

**ENERGY STATE CHARACTERISTIC OF RAW MATERIALS
FOR BUILDING NANO-COMPOSITES**

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Abstract

Samples of sand and basalt in nanodispersed state were experimentally obtained. The optimum regime of samples disintegration was defined. Using Zisman method, values of the critical surface tension of liquid on the border of the investigated materials and the complex Hamaker constant were calculated. The applicability of the thermodynamic approach to the assessment of the surface energy state of disperse systems was confirmed. The atomization energy and energy density of the dispersed samples were calculated.

Key words: *Zisman method, critical surface tension, complex Hamaker constant, free surface energy, energy density, atomization energy.*

1. INTRODUCTION

It is known that the material which is composed of two or more components, differing in composition and genesis, where the components are combined into a monolithic structure with the optimal combination of interface between the structural components, called the composite material. Different compound combination of composite material is providing a certain set of physicochemical and mechanical properties [1]. Nanocomposites are the objects where the nanoparticles are packed in a macroscopic sample with interparticle interactions of compound much stronger than individual particles of its components [2].

With respect to the using of micro-and nanosystems in building materials, recent studies were shown its suitability for continuous operation in extreme conditions. This approach allows to improve such quality characteristics of construction materials as: strength, durability, thermal and chemical resistance, fracture toughness. Thus nanotechnology using increases the operational period and productive life of structures [3-5].

Raw materials have a free internal energy reserve, therefore the work spent on the mechanical disintegration of the feedstock and the new formation synthesis is reducing. Thus, a significant goal of the building materials science is a selection of energy-saving materials with internal energy reserve, which can be used for obtaining a material with special properties. In regard to the building materials production, this energy criteria is used for ranking the raw materials [6]. Nano-dispersed material is a system with surface energy excess and high reactivity, which demands a detailed study of the changes in the properties of composites. The development of methods for creating surfaces nanomodified dispersed materials is required as well [7].

In our opinion the comprehensive approach to the nanocomposites formation with the optimum composition of nanoscale components, involves the algorithm designing for the surface energy parameters calculating. This algorithm must be based on the thermodynamic evaluation of the nanofillers surface energy properties. [7, 8].

The actual value of the energy of solid surface cannot be evaluated. Thus, the parameter σ for the solid body is a measure of energy reserve in the decompressed surface layer (a measure of the free surface energy) [5, 9, 10].

Research shows that the critical surface tension of the system (σ_c) determines the nature of the components, forming the material surface. Consequently, the critical surface tension σ_c defines the free surface energy reserve. The cohesive resistance of particles in the composite material is characterized by the complex Hamaker Constant (A^*). Hence, an algorithm was designed to determine the surface state energy of the nanodispersed materials through the critical surface tension and the complex Hamaker constant [11]. This algorithm includes the Zisman method [12] and implemented with up-to-date equipment (EasyDrop).

In according to the above, the main aims of the study were identified. They are:

- an experimental obtaining of nanosized systems from raw materials of the Arkhangelsk region,
- the definition of the critical surface tension and the complex Hamaker constant for these systems,
- comparative analysis of received data and the energy parameters, calculated on the thermodynamics basis.

2. EXPERIMENTAL

2.1. *Materials*

As investigated materials we selected polymineral river sand (the main minerals of its components are quartz, calcite, feldspar, gypsum, mica) and basalt grit, selected from the basalt deposit from mountain named 'Myanduha' near Arkhangelsk region [13]. The fineness of the sand grain ranges from 1.6 to 1.8 mm. Sand was pre-washed from the clay inclusions. The samples were dried and adjusted to a constant weight at 105°C.

2.2. *Methods*

The chemical composition of the samples was characterized by X-ray fluorescence spectroscopy with the spectrometer Shimadzu EDX-800 HS.

Dispersion process was carried out on a Planetary Ball Mill (Retsch PM100) and Colloidal Mill (IKA magic LAB).

