IOP Conference Series: Materials Science and Engineering

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To cite this article: Yulia Sokolova *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **365** 032036

Energy characteristics of finely dispersed rock systems

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Abstract. In their genesis, rocks accumulate their energy potential – free energy of rock-forming minerals and the rock in general that is an important criterion of raw material genetic classification for construction materials production. The free energy value for the macrostate of a substance (rock) is atomization energy. The critical surface tension value can be used as an energy characteristic for destroyed rock in a finely dispersed state. If condensed phase surfaces carry no significant electrostatic charge, then main surface forces that determine the interaction between solids are dispersion ones evaluated by the Hamaker constant value. These energy parameters can enable forecasting various physical and mechanical properties of minerals and rocks and thereby increase the efficiency of construction materials production where synthesis is based on the complete rock destruction. Since compared chemical compositions of minerals forming rocks revealed a predominant silicon dioxide content in them, the aim of this paper was to establish a possible relationship between the silicon dioxide content and energy characteristics for finely dispersed rock systems of various genetic types. The selected objects of research were different genesis rocks typically used in the construction materials industry and quartz as a main rock-forming mineral. Test samples of rocks in a finely dispersed state were obtained by dry milling. It is established that an increase in silicon dioxide content in the limestone – quartz series leads to higher atomization energy, specific mass atomization energy and free surface energy with intensified dispersion interaction between particles evaluated by an increase in the Hamaker constant.

1. Introduction

Rocks are complex polygenetic natural compounds formed as a result of physical and chemical natural processes in the Earth's interior and on the surface continually changing in time and making up a raw material basis for the construction materials industry [1].

The management of structure forming processes when synthesizing construction composites, evaluating and forecasting various material properties and determining ways of their sustainable use should take into account petrographic characteristics (mineral composition and typomorphic features: morphological and structural peculiarities) of rocks.

Studies presented in papers [2-4] have shown that petrographic characteristics are important parameters affecting physical and chemical properties of rocks. Many scientists studied a relationship between the mineral composition, grain size and strength of clastic sedimentary rocks with an undestroyed structure (sandstones, limestones) as most widespread silica-containing raw materials. It is found that as the quartz percentage increases, the strength improves and the less time is required for sample destruction.

In their genesis, rocks accumulate their energy potential, i.e. free energy of rock-forming minerals and the rock in general that is an important criterion of raw material genetic classification for construction materials production proposed by the author of the paper [1].

According to this approach, free energy is an integral characteristic connected with internal energy, entropy and surface energy and determined by the result of the motion and interaction of particles (clusters, molecules, atoms, ions), defects in crystalline lattices of rock-forming minerals, ore-forming fluid inclusions, air-gas and liquid phases, mineral crystallinity, rock structure and texture.

The production technology of construction materials includes such stages as raw material mining, transportation, dosing, special treatment resulting in failure of integrity, structure and texture of rocks, crystalline lattices of minerals, neogenesis and composite formation. At the same time, source rock disintegration and structural damage lead to free energy growing to its maximum when crystalline lattices of rock-forming minerals are destroyed, while synthesis of new minerals and structuring of new natural formations cause its decrease [1]. In addition, rock grinding forms a new surface and some part of free internal energy turns into surface energy (E_S, J/kg), i.e. excess energy of surface layer molecules equal to the product of surface tension by total interfacial area [5].

As shown in the study [6] for the macrostate of a substance – a solid, conglomerate rock – the free energy value is atomization energy. Atomization energy (E_a, kJ/mol) is an endoenergy effect created when one mole of a substance transforms into a state of free atoms not interacting with each other, energy generated by chemical bonds of a substance. Specific mass energy (E_m, kJ/g) and specific volumetric energy (E_v, kJ/cm^3) of atomization are used to correctly compare atomization energy values of simple and complex minerals and to determine relationships with various properties of minerals and rocks [7]. The method used to calculate these energy parameters is provided in the paper [6].

