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MEASUREMENT OF THE SURFACE FORCES IN A HIGHLY DISPERSED SYSTEMS

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Abstract

Scientifically justified and worked out methods for determining the energy characteristics of the surface of highly-dispersed raw rocks. The values of the energy density of the samples of rocks were calculated. The calculation of the surface activity for the highly-dispersed raw materials of rocks obtained by dispersing was suggested.

Key words: *criterion of surface activity, thermodynamic approach, dispersion, mineral fillers, atomization energy, free surface energy, critical surface tension*

1. INTRODUCTION

The composite building material is a heterogeneous system consisting of two or more individual components while maintaining the properties of each. Construction composites represent a new generation of materials with improved properties unattainable in the individual components. Optimization of the composite material is often associated with a significant amount of labor-intensive experiments on the selection of the quantitative content of components to give the material specified properties. Therefore, investigation of the possible relationship of the surface properties of the composite material with the physical and chemical characteristics of the final product, and selection criteria, which makes it possible to quantify the ability of the components to the transformation conversions , are an urgent task. This task is particular important for the building material science, as well as the main technological method of preparation of the raw material is its fragmentation. As a result, a new surface is formed with the excess surface energy.

Assessment of the overall tendency of the highly-dispersed system surface to the transformation conversions can be based on the thermodynamic characteristics of its energy state [Veshnyakova, 2012], which is defined as the level of the common stock of the potential energy of the rock (depending on the genesis) and as a part of it which is passed into the surface energy of the formation of new solid surface in the process of crushing material. It is important to keep in mind that the energy transition quantitatively determined by many factors: the size of the particles, their structure and shape, mineral composition, crystal lattice defects forming minerals, gas, air and other inclusions, chemical nature , etc. This is especially important for the material in a highly-dispersed state, which is characterized by the surface heterogeneity, consisting of particles of nano-and micron-sized fineness.

The rocks used in the manufacture of building materials, have a free supply of internal energy, which reduces the work expended in mechanical disintegration of raw materials and new formations synthesis of the final product. So an important task in building materials is a selection of energy-saving materials, which supply of internal energy can be used to produce a material with the pre-desined properties. The possibility of using the energy criterion suggested by the author [Lesovik, 2006] for the classification of raw materials used in the manufacture of building materials.

Ecologicall impact on the environment is reduced through the use of complex materials based on rocks with regard energy store of internal energy. Furthermore, the joint application of fine fillers through the rock occurs a synergistic effect which allows to obtain the adhesive strength of the composite.

Adhesive interaction for highly dispersed systems is determined by the following parameters [Lesovik, 2013; Veshnyakova, 2013]: the critical value of the surface tension ($\sigma_к$), the specific mass atomization energy (E_m, J/kg) , the atomization energy (E_a) and the criterion of surface activity k_s. The main criterion for ranking highly materials (ultra-and nano-dispersed), the coefficient of surface activity of the rock (k_s) can be used. The proposed surface activity coefficient shows the share of the surface free energy (E_S), the acquired system in the transition from the course to the highly dispersed state of the common stock of the internal energy (E_m) of the entire system of rock.

In studies [Frolova, 2011] the technique of determining the surface free energy value of the nanodisperse rocks materials by surface tension ($\sigma_к$ - surface energy per unit surface area, J/m^2). For the thermodynamic calculation of the surface free energy (E_s ,J/kg) finely system taking into account its specific surface area (S_{sp} , m^2/kg) must use the following relationship :

$$E_s = \sigma_к \cdot S_{sp} \quad (1)$$

Then the ratio E_s / E_m is a parameter (k_s), which characterizes the level of reserve potential energy contained in the rock due to the activation of its surface. So parameter (k_s) means the surface activity of a material in a highly dispersed state. According to calculated values the energy density (E_v)of rocks depended on their genesis and can be divided into high energy dense (igneous and metamorphic rocks) and average energy dense (sedimentary or effusive rocks) [Abramovskaya, 2012, 2013; Zuev, 2006].

The purpose of these studies is the experimental determination and evaluation of changes in the surface activity of the materials in a highly dispersed state, depending on the origin of rocks (igneous, metamorphic and effusive) as raw material for the building composites production.

2. EXPERIMENTAL

2.1. Materials

As objects of study we selected rock from the deposits of the Arkhangelsk region: igneous - granite from the deposit "Pokrovskoe" and basalt deposits from Myanduha mountain in Plesetsk district; metamorphic - amphibolite from the field "Kiyskoe"; effusive - river sand from the field "Kenitsy". The samples were pre-washed from clay particles, dried and made to constant weight at 105°C. 105^{0}C.

