Some aspects of the processes of obtaining and application of mineral powders as fillers for cement systems

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Abstract. The main theoretical prerequisites for the thermodynamic analysis of the process of grinding rocks are given. The structural-energetic relationships between the regularities of plastic deformation with energy characteristics that occur during the crushing of mineral substances are described. The evaluation of the grindability of rocks in a ball mill under different grinding modes was made. Rational operating modes of the mill have been determined to ensure the required degree of grinding, which makes it possible to significantly reduce the energy consumption of the grinding process. To assess the quantitative content of adsorption centers, a classification of the "indicator of reduced hydration activity" is proposed. (P_{pga}), allowing the most accurate assessment of the contribution of the surface activity of mineral fillers to the course of the processes of interactions and transformations occurring in a hydrated medium.

1 Introduction

The progressive development of the production of building materials is impossible without solving the problems of preparing high quality raw materials that meet the requirements of regulatory documents.

In the building materials industry, mechanical destruction of rocks creates raw materials that are crushed for further use.

The grinding process, depending on the fineness of the final product, is divided into crushing and grinding. In the first case, as a result of crushing, raw materials are formed with dimensions: large - up to 200 mm; medium - from 12 to 60 mm; small - from 3 to 15 mm. In the second, raw materials are formed with dimensions: coarse - 0.1-0.3 mm; thin - less than 0.1 mm; ultra-thin - less than 0.01 mm i.e. when an external force is applied to the rock, destruction products are formed, consisting of large and small fragments, which are a kind of "raw material" for further processing either in crushers or in mills.

The destruction of a solid body into pieces of derivative sizes is a consequence of the occurrence of deformations and stresses that are formed under the action of forces created

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by crushing equipment and leading to a rupture of intracrystalline and intercrystalline cohesive forces. A further increase in the processing time contributes to a change in their size with the formation of smaller fractions of the processed material up to sizes from 5 to 60 mm.

It should be noted that in the materials obtained in this way, freshly formed chips have a weak or practically absent surface activity and do not take part in the processes of structure formation in the manufacture of, for example, cement concretes, i.e. are inert [1, 2].

A somewhat different picture is observed when grinding the feedstock (after crushing) in order to obtain finely dispersed powders. The powders formed during processing in mills of various types differ significantly from materials processed in crushers both in size, the values of which can range from 500 to

10000 cm^2/g, and high surface activity. As a result, such particles are able to enter into chemical interactions and significantly affect the course of hydration processes occurring, for example, in systems with mineral binders.

The processes occurring during the mechanical destruction of various rocks have not been studied enough to date. The expansion of ideas about the mechanism of grinding and physical phenomena leading to destruction, in our opinion, will, to a certain extent, contribute to solving problems of choosing optimal grinding modes, coordinated decision-making when designing appropriate equipment for the production of powders of the required indicators of properties and surface activity of the material.

This article attempts, on the basis of well-known hypotheses of grinding theories, to describe the physical processes of separation of large particles into small ones, to explain the mechanism for the formation of new reactive centers on their surface, and to experimentally confirm the high efficiency of using finely dispersed mineral powders and binary fillers to address issues of directional structure formation in the development of cement concretes. new generation.

Numerous studies have confirmed that as a result of technological action (for example, grinding), the original substance remains unchanged, and new formations formed as a result of mechanical action on the surface have an increased reactivity [3–6].

Many researchers explain the activation of solid substances with the formation of new surfaces as a result of grinding as a process of changing the energy state, physical structure, and chemical properties of the feedstock [7–10].

It should be noted that the surface energy formed as a result of the division of large particles into small ones is a component of the total energy of a solid body formed by adding the effects of atomic vibrations, the kinetic energy of the chaotic translational or rotational motion of microparticles, the potential energy of interaction of these particles, the energy of the electron shells of atoms, intranuclear energies and etc. [eleven].

When grinding rocks in ball mills of various operating principles, the working body (balls of different diameters) deforms the material. The energy of deformation is concentrated in the components of the feedstock in the form of elastic or plastic deformations and, partially turning into heat, is dissipated. Further mechanical action contributes not only to the concentration of deformation, but also to the destruction of particles, which are kinetic processes from a microscopic point of view, representing a set of elementary acts, the totality of which manifests itself in a common system of interacting materials [12].

Thermodynamic analysis of plastic deformations that occur during grinding of solids, which is based on the structural-energy interpretation of the process, makes it possible to establish the relationship between the laws of plastic deformation with energy characteristics and describe the evolution of transition processes during crushing and grinding of large particles and their transformation into small ones [12].

