Energy characteristics of sands of deposits in the Ivanovo region

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Abstract. It is proposed to use the energy potential of rock-forming minerals obtained in the process of rock synthesis as an energy criterion for ranking raw materials for the production of construction materials. The energy of atomization and its specific values calculated based on the principles of crystal energy are used as a quantitative parameter. The estimation of two deposits of sands of the Ivanovo region on energy of atomization, specific mass energy of atomization, specific volume of energy of atomization (energy density) is carried out. It was found that, despite the difference in the chemical, mineral composition and origin of rocks, macro-energy parameters have similar values. The energy density value allows classifying the considered sands as high-energy-dense. The possible level of use of this energy reserve due to mechanical crushing of raw material is established. Quantifying potential energy of the system that fallen after crushing the material in the surface was carried out based on the values of critical surface tension and specific surface area of raw materials (formed after the process of mechanical grinding). The level of possible use of the potential energy reserve due to the formation of a new material surface was characterized by the activity of the surface of fine samples. The obtained values of surface tension and surface activity showed that the sands of the Nekhtskoe deposit, in comparison with the sands of the Khromtsovskoye deposit, are preferable to be used as an active fine-dispersed component for obtaining binding compositions.

1. Introduction

It is known that rocks have a reserve of free internal energy, which is determined by the method of their formation (igneous, sedimentary, metamorphic) [1]. The use of this energy reserve can reduce the work that must be performed during the technological transformation of raw materials in the production of building materials (mechanical disintegration of raw materials, destruction of crystal lattices of minerals, synthesis of new things, etc.) [2-4]. In addition, a significant interest for the construction materials industry is represented by fine-ground mineral powders [5-7], the addition of which in the production technology can improve the quality of building materials: strength, wear resistance, thermal and chemical resistance, fracture toughness, i.e., increase the operating period and life cycle of the product or structure as a whole [8 – 11]. Bringing powders to the nanoscale level of particles also leads to changes in a number of physical and chemical properties of the systems themselves [12-14].
When rocks are destroyed in the process of mechanical dispersion, according to the classical principles of thermodynamics, a certain amount of work is spent, because of which energy is released from the total energy potential of the rock, which is called free surface energy [3–4]. Moreover, this energy parameter is associated with the specific surface area ($S_{sp}$). A number of researchers have noted that when creating compositions of different composition, the greater $S_{sp}$, the better the interaction of the material particles with the composite matrix becomes (a more uniform distribution of nanoparticles in the material is achieved) [7, 8, 10, 15].

In addition, the dispersion of rocks to a micro- and nanoscale state is accompanied by the formation of an amorphous phase, which is an important component of increasing the reactivity of a highly dispersed material. For such systems, this capability is determined by surface activity ($k_s$). This parameter allows characterizing quantitatively the transition of potential energy accumulated by the rock during genesis to free surface energy due to activation of the surface of the raw material [6–7, 16].

The determination of the $k_s$ value is based on the macro-energy indicators of the rock. The first is the energy of atomization ($E_a$, kJ/mol), which is defined as the sum of the standard enthalpy of crystal formation and the heat of the formation of constituent atoms (the values are given in the reference literature [17]). The derivatives of this value are the specific mass energy of atomization ($E_m$, kJ/g) and the specific volume energy of atomization ($E_v$, kJ/cm$^3$), which allow comparing correctly rocks by energy parameters. In this case, the $E_v$ parameter, due to the specifics of its calculation, allows characterizing rocks by energy density [2–3].

Therefore, the calculation of the above parameters can help in ranking and selecting the most effective raw materials for the production of building materials (composition of composite binder, complex additive for concrete, active filler, etc.).

The aim of this work is to calculate the macro-energy indicators of polymineral sands of the most widely used deposits of the Ivanovo region, and a comparative assessment of fine-dispersed systems based on their surface activity.

The surface activity value was calculated using the working positions [3, 6, 11, 18], according to which this parameter is equal to the ratio $k_s = E_s / E_m$. The free surface energy ($E_s$, J/kg) was calculated by multiplying the surface tension ($\sigma$) of a highly dispersed system by its specific surface area. The OWRK method was used for experimental determination of $\sigma_s$ [13, 15–16, 18].

