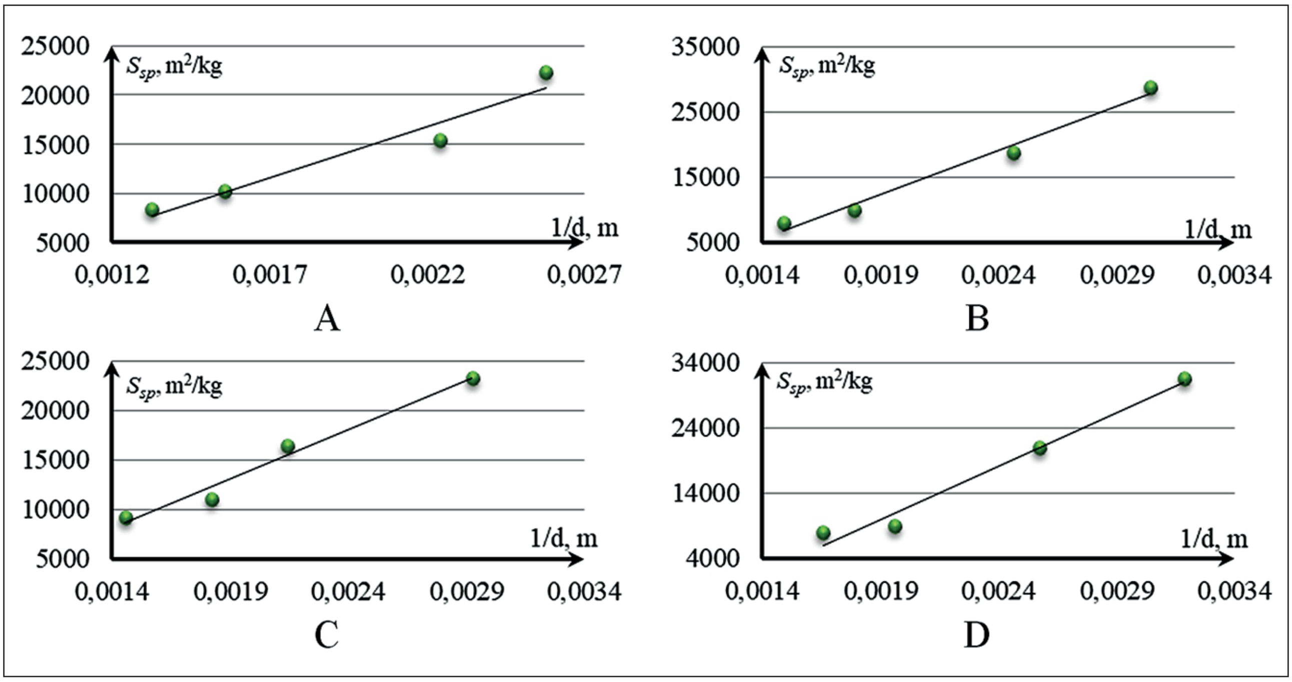

Fig. 1. **Functional dependence $S_{sp} = f(1/d)$ for polymineral sands powders:** A) "Krasnoflotsky-West" deposit; B) "Kenitsy" deposit; C) "Khromtsovskoye" deposit; D) "Nekhtskoye" deposit

Table 4
Values of coefficients for sands of different deposits

Sand deposit	Coefficients of the linear equation		R^2
	$a \cdot 10^7$	b	
S1	1	6111	0.95
S2	1	13 440	0.98
S3	1	5977	0.98
S4	2	21 030	0.98

acterizes the non-uniformity (roughness) of the surface formed by the powder particles.

For fine samples, the coefficients of these equations are shown in Table 4 (R^2 – approximation validity).

From the obtained data, it follows that as the value of b increases, the degree of roughness of the particles associated with their morphological structure and inhomogeneity of the surfaces formed by these particles increases. This fact was confirmed by the synchronism of the changes in the value of the coefficient b for the powders under study, and the corresponding values of the specific surface.

Figure 2 shows photographs that visually characterize the particle shapes of the studied powders of the fields under consideration.

According to the goal, in the continuation of the studies, an edge wetting angle (θ) was determined for each fine sand sample. Figure 3 shows as an example photographs of a water drop located on the surface of powders with different particle size characteristics ("Nekhtskoye" deposit).

The obtained photographs showed that as the dispersion time increases, the wetting edge angle of the samples changes. In this case, the hydrophilic surface of the powder ($\theta < 90^o$) begins to acquire hydrophobic properties ($\theta > 90^o$).

Table 5 shows the experimentally determined values of the wetting edge angle of the polyneral sands fine powders tested and the corresponding values of the free term (b) of the linear expression (2).