2.2. Methods

The process of dispersion was carried out on the planetary ball mill PM 100 («RetschGmbH») using dry method.

Particle size distribution of the samples in highly-dispersed state was determined with Delsa Nano Series Zeta Potential and Submicron Particle Size Analyzers by photon correlation spectroscopy based on the dynamic light scattering.

Determination of the specific surface area of the samples in highly-dispersed state was performed with volumetric adsorption method. The method deals with the analysis of gas trapping by solid at constant cryogenic temperature and gradual increase in pressure. The specific surface area was measured on the Autosorb-iQ-MP.

To determine individual energy characteristics of tested objects, the Zisman method was used. The $\cos\theta=f(\sigma)$ dependence was determined for water-ethanol mixture with alcohol concentration varying from 50 to 100 volume per cent for the surface formed by disperse system particles. Extrapolating the averaged curve to $\cos\theta=1$, critical value of surface tension σ_{cr} was obtained.

3. RESULTS AND DISCUSSION

Grinding of raw materials was carried out using the following operating parameters of the grinding machine (Figure 1): 50 -tungsten carbide grinding bodies with 10 mm diameter, rotor speed of 420 rev/min, grinding time for granite - 60 min., for basalt - 180 min., for amphibolite - 60 min., for polymineral sand - 60 min. Engine stop period of the ball mill rotor - 30 min. Duration stops - 1 min. After closure of these (first) step of dispersing a ball mill was turned off and the rotor is kept closed for 30 min to achieve a temperature of the rotor cup 30 ÷ 40^{0}C then removed synthesized rock sample. These operating parameters allow to obtain stable dispersion grinding results of the samples.

To estimate the size characteristics and properties of rocks obtained during the grinding of nano-to micron-sized state, the modern equipment was used (Figure 2). The average size of fine granite samples was 206 ± 57 nm (Figure 3) , basalt - 360 ± 98 nm (Figure 4) , amphibolite - 416 ± 114 nm (Figure 5), silica- rock - 266 ± 69 nm (Figure 6).



Figure 1 - Sampling preparation: Planetary Ball Mill Retsch PM100



Figure 2 - Up-to-date equipment of particle analysis: Delsa Nano by Beckman Coulter

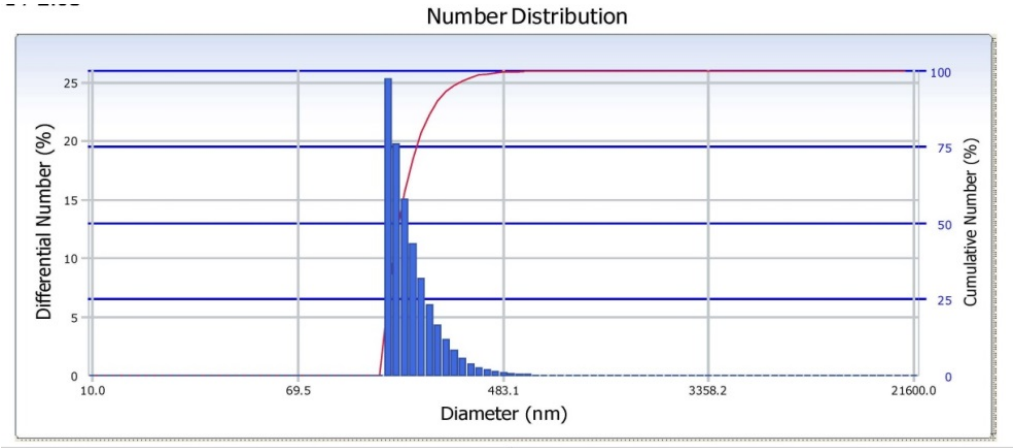


Figure 3 – The test report of the sample particle size determination of the granite (average particle size of 206±57 нм)