2. Materials and methods

2.1. Materials
Two deposits of polymineral quarry construction sands were selected as raw materials: Khromtsovskoye deposit (Khromtsovo village, Ivanovo region) and Nekhtskoye deposit (Teterinskoye village, Nerekhtsky district).

2.2. Methods
Before testing, the sand was washed and dried to a constant mass at a temperature of 105 °C. Determination of the main characteristics of the sands such as the size modulus and true density was carried out in accordance with GOST 8735-88.

The mineralogical composition of rocks was determined by recording x-ray diffractograms on a Shimadzu XRD-7000 S x-ray diffractometer (CCP “Arctic”, Northern (Arctic) Federal University named after M.V. Lomonosov). The chemical composition of the sands was determined using a MetExpert x-ray fluorescence analyzer.

To calculate the activity value of the surface of the sand sample, the method of dry dispersion of raw materials was ground to a highly dispersed state in a planetary ball mill “Retsch PM100”, whose grinding principle is based on the friction of particles and the impact of steel grinding bodies on them. The optimal dispersion parameters were selected experimentally to obtain the required particle size.
The size characteristics were determined using the submicron particle size analyzer Delsa Nano Series Zeta Potential and Submicron Particle Size Analyzers (“DelsaNano”) by photon-correlation spectroscopy based on the principle of dynamic light scattering.

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

To determine the edge angle of wetting on the “Easy Drop” installation at a temperature of 25±1 °C, we used samples-tablets made by pressing ground sand on a press “PLG-20” at a load of 20 kPa into a metal mold with a diameter of 20 mm.

The surface tension of the samples (σ, N/m) was calculated using the OWRK method (Ounce, Wendt, Rabel and Kjelble method), based on the measurement of the equilibrium wetting angle (θ) with liquids (distilled water, decane, glycerine and ethylene glycol) with known values of the surface tension (σ, N/m) and its dispersion (σ_D) and polarization (σ_P) components.

3. Results

The selected sand deposits do not differ significantly in size modulus (M_s), but they are medium-sized. Quarry polyminer.al sand deposits “Khromtsovskoe” (Kh) has a fineness modulus of 2.18 and for sand deposits “Nekhtskoe” (N) module size amounted to 2.43. The true densities (ρ_t) of the studied rocks also have similar values and are for sand “X” ρ = 2.50 g/cm³; for sand “H” ρ = 2.60 g/cm³.

The studied rocks have the same composition of the main rock-forming minerals, but their quantitative content differs. So, the sand field “Khromtsovskoe” contains 40% quartz, 11% albite; sand deposits “Nerehtskoe” - 84% quartz, and 14% albite.

When calculating the energy reserve of a rock, the atomization energy parameter was used as a criterion. Therefore, the initial data for calculating E_a are the results of chemical analysis of the rock presented in table 1.

Table 1. Chemical composition of sands in terms of oxides (%) and enthalpy of elements and oxides formations.

| Definite component | Sand deposit | Khromtsovskoe | Nerehtskoe | E_av, kJ/mol | Molar mass of oxide, g/mol |
|--------------------|--------------|---------------|------------|-------------|--------------------------|
| SiO_2 | 85.23 | 95.89 | 1861.34 | 60.084 |
| Al_2O_3 | 1.97 | 2.32 | 3081.90 | 100.181 |
| MgO | 0.46 | 0.16 | 997.80 | 40.311 |
| Fe_2O_3 | 5.75 | 0.56 | 2403.80 | 159.695 |
| CaO | 3.30 | 0.20 | 1062.10 | 56.079 |
| TiO_2 | 0.05 | 0.01 | 1916.00 | 79.954 |
| K_2O | 0.01 | 0.75 | 789.00 | 94.203 |
| SO_3 | 0.68 | 0.04 | 1463.60 | 80.061 |
| P_2O_5 | 0.08 | 0.02 | 3385.80 | 141.943 |
| Na_2O | 2.41 | 0.04 | 879.04 | 61.979 |
| MnO | 0.06 | 0.01 | 918.80 | 70.937 |

Based on the results of chemical analysis of the samples, the enthalpy of formation of the corresponding elements and chemical compounds, the energy of atomization for each oxide was calculated, taking into account its quantitative content in the sample. The sum of these values allowed calculating the energy of atomization for samples “Kh” and “N”.