The critical surface tension value can be used as an energy characteristic for destroyed rock in a dispersed state [8]. The critical surface tension value (σ_c, N/m) is a characteristic of the surface energy of a solid phase surface unit. There are various methods for surface tension determination, but the most common and effective one [5, 8-11] is the G.A. Zisman's non-destructive method ("neutral drop" method) based on measuring the contact angle of solid surface wetting (θ) with service fluids having known surface tension values (σ_l, N/m), plotting a functional dependence diagram $\cos\theta = f(\sigma_l)$ and extrapolating this dependence to $\cos\theta = 1$.

If condensed phase surfaces carry no significant electrostatic charge, then main surface forces that determine the interaction between solids are dispersion ones (van der Waals attraction forces). According to the DLVO theory, the dispersion component of surface energy between particles is expressed in terms of the Hamaker constant (A, J), a value that takes into account the interparticle interaction between homogeneous particles and the interfacial interaction at the solid-solution interface. Based on the cohesion behavior (energy) definition, the Hamaker constant value for a solid surface can be calculated by the formula:

$$A = 24\pi h^2 \sigma_c \tag{1}$$

where h is the van der Waals radius (the minimum distance between interacting particles, 0.24 nm); σ_c is the critical surface tension value, N/m [12, 13].

In our opinion, these energy parameters can enable forecasting various physical and mechanical properties of minerals and rocks and thereby increase the efficiency of construction materials production where synthesis is based on the complete rock destruction.

It should be noted that compared chemical compositions of minerals forming igneous and sedimentary rocks revealed a predominant silicon dioxide content in them. Metamorphic rocks are formed from sedimentary and igneous rocks exposed to the impact of temperatures, pressure and fluids. However, quartz is one of the most transformation-resistant rock-forming minerals which changes and acquires a maximum amount of defects and inclusions at early metamorphism stages (lower stage) and is characterized by less mineral inclusions and a defect-free structure formed at the highest metamorphism stage. Additionally, silicon dioxide not only forms quartz as a mineral, but also is a part of other rock-forming minerals [1].

Therefore, this paper focuses on establishing a possible relationship between the silicon dioxide content and energy characteristics (E_a, E_m, E_v, E_S and A) for finely dispersed rock systems of various genetic types.

2. Materials

The selected objects of research were different genesis rocks typically used in the construction materials industry and quartz as a main rock-forming mineral.

Quartz – a natural polycrystalline mineral.

Basalt – an effusive cryptocrystalline igneous basic rock, Myandukha Mountain deposit in the Plesetsk district of the Arkhangelsk region.

Sand S1 – clastic sedimentary rock; belongs to modern alluvial quaternary deposits (aIV), Lower Carboniferous, polymineral river sand, medium-grained, fineness modulus is 2.23; Class I, Kenitsy deposit, Arkhangelsk region.

Sand S2 – clastic sedimentary rock; belongs to modern marine alluvial quaternary deposits (amIV), Baltic Lower Cambrian, polymineral river sand, very fine-grained, fineness modulus is 1.70; Class II; Krasnoflotsky-Zapad deposit, Arkhangelsk region.

Granite – intrusive deep-seated even-grained igneous acid rock, Pokrovskoe deposit, Arkhangelsk region.

Amphibolite – lowest and medium stage of metamorphic rocks, epidot-amphibolitic facies, source rocks are basic and intermediate igneous rocks, Kiyskoe deposit, Arkhangelsk region.

Limestone – sedimentary rock – carbonate rocks, Savinskoe deposit, Arkhangelsk region.

Diabase – intrusive hypabyssal finely-crystalline igneous basic rock, Drugoretskoe-Yuzhnoe deposit in Karelia, Prionezhsky district, Rybreka village.

Quartzitic sandstone – lowest stage of metamorphic rocks, source rock is quartz sandstone with siliceous cement, Lebedinskoe deposit, Belgorod region, near the city of Gubkin, in the Starooskolsky iron-ore district of the Kursk Magnetic Anomaly.

Diorite – intrusive hypabyssal igneous intermediate rock, crystalline unequigranular –finely to coarse-grained – structure, Sangalykskoe deposit in the Uchalinsky district of the Republic of Bashkortostan, in Mansurovo village.