The particle size was tested on the system for determination particle size and zeta potential (Delsa Nano Series Zeta Potential and Submicron Particle Size Analyzers) by measuring the dynamic and electrophoretic light scattering.

EasyDrop system was used for implementing the contact angle measurements and assessment of surface quality of treated materials.

Zisman method was applied for defining of individual energy characteristics of the investigated materials. As the result, the dependence of $\cos\theta = f(\sigma)$ for the water-ethanol mixture with alcohol volume range 50-100 percent, in case the surface was formed by the particles of the dispersed system, was obtained. The critical surface tension σ_c was defined by the averaged curve extrapolation to $\cos\theta=1$.

The density of the sand was determined by pycnometer test. The basalt density was tested by weighing waxed samples in water.

3. RESULTS AND DISCUSSION

The investigated samples are similar in amount content (in terms of oxides) such components as SiO₂ (47-56%), MgO (8-19%), Fe₂O₃ (5-13%), CaO (4-14%), Al₂O₃ (9-14%). The chemical composition of sand and basalt samples in terms of oxides, as well as the molar mass of the oxides is presented in Table 1.

Table 1. The composition of the samples in terms of oxides, %.

Analyte	Sample		Molar mass of the oxide, g/mol
	Sand	Basalt	
SiO ₂	58,111	47,752	60,1
MgO	8,473	14,599	40,3
Al ₂ O ₃	9,291	13,803	102,0
Fe ₂ O ₃	5,053	13,094	159,6
CaO	14,663	8,289	56,1
Na ₂ O	- *	0,891	62,0
TiO ₂	0,783	0,531	81,9
K ₂ O	2,402	0,317	94,2
SO ₃	0,146	- *	80,1
P ₂ O ₅	0,618	- *	142,0
Cr ₂ O ₃	- *	0,266	152,0
ZrO ₂	0,040	- *	123,2
ZnO	0,024	- *	81,4
BaO	- *	0,221	153,3
MnO	0,319	0,218	70,9
SrO	0,022	0,019	103,6
NiO	0,055	- *	79,5

* - component is not detected

The optimum regime of samples disintegration was defined. This regime means that the minimum particle size of dispersed samples and the high reproducibility of results for each of the investigated samples were obtained.

The required reduction ratio of sand was achieved due to dry disintegration by Planetary Ball Mill. The grinding duration was 120 minutes with the rotary speed 420 rpm. As the result we got dispersed material with average size 313.4 ± 89.9 nm. The subsequent fragmentation of the aqueous suspension of the sand sample was carried out on a Colloidal Mill. The grinding duration of the second disintegration was 30 minutes with the rotary speed 16,000 rpm. The final reduction ratio of the sample amounted to 102.0 ± 29.9 nm. Fractional composition of the dispersed sample (95%) presented in Table 2. The test report of sand size determination is shown on Fig. 1.

Table 2. Fractional composition of the **sand**.

Grind time t, min	Fraction size, nm / Content, %							Average size, nm
	№ 1	№ 2	№ 3	№ 4	№ 5	№ 6	№ 7	
120	240,5/21	259,9/18	280,9/15	303,6/12	328,2/9	354,7/7	383,4/5	313,4±89,9
30	81,1/25	88,7/20	97,1/16	106,2/12	116,2/9	127,1/6	139,0/4	102,0±29,9