The presented results show that for the mineral powder systems under study, the wetting angle (surface hydrophobicity) increases with increasing grinding time (and therefore decreased particle size characteristics). In our opinion, this is due to the formation of a tighter package

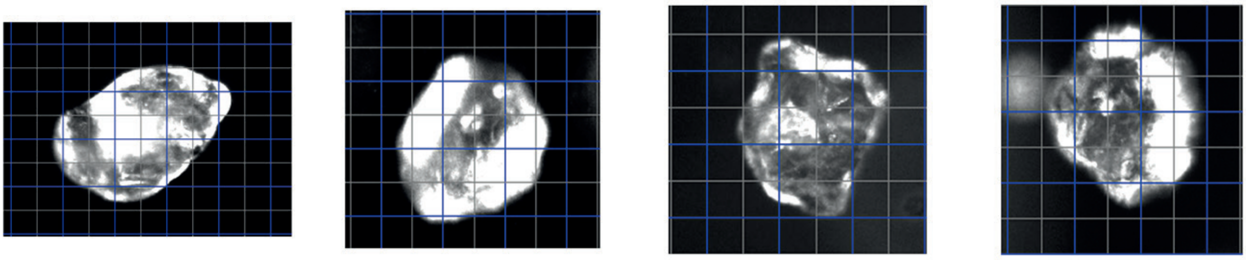

Fig. 2. **Particle shape of fine sand samples (grinding time 30 minutes):** A) "Krasnoflotsky-West" deposit; B) "Kenitsy" deposit; C) "Khromtsovskoye" deposit; D) "Nekhtskoye" deposit

Table 5
Change of coefficient b depending on wetting angle θ

Powder	Coefficient b	Wetting angle (θ^o) for samples with grinding time			
		5 min	10 min	20 min	30 min
S1	6111	12.6	44.3	59.8	90.4
S2	13 440	10.6	39.7	77.8	98.4
S3	5977	13.7	50.8	60.9	97.6
S4	21 030	11.8	33.9	85.8	114.3

Fig. 3. **Water drop on the surface of fine powder:** A) 604 nm fraction (grinding time 5 min); B) 314 nm fraction (milling time 30 min)

of particles on the surface of the substrate and its definite roughness due to the angular shape of the particles while reducing their linear size. Figure 4 shows the functional relationship of type $b = f(\theta)$ for the series of experiments combined by powders of a certain deposit, but obtained at different grinding times.

These results show that the surface of the fine test powders has the ability to increase their hydrophobicity. So, for these systems, a positive correlation between parameter b and the edge wetting angle is observed (Figure 4, lines 3 and 4). For surfaces formed by powder systems with larger particle dimensional characteristics, there is a negative correlation (Figure 4, line 2) between these parameters or there is no such functional connection (Figure 4, line 1).

In addition, it can be noted that for the surface of the fine powder formed by the polymineral sand of the "Nekhtskoye" deposit, the wetting edge angle reaches a value (114^o) close in magnitude to superhydrophobicity (120^o).

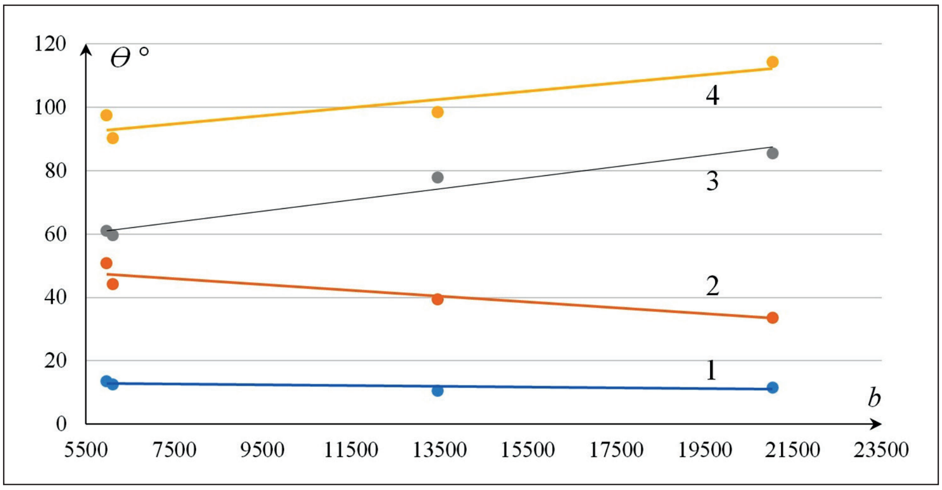

Fig. 4. **Dependence of variation of wetting edge angle on specific surface value of fine sand powders:** 1) grinding time 5 minutes; 2) grinding time 10 minutes; 3) grinding time 20 minutes; 4) grinding time 30 min.