3. Methods

Samples of the rocks under investigation (polycrystalline quartz, basalt, granite, amphibolite, limestone, diabase, quartzitic sandstone, diorite) were preliminary sieved to separate large inclusions through Sieve No. 10. Sands S1, S2 were washed from clay particles. Then the samples were brought to constant weight at a temperature of 105±5°C.

The composition of the objects selected was determined using the X-ray fluorescence spectroscopy on the Shimadzu EDX-800 HS spectrometer at the NArFU “Arktika” Common Use Center (“Arktika” CUC).

Dry milling at the Retsch PM100 planetary ball mill was used to obtain rocks in a finely dispersed state. Mode parameters (rotor speed, milling time, grinding ball number) were selected experimentally based on the target sizes of finely dispersed systems (10^{-7}-10^{-9} m).

Particle sizes (d, nm) were determined at the Delsa Nano Series Zeta Potential and Submicron Particle Size Analyzer by photon-correlation spectroscopy based on the dynamic light scattering principle. Specific surface (S_{sp}, m^2/kg) was measured using a sorption method on the Autosorb-iQ-MP automatic analyzer. True density (ρ, kg/m^3) was determined using a pycnometer test.

Free energy values for undisturbed-structure rocks (atomization energy and its specific values) were determined by calculation based on the chemical composition with standard enthalpies of chemical compound formation.

Test samples were made by sample compaction in molds on the PLG-20 laboratory hydraulic press to determine energy characteristics of the studied rocks in a finely dispersed state.

The critical surface tension value for materials under investigation was determined using the G.A. Zisman's method. Aqueous ethanol solutions with different water volume contents (4÷50%) were selected as service fluids. The KRUSS Easy Drop unit was used to measure the contact angle of surface wetting and surface tension of service fluids at 20±2°C. The time of the first service fluid contact with the surface of the sample studied (1.0±0.5 s) was selected during experiments conducted to determine the contact angle. This is because the processes of liquid diffusion into a bulk phase, capillary phenomena and other effects associated with the irregularity of the solid sample surface can be neglected in the specified period of time. This time interval demonstrates a pseudo-equilibrium state on the phase boundary evidenced by good reproducibility of measurement results. After a series of experiments consisting in three mandatory measurements made simultaneously, the critical surface tension value was calculated by plotting a functional dependence diagram $\cos\theta = f(\sigma_l)$ and extrapolating this dependence to $\cos\theta = 1$.

The Hamaker constant was calculated using the formula (1). Free surface energy was calculated as a production of critical surface tension by specific surface (expression (2)):

$$E_S = \sigma_c S_{sp} \tag{2}$$

where σ_c is the critical surface tension value, N/m; S_{sp} is specific surface, m^2/kg.

4. Results

Tables 1 and 2 specify the characteristics of basic rocks and finely-dispersed rocks, respectively. However, diagrams plotted to establish the dependence of different energy characteristics on silicon dioxide content in rock (C_{SiO_2}) revealed significant approximation certainty factors (R^2>0.8) for the functions $E_m = f(C_{SiO_2})$ and $A = f(C_{SiO_2})$ only (Figures 1 and 2). Figure 3 graphically represents the E_a calculation data for the studied rocks with different silicon dioxide contents. Digits in figures designate the objects of research in accordance with Tables 1-2.

Table 1. Characteristics of the undisturbed-structure rocks

№	Studied samples	True density ρ, kg/m^3	Silicon dioxide content C_{SiO_2}, %	Atomization energy E_a, kJ/mol	Specific volumetric atomization energy E_v, kJ/cm^3	Specific mass atomization energy E_m, kJ/g
1	Quartz	2650	98	1859.04	81.97	30.93
2	Basalt	3050	48	1892.00	80.97	26.60
3	Sand S1	2577	90	1879.00	78.30	30.40
4	Sand S2	2594	91	1872.40	72.90	28.10
5	Granite	2600	76	1909.03	75.43	29.00
6	Amphibolite	3000	53	1867.51	80.01	26.70
7	Limestone	2850	0	1300.62	75.20	26.39
8	Diabase	2523	50	1847.08	83.02	26.39
9	Quartzitic sandstone	2650	90	1834.30	78.25	29.52
10	Diorite	2820	57	1889.07	77.95	27.64