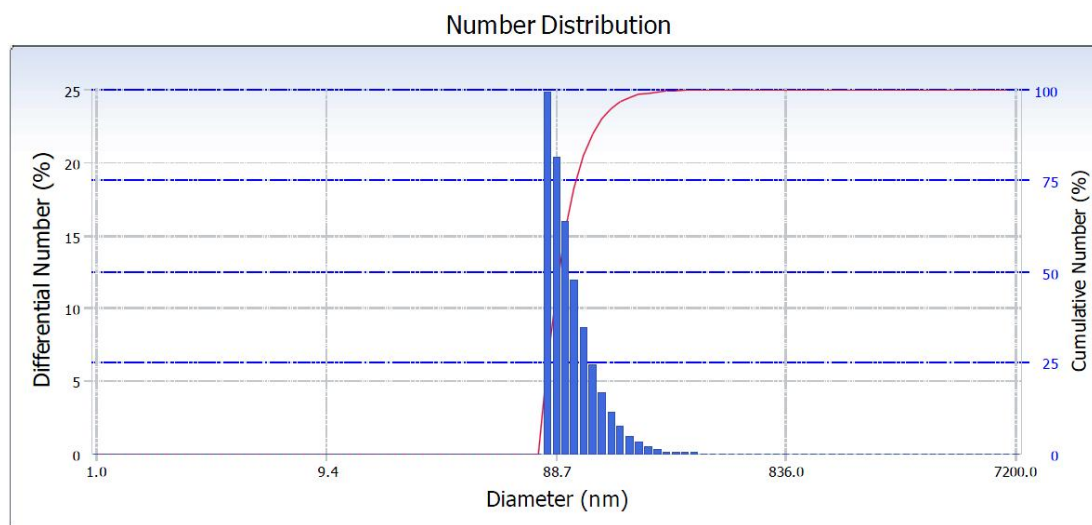


Fig. 1 - Average particle size of **sand** implemented by Delsa Nano

Basalt is rather stable, hard and abrasive rock. Owing to these causes basalt has a grinding limitation of using the Colloidal Mill. Therefore, the required reduction ratio of basalt was attained by wet disintegration on the Planetary Ball Mill for 120 minutes with the rotary speed 420 rpm. In total, average size of the dispersed basalt grit was 102.8 ± 28.2 nm. Fractional composition of the dispersed sample (89%) of basalt is presented in Table 3. The test report of basalt size determination is shown on Fig. 2.

Table 3. Fractional composition of **basalt**.

Grind time t, min	Fraction size, nm / Content, %							Average size, nm
	№ 1	№ 2	№ 3	№ 4	№ 5	№ 6	№ 7	
120	77,0/17	83,7/17	90,9/16	98,9/ 14	107,5/11	116,8/8	127,0/6	102,8 ±28,2

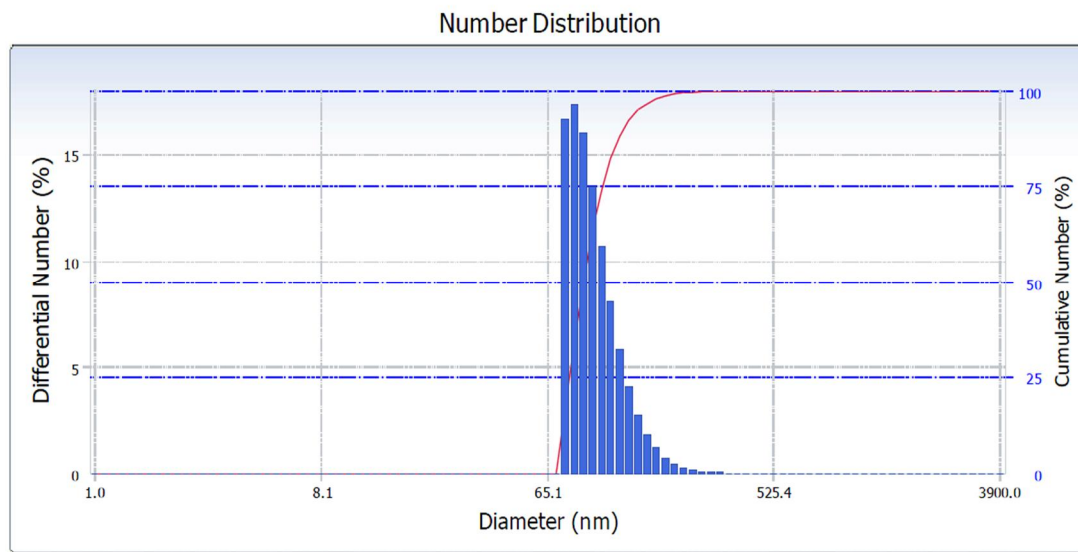


Fig. 2 - Average particle size of **basalt** implemented by Delsa Nano

In order to determination individual energy characteristics of the dispersed objects there are test models were made. These modelss were produced by compaction of the dispersed samples to the metal mould with the diameter 10 mm. The compaction value was 1.5 kPa.