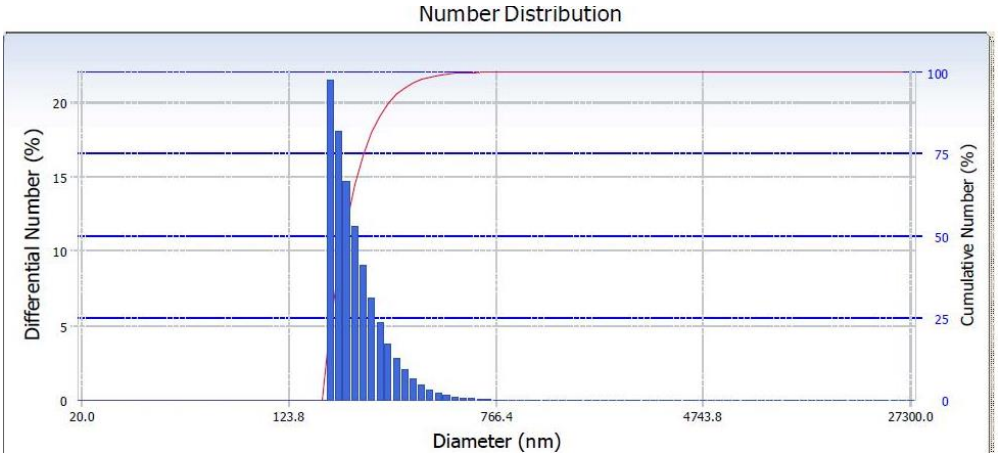


Figure 4 – The test report of the sample particle size determination of the basalt (average particle size of 360±98 нм)

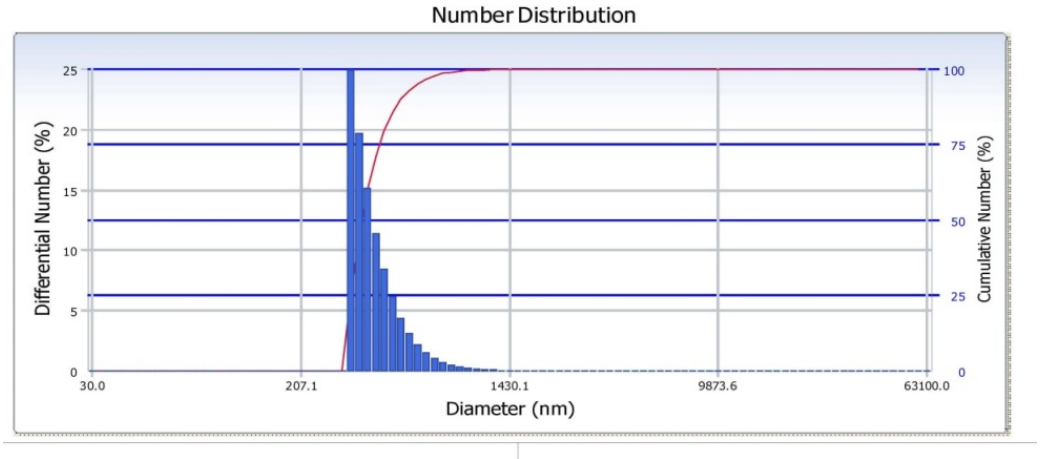


Figure 5 – The test report of the sample particle size determination of the amphibolite (average particle size of 416±114 нм)

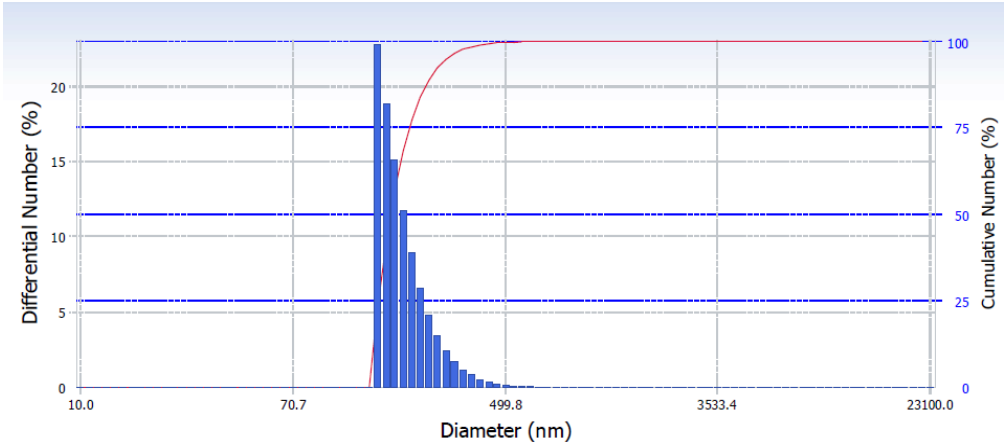


Figure 6 - The test report of the sample particle size determination of the sand (average particle size of 266 ± 69 nm)

Determination of the surface contact angle was implemented on KRUSS Easy Drop at 20 $\pm 2^0$C. In the experiments for the contact angle determination, the first contact with the surface of the liquid and the sample surface was chosen. The critical surface tension of the tested materials was determined by the method [7, 9]. The actual value of the surface tension of the solid body cannot be identified, however, the surface energy of such substance can be calculated by the critical surface tension ($\sigma_к$) bordering the rigid body (G.A. Zisman method). According to Zisman method, the dependence $\cos\theta = f(\sigma)$ for various liquids is obtained and then is extrapolated to the average curve to $\cos\theta = 1$. Thus the critical value of the surface tension, σ_k, which is the characteristic of the surface energy per surface of the solid phase unit was determined.