Table 2. Characteristics of the rocks in a finely dispersed state

№	Studied samples	Particle sizes *d*, nm	Critical surface tension value σ_c, mN/m	Hamaker constant $A\cdot10^{20}$, J	Specific surface S_{sp}, m^2/kg	Free surface energy E_S, J/kg
1	Quartz	230±25	24.0	10.4	16169±127	388.06
2	Basalt	360±98	17.3	7.5	6446±774	111.50
3	Sand S1	102±34	23.7	10.3	8580±43	203.35
4	Sand S2	102±30	22.6	9.8	7532±211	170.22
5	Granite	206±57	21.2	9.2	9159±54	194.17
6	Amphibolite	416±114	19.4	8.4	2750±14	53.35
7	Limestone	632±69	16.4	7.1	6260±31	102.66
8	Diabase	252±71	17.9	7.8	1525±18	27.29
9	Quartzitic sandstone	233±59	21.1	9.2	4994±28	105.42
10	Diorite	464±120	18.8	8.2	1567±23	29.47

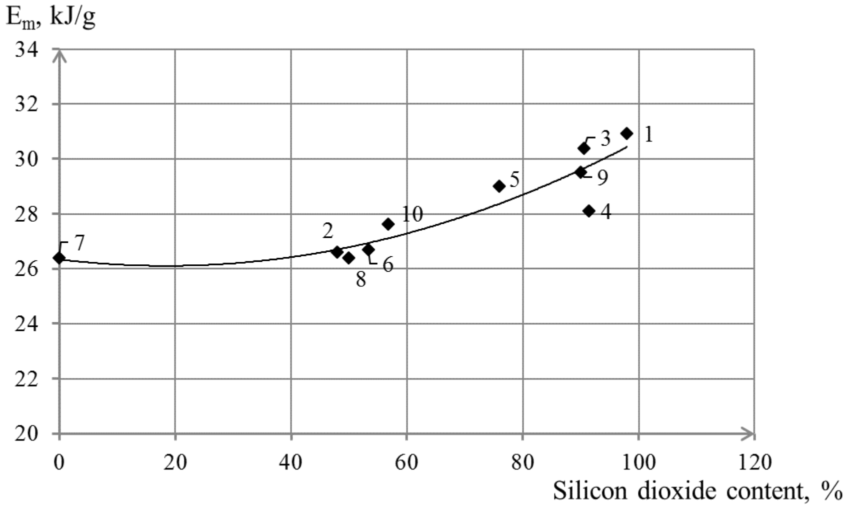

Figure 1. The dependence of specific mass atomization energy on silicon dioxide content