CONCLUSION

The experiments showed the validity of the proposed working hypothesis related to the possible assessment of surface hydrophobicity by the experimentally determined dependence of $S_{sp} = f(1/d)$. This technique can be used to select mineral powders whose fine systems are capable of hydrophobizing (if necessary hydrophilizing) the surface of the material. It should be noted that hydrophobizers based on polymineral sands are characterized by high environmental friendliness and their production is not associated with the implementation of complex technological processes and the high cost of raw material.

REFERENCES

1. Yakovleva M.Ya. Protection of construction structures against water-salt loads. *Roofing and insulation materials*. 2015; 4: 32–35. (In Russian).

2. Fedosov S.V., Rumyantseva V.E., Krasilnikov I.V., Manohina Yu.V., Hrunov V.A. Mathematical modeling of the initial periods of corrosion destruction of the first type of cement concrete. *Architecture. Construction. Education*. 2013; 2: 210-221.

3. Baranov O.V., Komarova L.G., Golubkov S.S. Hydrophobic coatings based on octyltriethoxysiloxane. *News of the Academy of Sciences. Chemical Series*. 2020; 6: 1165–1168.

4. Kravets L.I., Yarmolenko M.A., Rogachev A.A., Gaynutdinov R.V., Altyinov V.A., Lizunov N.E. Formation of hydrophobic coatings on the surface of track membranes by electron beam dispersion of polyvinyl chloride in vacuum. *Nanoindustrium*. 2021; 14(S6): 44–54.

5. Kozhuhova M.I., Chulkova I.L., Harhardin A.N., Sobolev K.G. Evaluation of the effectiveness of the use of hydrophobic aqueous emulsions with the content of nano- and micro-sized particles for modifying fine-grained concrete. *Construction materials*. 2017; 5: 92–97.

6. Loganina V.I., Sergeeva K.A. Assessment of superhydrophobic properties of acrylic resin-based coatings. *Regional architecture and construction*. 2020; 1(42): 98–103.

7. Massalimov I.A., Chuykin A.E., Massalimov B.I., Akhmetshin B.S., Urakaev F.H., Burkitbaev M.M., Mustafin A.G. Longterm protection of building structures with sulfur-based nanoscale coatings. *Nanotechnologies in Construction*. 2019; 11(3): 276–287. Available from: doi: 10.15828/2075-8545-2019-11-3-276-287.

8. Li K., Wang Y., Zhang X., Wu J., Wang X., Zhang A. Multifunctional magnesium oxychloride based composite with stable superhydrophobicity, self-luminescence and reusability. *Construction and Building Materials*. 2021; 286. Available from: doi: 10.1016/j.conbuildmat.2021.122978.

9. Rudakova A.V., Emeline A.V., Romanychev A.I., Bahnemann D.W. Photoinduced hydrophilic behavior of TiO_2 thin film on si substrate. *Journal of Alloys and Compounds*. 2021; 872. Available from: doi: 10.1016/j.jallcom.2021.159746.

10. Tian J., Zhao Y., Wu L., Deng X., Zhao Z., Zhang C. Preparation of refreshable membrane by partially sacrificial hydrophilic coating. *Journal of Materials Science*. 2021; 56(17): 10676–10690. Available from: doi: 10.1007/s10853-021-05960-9.

11. Orekhov S.A., Dergunov S.A., Rubisova V.N. *Erhöhung der Effektivität der Anwendung der hydrophoben Zusätze in den Bindemittel auf Zementbasis*. Internationale Baustofftagung Die 18. Ibausil – Institut für Baustoffkunde der Bauhaus-Universität Weimar. 2012; 1.07.

12. Zheng H., Liu L., Meng F., Cui Y., Li Z., Oguzie E.E., Wang F. Multifunctional superhydrophobic coatings fabricated from basalt scales on a fluorocarbon coating base. *Journal of Materials Science and Technology*. 2021; (84): 86–96. Available from: doi: 10.1016/j.jmst.2020.12.022.

13. Blushan B. (ed.). *Springer's Handbook on Nanotechnology*. 2nd ed. Moscow: Technosphere; 2010.

14. Lidiya Mishchenko, Benjamin Hatton, Vaibhav Bahadur, J. Ashley Taylor, Tom Krupenkin, Joanna Aizenberg. Design of Ice-free Nanostructured Surfaces Based on Repulsion of Impacting Water Droplets. *Nanoletters*. 2010; 4(12): 7699–7707.

15. Danilov V.E., Ayzenshtadt A.M. Integrated approach to the assessment of nanoscale fractions of polydisperse systems of crushed rocks. *Nanotechnologies in Construction*. 2016; 8(3): 97–110. Available from: doi: 10.15828/2075-8545-2016-8-3-97-110.

16. Summ B.D. Hysteresis of wetting. *Soros educational journal*. 1999; (7): 98–102.

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