There is a limitation associated with the use of the Zisman method. This limitation is based on that the liquids for measuring the contact angle should be poorly polar or nonpolar. Based on the above mentioned limitation of the Zisman method, the first experimental problem to be solved at the stage of preliminary experiments is the selection of the reference solution. The surface tension of this reference solution will be used in determination of the critical surface tension of the solid surface. The second experimental problem to be solved is the choice of determining method for σ. Most appropriate to apply a homologous series of liquids. With the amount of surface tension over $35 \cdot 10^{-3}$ N/m Zisman method gives high inaccuracy, since in this case it is necessary to take into account the contribution of polar forces in an adhesive interaction. During the experiments an aqueous solution of industrial alcohol at a concentration of 4 to 50 % by volume of water were used. In tests physical parameters

of drops was empirically chosen (capillary diameter - 1,821 mm). The test report of the sample particle size determination is shown in Figure 7.

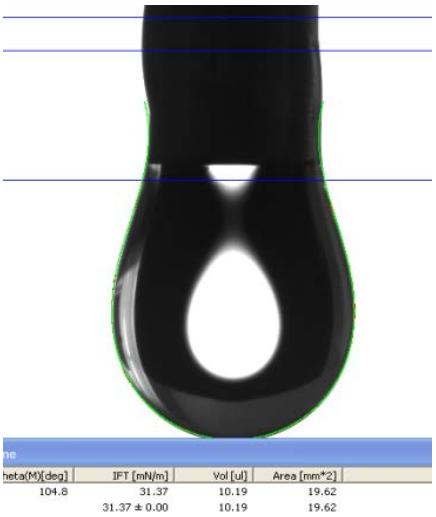


Figure 7 – Determination of surface tension of aqueous ethanol solution

To implement the Zisman method, we used the ethanol solutions with different contents of water fraction and water fraction in the concentration of the solution did not exceed 50%. The required test samples were prepared by compacting into a metal mold 25 mm in diameter with a 1.5 kPa load during 1min. Preformed composite samples were made in special molds and compacted on a laboratory hydraulic press PLG-20 (Figure 8 and 9).



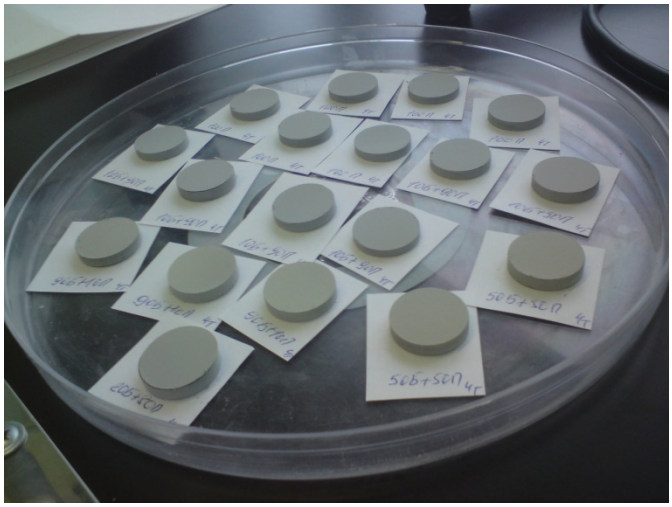


Figure 8 - Manual hydraulic press PLG-20 Figure 9 - The samples for the determination of the contact angle

In experiments of contact angle determination, the first contact of the liquid with the surface sample was analyzed according to a specialized computer program, which in all experiments varied in the range from 1,0 ± 0,5 (Figure 10). This is due to the fact that during this period of time the processes of diffusion in the liquid bulk phase, capillary phenomena and other processes related to the heterogeneity of the surface can be disregarded. Furthermore, a good reproducibility of the measurement results may indicate the existence of a given time interval as it were equilibrium state at the interface.