The emerging microscopic interactions in such systems are proposed to be classified according to the following features:

• elementary acts of atomic-molecular rearrangements associated with the breaking of interatomic bonds, reproduction and accumulation of elementary defects in deformable volumes;

• elementary acts of atomic and molecular rearrangements associated with the movement and destruction of elementary defects.

The ongoing microscopic acts cause the release of free energy of various kinds of defects and their interactions. The occurrence of such acts is estimated by the flow rates of these processes and characterizes the adaptability of the system to external influences [12].

The frequency of forming interactions and transformations with the formation of new phases is well described from the standpoint of the theory of absolute reaction rates [8], according to which the number of elementary events Ni in one mole of a substance per unit time τ can be determined from the equation:

$$J_o = \frac{dN_i}{d\tau} = \varkappa \frac{RT}{h} \exp\left(-\frac{U_{oi}}{RT_0}\right), \quad (1)$$

where $\varkappa$ is the transmission coefficient; R is the universal constant; h - constant bar;U_{oi} – free energy of activation of an elementary act per one mole of substance.

Preexponential multiplier $\frac{RT}{h}$ corresponds to the frequency of transitions of activated complexes through the energy barrier, while the exponential factor $exp(-\frac{U_{oi}}{RT})$ considered as a measure of the probabilities of the existence of an activated complex [14].

To understand the mechanism of formation of an activated state during grinding of solid materials in the theory of absolute reaction rates, a single elementary act is usually represented graphically using an energy barrier (Fig. 1).

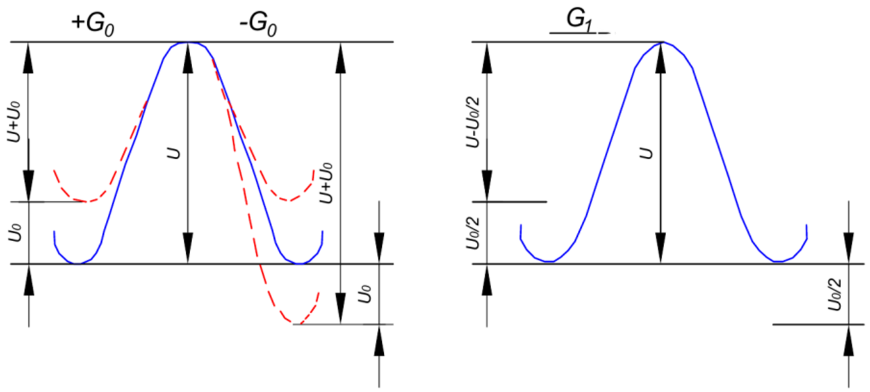

Fig. 1. Scheme of modification of the energy barrier during grinding of solids

For particles in an equilibrium state, in the absence of an external force action, the energy barrier is symmetrical. In this case, the probabilities of overcoming the barrier by an atom or ion in all directions are equal and, consequently, the effective rate of reproduction of elementary defects in accordance with Eq. (1) is equal to zero, i.e. an equilibrium of various kinds of elementary defects Ci is established, which is determined by the relation:

$$C_i = \frac{N_i'}{N_o} = exp\left(-\frac{U_{oi}}{kT}\right), \quad (2)$$

where N_o – is the number of elementary particles of the material system;
N_i' - the number of elementary defects of the i-th body;;
U_{oi} – is the activation energy of the elementary act of formation of the i-th defect;
k – Boltzmann constant.

When an external force is applied as a result of a change in the energy of accumulated defects, the energy barrier is modified. The integral measure of the impact of external forces on a particle is the potential energy of elastic deformations W obtained by integrating the specific energy of deformations expressed through the components of the principal stresses U. According to the theory of elasticity [9], this energy is represented as the sum of two components: U_o – volume change energy and $U_ф$ – energy of shape change, associated respectively with the spherical tensor (σ_o) and voltage deviator (σ_i). As a result of an activating external action on the particle, the modification of the energy barrier can be represented as a combination of the action of the stress tensor: spherical (σ_o) depending on the sign increases or decreases the height of the energy barrier, without violating its symmetry, by the value U_o (fig. 1.b.), stress deviator (σ_i) leads to a modification of the energy barrier in such a way that its height in the direction increases by $\frac{U_Ф}{2}$ (рис. 1.б.).