The calculation of the critical surface tension (as well as surface energy) σ_c produced due to the $\cos\theta = f(\sigma_{zh})$ graph construction for the samples (extrapolation at $\cos\theta \rightarrow 1$). Also the complex Hamaker constant was defined owing to the $\cos\theta-1 = f(1/\sigma_{zh})$ graph construction. Those experimental data, namely the tangent of the inclination line of $\cos\theta-1 = f(1/\sigma_{zh})$, which is multiplied by the constant $12\pi h_{\min}^2$, is equal to the value of A^* [8] ($h_{\min} = 0.24$ nm). Functional dependences of $\cos\theta = f(\sigma_{zh})$ and $\cos\theta-1 = f(1/\sigma_{zh})$ for the samples of sand and basalt, derived from experimental and calculated data, are shown on Fig. 3 and 4. The Tables 4 and 5 includes values of calculated and experimental data.

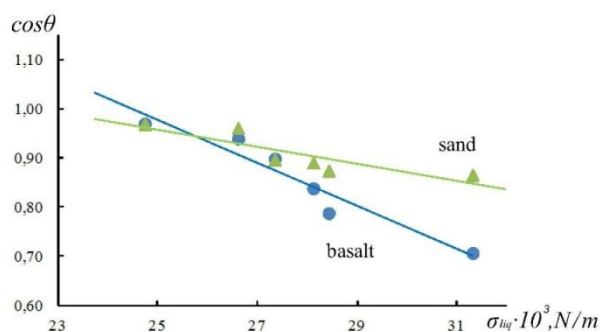


Figure 3 - Functional dependence of $\cos\theta = f(\sigma_{liq})$ for dispersed samples of sand and basalt.

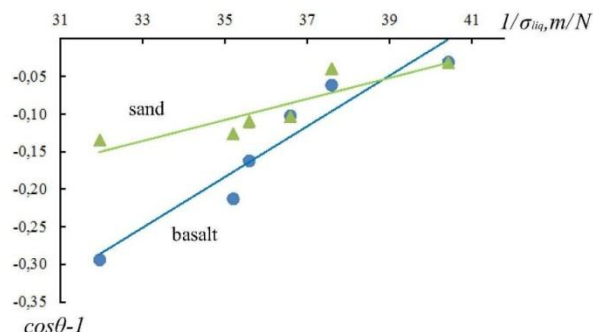


Figure 4 - Functional dependence of $\cos\theta-1 = f(1/\sigma_{liq})$ for dispersed samples of sand and basalt.

Table 4. Coefficients in the equation $\cos\theta=a\sigma_{liq}+b$ and σ_c value for the samples

Dispersed sample	Coefficient		Approximation accuracy, R^2	σ_c , N/m
	a	b		
Sand	-0,018	1,4	0,8	22,6
Basalt	-0,044	2,1	0,9	24,5

Table 5. Coefficients in the equation $\cos\theta-1=a/\sigma_{liq}+b$ and complex Hamaker constant for the samples

Dispersed sample	Coefficient		Approximation accuracy, R^2	$A*10^{20}$, J
	a	b		
Sand	0,018	-0,8	0,8	4,0
Basalt	0,034	-1,4	0,9	7,3

With respect to the physic-chemical bases of the crystal energy science of solid materials, energy density is known as one of the characteristic of the free energy value of solids (minerals) [14]. The energy density calculation is based on the values of the atomization energy of the substance.

$$E_v = \frac{E_a}{V} \quad (1)$$

where E_a – calculated atomization energy, kJ/ mol

V – molar volume of the compound, m^3/mol , which is determined according to:

$$V = \frac{M}{\rho} \quad (2)$$

where M - molar mass of the sample, kg/mol

ρ - density of the sample, kg/m^3 .