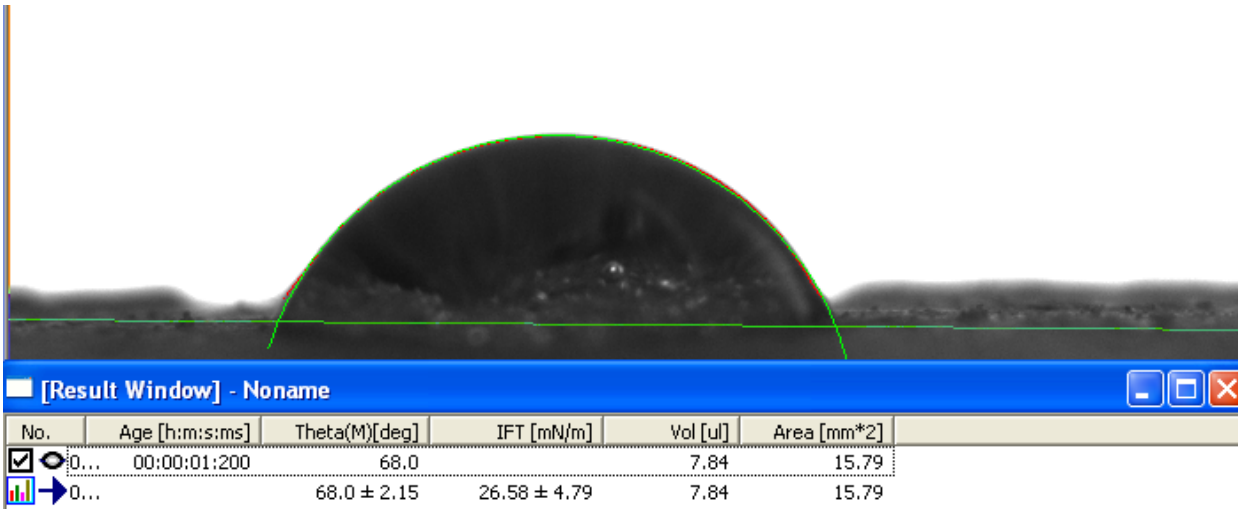


Figure 10 - Water-alcohol solution on the surface of the sand

Additionally, to confirm the size characteristics of highly-dispersed samples, the photos of samples of rocks in a highly dispersed state were obtained by scanning electron microscopy (SEM) with an electron microscope Zeiss SIGMA VP (Figure 11 and 12).

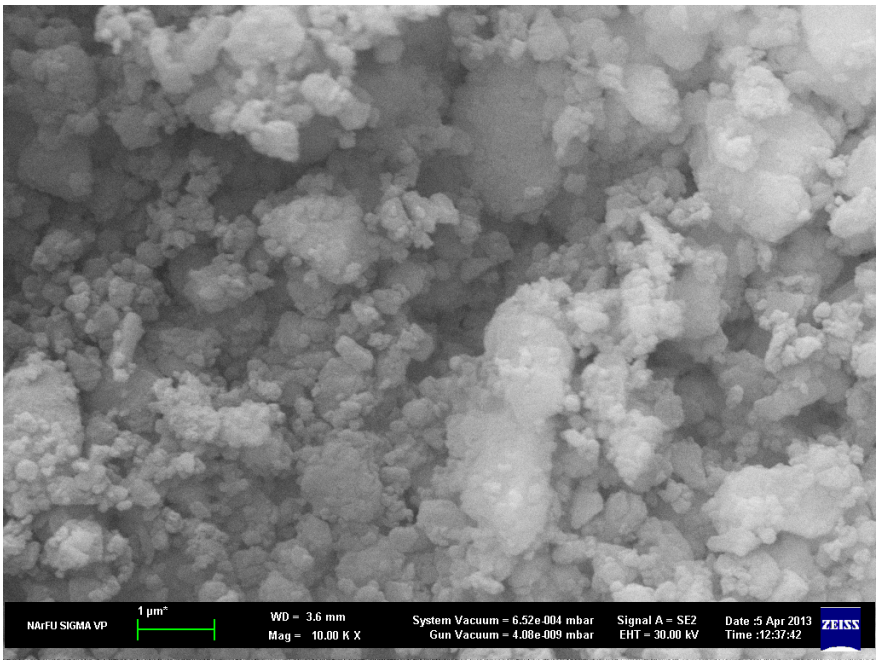


Figure 11 - SEM sample basalt with an average particle size of 360 ± 98 nm.