The above theoretical justifications allow us to conclude that in order to increase the mobility of atoms and create prerequisites for the implementation of rapid grinding of solid particles, it is necessary to increase the kinetic energy of atoms. For example, when grinding various rocks in ball mills, it is necessary to optimize: the speed modes of rotation of the mill drum, the ratio of grinding balls by size and quantity.

Optimization of technological stages will significantly reduce the duration of the grinding cycle and ensure the required performance of the crushed materials.

The above materials highlight the theoretical background of the mechanism of grinding hard rocks. Further physical and mechanical effects on small particles, as studies show, lead to surface modification of dispersed powders - mechanical activation (MA).

2 Research methods

In the grinding process, the speed mode of the mill plays an important role. The rotation speed predetermines the dynamics of the drum loading, which provides a destructive effect on the crushed material. Basically, in ball mills, grinding of rocks is carried out in three ways: attrition, impact-attrition and impact methods.

Considering the foregoing, the influence of grinding modes on the change in the specific surface area and reactivity of particles was studied using the example of a filler made of quartz sand (CS) from the Maysky quarry (Uzbekistan) in various operating modes of a ball mill.

The process of grinding CP was carried out in a laboratory ball mill ShLM-100 in three modes: abrasive, shock-abrasive and impact. The mass and number of balls of the mill are given in fig. 2. In the study, the initial raw material was dried to constant weight at a temperature of ±105ºC.

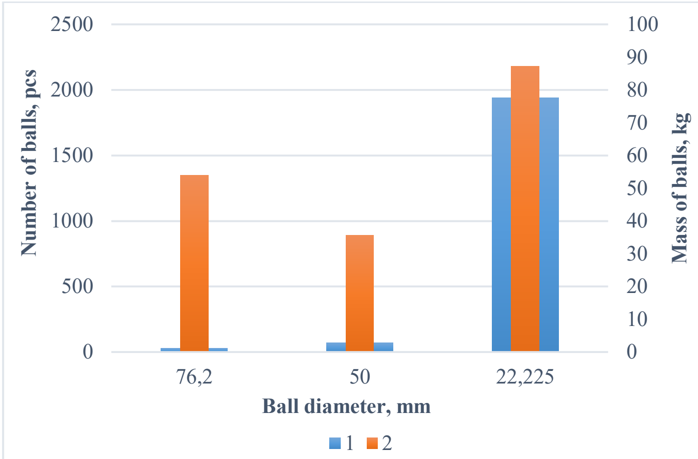

Fig. 2. Number and diameter of balls when loading into a ball mill: 1-number of balls; 2-mass of balls

The fineness of grinding was evaluated by the specific surface on a PSKh-11A surface meter.

The results of studies of the grinding capacity of CP are shown in fig. 3.

3 The results of the study of the first direction

An analysis of the dependence of the increase in the specific surface of the CP on the duration of grinding showed that an intensive increase in the value of Ssp occurs in the range from 10 to 60 min of grinding in all operating modes of the ball mill, after which the kinetics of the increase in Ssp slows down.

For 60 min of CP grinding in impact mode, the specific surface area reaches the value 3450 cm^2/g. During the same period, in the shock-abrasive mode, it is possible to bring only to the fineness Ssp = 3100 cm^2/g. In turn, the abrasive mode allows you to create dispersion Ssp=2700 cm^2/g. Grinding in the next 20 min in all CP grinding modes leads to an increase in the value of Ssp by 2%, 1.5% and 1%, respectively.

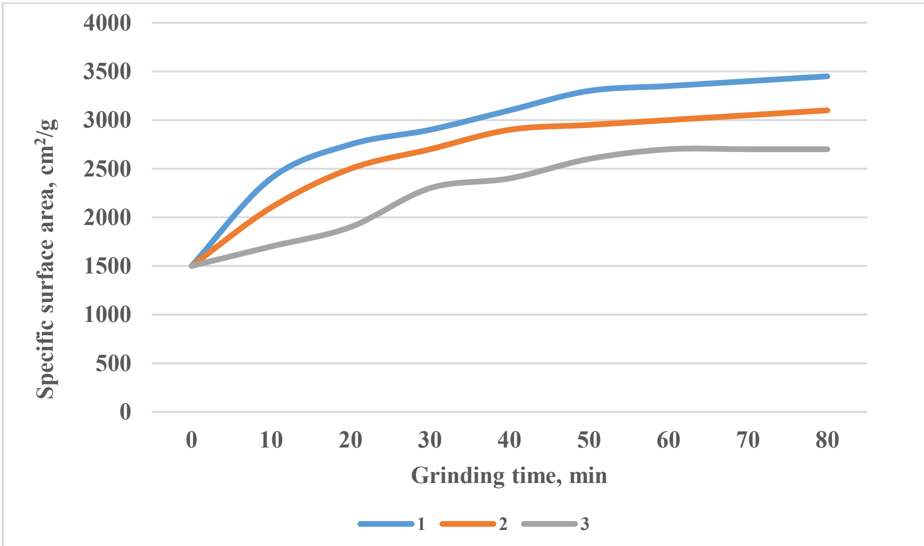

Fig. 3. Influence of the duration of grinding on the value of the specific surface of the CP 1-impact, 2-impact-attrition, 3-attrition mode grinding ball mill