Then the specific mass energy of atomization (E_m) was calculated based on the molar mass of the oxide and its percentage content in the analyzed sample. Table 2 summarizes all calculated energy parameters for sedimentary rocks of the studied fields.
Table 2. Calculation of atomization energy and specific mass energy of atomization.

| Oxides | \(E_a\) oxide in the mixture, kJ/mol Khromtsovskoe | \(E_m\) oxide, kJ/g Khromtsovskoe | \(E_a\) oxide in the mixture, kJ/g Nerekhtskoe | \(E_m\) oxide, kJ/g Nerekhtskoe |
|--------|--------------------------------|----------------------------|--------------------------------|----------------------------|
| SiO\(_2\) | 1586.42 | 30.979 | 26.403 | 29.706 |
| Al\(_2\)O\(_3\) | 60.71 | 30.763 | 0.606 | 0.714 |
| MgO | 4.59 | 24.753 | 0.114 | 0.040 |
| Fe\(_2\)O\(_3\) | 138.22 | 15.052 | 0.866 | 0.084 |
| CaO | 35.05 | 18.939 | 0.625 | 0.038 |
| TiO\(_2\) | 0.96 | 23.964 | 0.012 | 0.002 |
| K\(_2\)O | 0.08 | 8.376 | 0.001 | 0.063 |
| SO\(_3\) | 9.95 | 18.281 | 0.124 | 0.007 |
| P\(_2\)O\(_5\) | 2.71 | 23.853 | 0.019 | 0.005 |
| Na\(_2\)O | 21.18 | 14.183 | 0.342 | 0.006 |
| MnO | 0.55 | 12.952 | 0.008 | 0.001 |

Based on experimentally determined values of rock density, the energy density values of the sands were calculated. All the obtained data on atomization energy, specific mass energy, and specific volume energy (energy density) are presented in table 3.

Table 3. Energy parameters of sedimentary rocks.

| Energy parameter | Sand of the deposit |
|------------------|---------------------|
|                  | Khromtsovskoe | Nerekhtskoe |
| Energy of atomization, \(E_a\), kJ/mol | 1860.43 | 1881.34 |
| Specific mass energy, \(E_m\) \(10^3\), kJ/kg | 29.12 | 30.67 |
| Specific volume energy, \(E_v\), kJ/cm\(^3\) | 72.80 | 79.73 |

Based on the data obtained (table 3), it is established that the energy parameters of the considered sands, despite the distinctive features of the processes of formation of these rocks, can have similar values due to similar chemical composition. At the same time, the calculated \(E_a\) allows characterizing materials by energy density. Based on the existing classification, all minerals and artificial compounds are divided into: super-dense (\(E_a=150 \ldots 230\) kJ/cm\(^3\)), high-energy (\(E_a=60 \ldots 150\) kJ/cm\(^3\)), medium-energy (\(E_a=30 \ldots 60\) kJ/cm\(^3\)) and low-energy (\(E_a=1 \ldots 30\) kJ/cm\(^3\)). Consequently, the considered deposits of sands of the Ivanovo region can be used as an active fine-dispersed additive in production, as the energy density of these rocks allows classifying them as high-energy dense.

The surface activity value of the studied sands was calculated for fractions with different dimensional characteristics and corresponding specific surface values (table 4).

Table 4. Grinding time and dispersion characteristics of sand fractions.

| Parameter | Sand of the deposit |
|-----------|---------------------|
|            | Khromtsovskoe | Nerekhtskoe |
| Grinding time, min | 5 | 10 | 20 | 30 | 5 | 10 | 20 | 30 |
| Average particle, nm | 687 | 549 | 467 | 341.7 | 603.7 | 510.6 | 389.4 | 313.9 |
| Specific surface, m\(^2\)/kg | 910 | 1089 | 1638 | 2319 | 778 | 887 | 2085 | 3154 |