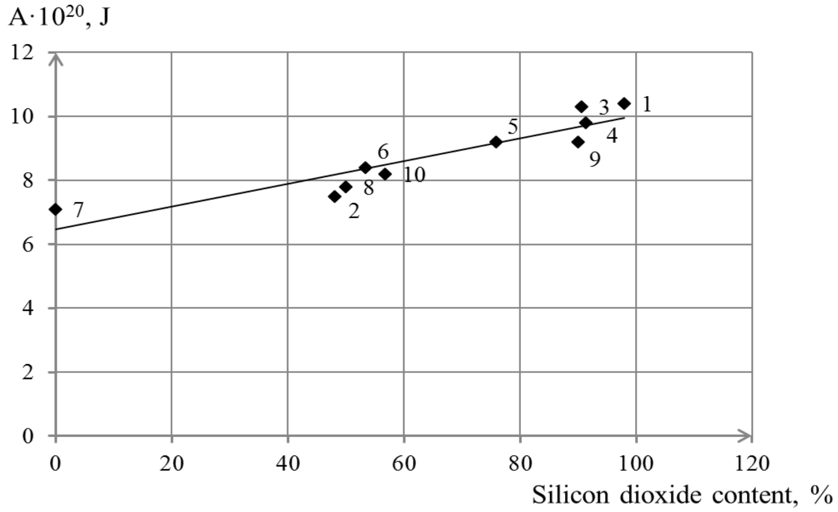

Figure 2. The dependence of the Hamaker constant on silicon dioxide content

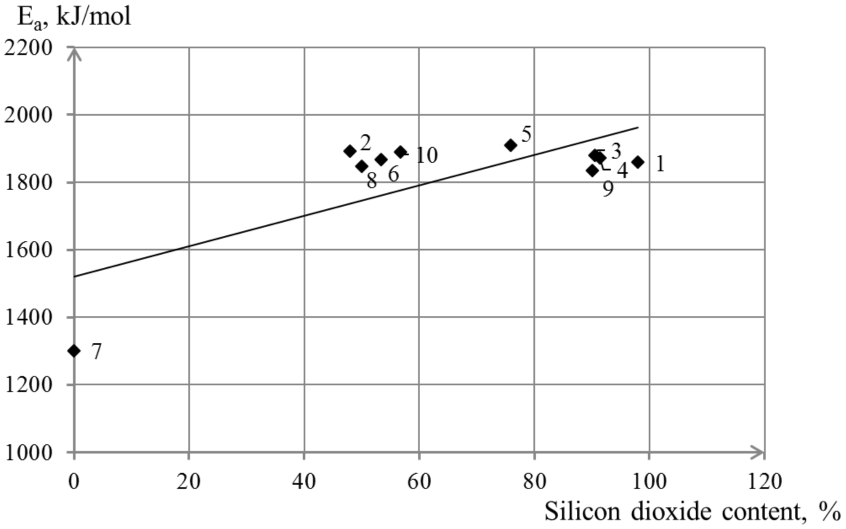

Figure 3. The dependence of atomization energy on silicon dioxide content

5. Discussion

The experimental results obtained have allowed to establish that the dependence of specific mass atomization energy for the studied rock samples on their silicon dioxide contents (Figure 1) is of a power mode and approximated by the second-degree equation where R^2=0.83:

$$E_m = 0.0007C_{SiO_2}^2 - 0.0253C_{SiO_2} + 26.339 \tag{3}$$

where E_m is specific mass atomization energy, kJ/g; C_{SiO_2} is silicon dioxide content in rock, %:

At the same time, conspicuous is the fact that atomization energy of the quartz-containing rocks under investigation (Figure 3) has a nearly constant value equal to 1872±37 kJ/mol.

The dependence of the Hamaker constant calculated by the expression (1) on silicon dioxide content for finely dispersed rock systems has a linear nature (R^2=0.83). In this case, the analytic expression is as follows:

$$A = 4 \cdot 10^{-22} C_{SiO_2} + 6 \cdot 10^{-20} \tag{4}$$

where A is the Hamaker constant, J; C_{SiO_2} is silicon dioxide content in rock, %.

The obtained results shown in Figure 2 demonstrate that different-genesis rocks in a finely dispersed state exhibit intensified dispersion interaction between particles with an increase in the Hamaker constant as silicon dioxide content rises in the limestone (carbonate rocks) – quartz (silica-containing rocks) series.

6. Conclusions

Therefore, the studies performed allow us to draw the following conclusions:

An increase in silicon dioxide content in the limestone (carbonate rocks) – quartz (silica-containing rocks) series leads to higher atomization energy, specific mass atomization energy and free surface energy with intensified dispersion interaction between particles evaluated by an increase in the Hamaker constant.

Acknowledgments

This work is realized under financial support of the Ministry of Education and Science of the Russian Federation, Federal Action Program "Research and Development in Priority Fields of Science and Technology of Russian Federation for 2014-2020", unique agreement identifier RFMEFI58317X0063 using the Unique Equipment "Physicochemistry of surface for nanodisperse system" of Northen (Arctic) Federal University named after M V Lomonosov.

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