It is natural to assume that the process of mechanical activation of CP by grinding, associated with a change in the specific surface area of the fillers, will positively affect the strength of concrete (Table 1).

Table 1. Influence of specific surface area of quartz filler on compressive strength of fine-grained concrete after 28 days of normal hardening

Grinding time, min	Specific surface area, cm^2/g, when grinding			Ultimate compressive strength, MPa, grinding		
	shock mode	shock-abrasive mode	abrasive mode	shock mode	shock-abrasive mode	abrasive mode
10	2400	2100	1700	27,1	22,1	19,5
30	2900	2700	2300	31,3	32,5	24,9
60	3350	3000	2700	37,4	42,1	32
80	3450	3100	2700	37,8	42,3	32,5

The results of tests of fine-grained concrete (FCM) for compression after 28 days of normal hardening indicate that the best indicator of strength ($R^{28}_{сж}$) possesses samples with the content of filler from the CP obtained in the shock-abrasive mode of operation of the ball mill.

4 The results of the study of the second direction

The method of mechanical activation of powdered substances in mills, disintegrators and similar grinding devices has long been known and actively used, where, in addition to dispersion, such effects as crystal deformation, the formation of a large number of defects, a change in the size of microblocks forming a crystal, a local rise in temperature and pressure, phase transformations, and amorphization are observed. , breaking of chemical bonds, acceleration of diffusion processes, etc., leading to a significant increase in reactivity and, as a result, to acceleration of physicochemical processes.

According to the definition given by Acad. Rebinder P.A. "The goal of mechanochemistry is to use or prevent those chemical reactions that are caused or accelerated by mechanical activation." After grinding (mechanoactivation), the free energy is not in equilibrium and is not statically stable. In the near-surface layer, rearrangement processes begin towards the equilibrium state, i.e. mechanoactivation allows you to achieve the following positive effects:

- formation of active centers on a freshly formed surface;
- change in reactivity;
- a surface layer is formed on the surface of a solid body, in which “excess” energy is concentrated;
- change in free energy due to mechanochemical activation causes a change in the sum of surface and internal energy;
- the change in internal energy due to structural defects exceeds the increase in surface energy and, as a result, favorable conditions are created for a deeper course of hydration processes.

Numerous studies, in particular [17], have shown that the concentration of active surface centers can be increased by physical and mechanical processing of fillers in ball mills. As a result, the active sites that are formed on the surface of the fillers will determine their reactivity and participate in interactions with the hydrating binder. Therefore, the assessment of the quality indicators of mineral fillers only from the standpoint of increasing the dispersion of the ground material is insufficient. Of greater interest is the study of the mechanism of formation of reactive centers on the surface of mineral particles and their influence in solving the issues of directed structure formation of the projected composite.

Modern physical chemistry of solids proceeds from the fact that in order to assess the activity of materials, it is necessary to take into account the following groups of their physicochemical properties:

- properties directly determined by their composition and structure, the presence of defects and impurities (for example, Brönsted or Lewis acidity and redox properties of functional groups, d characteristics of metal ions [11].
- chemical affinity to the substrate, which can be characterized by thermodynamic quantities (for example, the energy of adsorption processes [10], the dissociation energy of the bond developing in the limiting stage), empirical indices of reactivity [11], potential reaction surfaces [11].
- spatial structure and texture (core dimension, type of crystal lattice, specific surface area, shape of particles or pores and their size distribution) [8].

Taking this into account, we have proposed a new classification of mineral fillers for cement concretes and mortars.

The new classification of mineral fillers, described in detail in [12], is based on a new criterion, the “reduced hydration activity index”, which makes it possible to most accurately assess the contribution of the surface activity of mineral fillers to the course of the processes of interactions and transformations occurring in a hydrated medium. To calculate the indicator of the reduced hydration activity of mineral fillers, experimentally obtained graphic dependences of the distribution of adsorption centers located on the surface of these fillers are used.