To calculate the value of free surface energy (\(E_{sf}\), J/kg), the surface tension values (\(\sigma_s\), N/m) were additionally calculated for samples with different values of \(S_{sp}\). In this case, the obtained functional dependencies of the OWRK method:
are well described by linear equations with a high value of the approximation confidence coefficient 
($R^2$), where $\theta$ is the edge angle of wetting of the material under study; $\sigma_L$, $\sigma_D^t$ and $\sigma_D^p$ are the total, 
dispersion, and polarization surface tensions of working fluids (respectively). A total surface tension 
of the system $\sigma_S = \sigma_S^p + \sigma_S^D$, where $\sigma_S^p$ and $\sigma_S^D$ – polar and dispersion components of the surface tension 
of the studied material.

So, for the sand of the Khromtsovskoe deposit, these equations have the following form: at 5 minute grinding: 
$y = 6.97\cdot x + 4.35$ ($R^2=0.98$); at 10 minute grinding: $y = 6.99\cdot x + 4.37$ ($R^2=0.98$); at 20 minute 
grinding: $y = 7.00\cdot x + 4.35$ ($R^2=0.98$); at 30 minute grinding: $y = 7.05\cdot x + 4.29$ ($R^2=0.99$). For the sand of the Nerekhtskoe deposits are the following: at 5 minute grinding: 
$y = 6.76\cdot x + 4.41$ ($R^2=0.98$); at 10 minute grinding: $y = 6.83\cdot x + 4.39$ ($R^2=0.98$); at 20 minute grinding: $y = 6.94\cdot x + 4.39$ ($R^2=0.98$); at 30 minute grinding: $y = 6.95\cdot x + 4.38$ ($R^2=0.98$).

The values of the surface tension of the sands and the characteristic of their surface activity are presented in table 5.

Table 5. Characteristics of the surface tension of sands.

| Defined parameter | The sand of the deposit | Khromtsovskoe | Nerekhtskoe |
|-------------------|-------------------------|---------------|-------------|
| Polar component $\sigma_S^p$, mm/m | 48.56 | 48.81 | 49.05 | 49.72 | 45.74 | 46.61 | 48.12 | 48.80 |
| Dispersed component $\sigma_S^D$, mm/m | 18.96 | 19.11 | 18.94 | 18.39 | 19.48 | 19.23 | 19.27 | 19.22 |
| Surface tension $\sigma_S$, mm/m | 67.51 | 67.91 | 67.98 | 68.11 | 65.22 | 65.84 | 67.39 | 67.51 |
| Free surface energy $E_S$, J/kg | 61.89 | 74.07 | 111.41 | 157.67 | 50.59 | 58.54 | 139.72 | 214.49 |
| Surface activity $k_S \cdot 10^6$ | 2.13 | 2.54 | 3.83 | 5.41 | 1.65 | 1.91 | 4.56 | 6.99 |

4. Discussion
The obtained results show that the polar components of the surface tension of the samples prevail over the dispersion ones. This indicates the advantage of transformations associated with active surface centers. For highly dispersed samples “Kh” and “N”, a fairly similar specific surface was obtained at the same grinding time. The free surface energy of the surface unit (surface tension) increases as the grinding time increases. It should be noted that the sands of the studied deposits, despite the difference in mineral composition, have similar values of surface activity of fine-dispersed systems obtained by mechanical grinding.

5. Summary
The calculated energy of atomization for the sands of the studied deposits in the Ivanovo region showed similar values and amounted to 1860.43 kJ/mol for the Khromtsovskoe deposit, and 1881.34 kJ/mol for the Nerekhtskoe deposit. The specific values of mass and volume atomization energy also have similar values. Thus, the energy density of these sands was: for the Khromtsovskoe deposit $E_v = 72.80$ kJ/cm$^3$, for the Nerekhtskoe deposit $E_v = 79.73$ kJ/cm$^3$. Based on this, the considered rocks can be classified as high-energy dense by their potential energy reserve.
The grinding ability of sands of Khromtsovskoe deposit lower than sands of Nerekhtskoe deposit, which is reflected in the increase in the activity of the surface with increasing time of grinding. Construction sands of this quarry (in comparison with the sands of the Khromtsovskoe deposit) are more active components for obtaining binding compositions.

6. References
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