For the majority of minerals the energy density is already calculated [14]. However, for the raw materials rock with multicomponent structure, this approach was tested for the first time. The atomization energy means endoergic effect, with transformation of one mole of a simple substance into non interacting atoms with free state. Thus, the atomization energy of the crystal is consists of the total amount of its standard enthalpy of formation and heat of formation of the constituent atoms [15].

The atomization energy E_a of sand and basalt was counted. According to the percentage in the complex compound, the molar ratio values were used in this calculation (Table 1). The density of the dispersed samples of basalt and sand was 3050 kg/m^3 and 2070 kg/m^3 , respectively. Computed values of the heating effects are shown in Table 6.

Table 6. Enthalpy of formation of elements and their compounds

Element	The enthalpy of formation of the element, ΔH_f , 298,15 K	Source	Oxide	The enthalpy of formation of the element, ΔH_f , 298,15 K	Source	Calculated atomization energy E_a , kJ/mol
Al	329,7	[16]	Al_2O_3	-1675,7	[16]	3082,61
Ba	179	[16]	BaO	-548	[16]	976,17
Ca	177,8	[16]	CaO	-635,09	[16]	1062,06
Cr	397,147	[17]	Cr_2O_3	-1140,6	[17]	2682,404
Cu	337,6	[18]	CuO	-156,1	[18]	742,87
Fe	413,3	[18]	Fe_2O_3	-823,4	[18]	2397,51
K	89	[17]	K_2O	-361,7	[17]	788,87
Mg	147,1	[16]	MgO	-601,5	[16]	997,77
Mn	283,3	[18]	MnO	-382,5	[18]	914,97
Na	107,5	[17]	Na_2O	-414,57	[17]	878,74
Ni	430,1	[18]	NiO	-239,7	[18]	918,97
O	249,17	[19]	-	-	-	-
P	316,4	[19]	P_2O_5	-1498,12	[21]	3376,77
S	277,03	[19]	SO_3	-438,4	[18]	1462,94
Si	450	[20]	SiO_2	-910,7	[20]	1859,04
Sr	160,5	[16]	SrO	-590,5	[16]	1000,17
Ti	473,715	[17]	TiO_2	-944	[17]	1916,055
Zn	130,4	[18]	ZnO	-350,46	[21]	730,03
Zr	599,293	[17]	ZrO_2	-1100,3	[17]	2197,933

Table 7 presents the calculation data such as atomization energy E_a and the energy density E_v defined for the test models. These data indicate a significant free energy reserve of dispersed basalt. That means, basalt is a material with a high value of energy density. This property can be used to strengthen the structure of composite materials based on basalt. The dispersed sand can be attributed to the material with a middle value of energy density [14].

Table 7. The calculated energy characteristics of the investigated materials

Sample	σ_c , N/m	$A^* \cdot 10^{20}$, J	E_a , kJ/mol	E_v , kJ/cm ³
Sand	22,6	4,0	1789,8	55,96
Basalt	24,5	7,3	1892	80,97

4. CONCLUSION

The calculation of the energy density values and the complex Hamaker constant for nanosized materials were performed. The complex Hamaker constant for the nanosized materials was calculated, its value for basalt and sand was $7.3 \cdot 10^{-20}$ J and $4.0 \cdot 10^{-20}$ J, respectively. In the comparison of nanosized basalt to nanosized sand, basalt has a more pronounced ability to form rigid interparticle interactions.

Moreover, obtained data are comparable with the classification of rocks, resulting the dependence of the surface free energy with the raw material genesis [6]. Thus, a good convergence of our results with classical ideas about rock energy content, depending on the genesis and the thermodynamic parameters of the energy density, shows the selected criteria (σ_c and A^*) as characteristic of the surface energy state of nanosized materials.

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