Based on these data, the quantitative content of adsorption centers on the surface of mineral fillers is established (Table 2).

The proposed indicator is denoted by the symbol – P_{pga} and is determined by the formula:

$$P_{pga}= P_{кв}+P_{кl}+0.33P_{ol}-0.1P_{ob},$$

where, $P_{кв}$, $P_{кl}$, P_{ol}, P_{ob} – number of adsorption centers in areas 0<pKa<7; pKa>13,0; -4<pKa<0; 7<pKa<13,0 в 10^{-3} mg-eq/g. respectively.

This criterion, which characterizes the acid-base properties of the surface of mineral fillers, allows scientifically substantiated classification of mineral fillers according to the degree of their impact on the properties of cement systems. In the general case, the following classification of mineral fillers is proposed according to the criterion - Ppga, that is, according to the calculated indicator of the reduced hydration activity (Table 3).

For the powders accepted for the study, the indicator of the reduced hydration activity is presented in Table. 4.

Table 2. The content of adsorption centers of the surface of mineral fillers

№ п/п	Name of mineral filler	Number of centers, 10^3 mg-eq/m ^{2}				General quantity centers
		-4…0	0…7	7…12,8	>12,8	
		P_{ol}	P_{kb}	P_{ob}	P_{kl}	
1.	Sand	8,04	9,11	8,75	1,88	27,78
2.	Quartz	4,12	7,08	9,95	1,07	22,22
3.	Dune sand	13,22	16,47	10,08	2,87	42,64
4.	Gliezh	23,41	22,15	11,16	1,96	58,68
5.	Basalt	41,18	5,48	9,34	1,14	57,14
6.	EEP (electrical smelting waste) production	6,61	23,88	16,37	4,32	51,18
7.	WMD (copper smelter waste)	43,14	27,61	11,77	5,32	87,84
8.	Fly ash TPP	102,08	24,88	12,62	2,14	141,72

Table 3. Classification of mineral fillers in terms of reduced hydration activity $P_{pga.}$

№ п/п	Type of mineral filler	Criteria values $P_{pga.}$	Potential efficiency in cement systems, cement savings in %
1.	Weakly active	от 0< до. <10	До 10%
2.	Medium active	от 10< до. <25	10-20%
3.	Highly active	от 25< до <50	20-30%
4.	Superactive	Over to >50	До 50%

Table 4. Criteria value P_{pga} for various mineral fillers

№ п/п	Name of mineral filler	Initial data				Converted data		Criterion$P_{pga.}$
		-4…0	0…7	7…13,0	>13,0			
		P_{ol}	P_{kb}	P_{ob}	P_{kl}	0,33P_{ob}	0.1 P_{ol}	
1.	Sand	8,04	9,11	8,75	1,88	2,65	0,87	12,77
2.	Quartz	4,12	7,08	9,95	1,07	1,36	0,99	8,52
3.	Dune sand	13,22	16,47	10,08	2,87	4,36	1,01	22,39
4.	Gliezh	23,41	22,15	11,16	1,96	7,72	1,12	30,71
5.	Basalt	41,18	5,48	9,34	1,14	13,59	0,93	19,28
6.	OEP waste of electrosmelting production	6,61	23,88	16,37	4,32	2,18	1,64	28,74
7.	Copper smelter waste	43,14	27,61	11,77	5,32	14,23	1,18	46,68
8.	fly ash	102,08	24,88	12,62	2,14	33,68	1,26	59,44

Comparative analysis of mineral fillers according to the criterion P_{pga} allows you to objectively assess their reactivity and make a ranking according to the degree of effectiveness of the effect of fillers on the properties of cement systems, as well as to characterize them according to the degree of activity, for example: dune sand - weakly active; quartz sand, gliez, EEP-medium activity; basalt, WMD, fly ash from the Angren TPP are highly active and zeolite-containing rock is super active.

5 Conclusions

The developed classification of mineral fillers according to the proposed criterion for assessing the acid-base properties of the surface of mineral fillers - Ppga, showed a high convergence of the results obtained with the data of previously performed studies, from the standpoint of assessing their effectiveness in the compositions of various types of cement concretes and mortars, and formed the basis for the development of new scientific methods. justified choice of modifying additives in the composition of BCM [23–25]. The obtained results of experimental and theoretical studies suggest that the use of active mineral fillers in cement systems will allow replacing part of the binder without compromising the strength characteristics of the material and improving their performance properties, which is one of the aspects of creating energy and resource-saving technology in the field of building materials science.

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