To calculate specific quantities of atomization energy (E_m) of the fine materials source and composite mixtures, the true density (ρ) were determined for all test samples by pycnometer test according to GOST (all-Union state standard) 5180-84. Specific surface area was measured on Autosorb-iQ-MP with sorption method nitrogen. The magnitude of the surface energy Es was calculated from the total surface area of the dispersed sample.

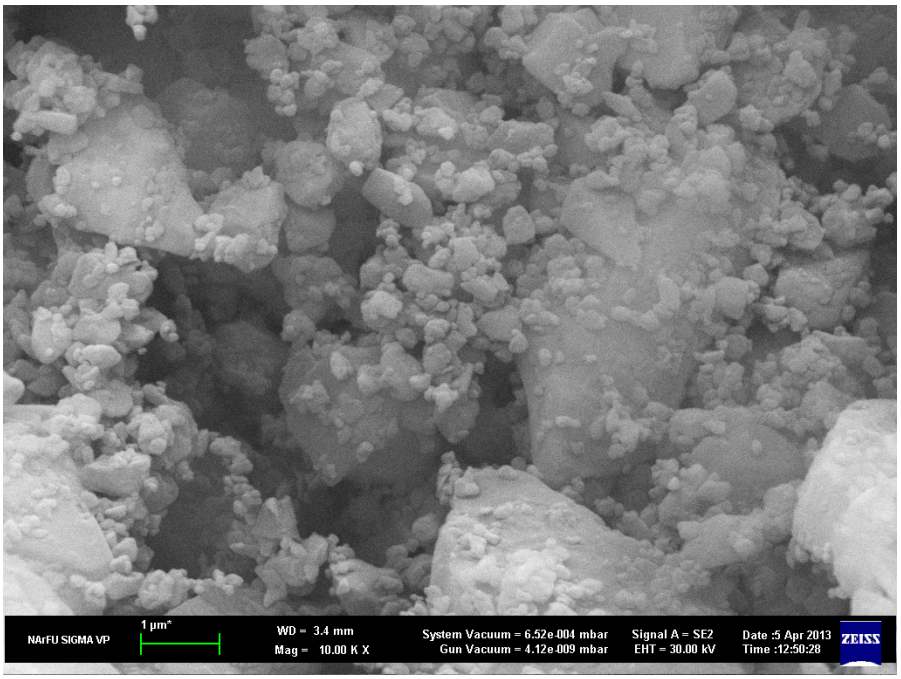


Figure 12 - SEM sample of sand having an average particle size of 266 ± 69 nm.

The data obtained in the experiments for determination of σ_k , S_{sp} and ρ, and also as a result of calculations of the energy characteristics of E_a, E_m, are presented in table 1.

Table 1. The experimental data and calculated the energy characteristics of test samples

Rock	Characteristic	ρ, kg/ m^3	Macro energy characteristics				Surface properties of highly dispersed systems (d=200÷400 nm)		
			E_a, kJ/ mole	E_v, kJ/ sm^3	$E_{m,}$ kJ/kg	class on E_v	S_{sp}, m^2/kg	$\sigma_к \cdot 10^3$, J/m^2	E_S, kJ/kg
Igneous rocks									
Granite	Intrusive abyssal uniformly granular	2600	1909	75	29	High energy dense	9159 ±54	21,2	0,19
Basalt	Effusive cryptocrystalline	3050	1892	81	27	High energy dense	7145±36	24,5	0,18
Metamorphic rocks									
Amphi bolite	Epidote-amphibolite facies	3000	1868	80	27	High energy dense	2750 ±14	19,4	0,05
Sedimentary (effusive) rocks									
Sand	Amorphous	2070	1790	56	27	Average energy dense	8580±43	22,2	0,19

The experimental results allowed us to calculate the surface activity of highly-dispersed granite samples (k_s=0,67·10^{-5}), basalt (k_s=0,42·10^{-5}), amphibolite (k_s=0,20·10^{-5}) and polymineral river sand (k_s=0,70·10^{-5}). These obtained values agrees well with the origin of the samples.

4. CONCLUSION

Calculations showed that as the main criterion for quantifying energy classification of raw materials on the basis of rocks for building composites, the value of the surface activity (k_s) can be used. Consequently, it can be assumed that the surface activity characterizes the material genesis. In addition, based on the physical meaning of the surface activity (k_s numerically equal to the ratio of the surface energy to the specific mass atomization energy) we can conclude that energetically more favorable raw material for building highly-dispersed composites are igneous rocks.

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