METHODS OF INFLUENCE ON THE SYSTEM TO CHANGE THE ENERGY STATE OF SUBSTANCE: EXPERIENCE, STATE OF THE ISSUE


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Abstract. Methods of influencing the system, the ultimate goal of which is to destruct the natural structure of the material, can be divided as mechanical, physical, chemical, biological and complex. The changing the energy state of a substance is called activation. The current scientific field of ultradispersed materials and physical and chemical processes caused by dispersion is created by the researches of many scientists. Detailed consideration for the increasing reactivity of a solid substance compared to the change in its specific surface area during its mechanical activation showed that the share attributable to the growth of the specific surface area is only a few percent of the mechanical activation effect. The other part is due to the accumulation of defects in the crystals during the grinding process. According to the law of conservation of energy, when a crystal splits, the potential energy of interaction between lattice nodes is transferred to uncompensated surface energy. In addition, the value of the specific surface energy depends on the type of flat lattice used to split the crystal. Therefore, the activation processes and the application of the substance in the active state are relevant in the development of modern binders and concretes. The purpose of the article is to analyse the advantages and disadvantages of the existing methods of influencing the system with the ultimate goal of destruction of the natural structure of the material to changing the energy state of the substance, i.e. its activation. Conclusions. During the destruction of solids, the formation of new cleavage surfaces is accompanied by the breaking of bonds between the substance structural elements and the transition of the potential bond energy into surface energy. Ceteris paribus, the higher the ionic charges and the smaller the distance between them (between adjacent flat grids in the lattice), the greater the value of $\sigma$. In addition, the value of the specific surface energy depends on the type of flat grids used to split the crystal. It is worth mentioning that not all methods of activation for binder and concrete (soluble) mixtures are currently implemented on an industry level. This is due to various reasons. The main method of activation used on an industry level is mechanochemical activation in various types of mills.

Keywords: influence on the system; destruction of the structure; specific surface area; methods of activation

СПОСОБИ ВПЛИВУ НА СИСТЕМУ ДЛЯ ЗМІНИ ЕНЕРГЕТИЧНОГО СТАНУ РЕЧОВИНИ: ДОСВІД, СТАН ПИТАННЯ

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Анотація. Способи впливу на систему, кінцева мета яких – руйнування природної структури матеріалу, можна поділити на механічні, фізичні, хімічні, біологічні і комплексні. Зміну енергетичного стану речовини прийнято називати активацією. Сучасний науковий напрям у галузі отримання ультрадисперсних матеріалів та фізико-хімічних процесів, зумовлених диспергуванням, створено працями багатьох учених. Детальній облік підвищення реакційної здатності твердої речовини порівняно зі зміною величини його питомої поверхні в ході його механічної активації показав, що частина, яка припадає на збільшення питомої поверхні, становить лише кілька відсотків від ефекту механоактивації. Разом з накопиченням дефектів у кристалах у процесі
Problem statement. Methods of influencing the system, the ultimate goal of which is to destruct the natural structure of the material, can be divided as mechanical, physical, chemical, biological and complex. The changing the energy state of a substance is called activation.

The current scientific field of ultradispersed materials and physical and chemical processes caused by dispersion is created by the researches of many scientists.

Detailed consideration for the increasing reactivity of a solid substance compared to the change in its specific surface area during its mechanical activation showed that the share attributable to the growth of the specific surface area is only a few percent of the mechanical activation effect. The other part is due to the accumulation of defects in the crystals during the grinding process.

According to the law of conservation of energy, when a crystal splits, the potential energy of interaction between lattice nodes is transferred to uncompensated surface energy. In addition, the value of the specific surface energy depends on the type of flat lattice used to split the crystal. Therefore, the activation processes and the application of the substance in the active state are relevant in the development of modern binders and concretes.

The purpose of the article is to analyse the advantages and disadvantages of the existing methods of influencing the system with the ultimate goal of destruction of the natural structure of the material to changing the energy state of the substance, i.e. its activation.

Analysis of publications. The current scientific field of ultradispersed materials and physical and chemical processes caused by dispersion is created by the researches of many scientists [1−10].

The process of grinding solids in practice is very complicated due to the set of phenomena that accompany it, such as:

- mechanical (movement of the grinding device body, the grinder itself, friction in bearings, friction of the material to be crushed against the grinding device body, etc);
- physical (deformation of the crystal lattice of the material to be grinded without its significant destruction, heat generation and heating of the particles of the material to be grinded, emission of electrons, etc);
- physical and chemical (breaking of bonds between the lattice nodes, i. e. its destruction, adsorption of gas molecules and surfactants from the environment by the surfaces of the newly formed grains, aggregation of grains with each other, etc);
- chemical phenomena (possible interaction of new surfaces with environmental molecules up to the formation of surface compounds, i. e. mechanochemical phenomena).

During the destruction of solids, the formation of new cleavage surfaces is accompanied by the breakdown of bonds between the structural elements of the substance and the transition of the potential binding energy into surface energy [11]. The presence of surface energy in a solid is caused by the uncompensated force field of ions or the unpaired electron spins on the outer orbitals of
the atoms of the surface nodes of the substance (Fig. 1) [11].

The specific surface energy $\sigma$ of a solid is considered as the total energy reserve of uncompensated bonds of surface nodes $E$ per unit area of the grain surface:

$$\sigma = \frac{E}{S}.$$ \hspace{1cm} (1)

Theoretically, the value of $\sigma$ can be estimated by knowing the structure of the crystal lattice of a solid.

During the destruction of solids, which is accompanied by the appearance of a new surface, the energy consumption for cleavage is equal to the amount of surface energy $E_r = \sigma \Delta S$.

Here, $\sigma$ is assumed to be a constant average value, although it is known that the specific surface energy is anisotropic.

During the crystal cleaves, two cleavage surfaces are formed, and the new surface for one lattice node is $S = 2a^2$. Then $E_p = \sigma \cdot 2a^2$ ($E_p$ is the surface energy). According to the law of conservation of energy, during the crystal cleaves, the potential energy of interaction between lattice nodes is transferred to surface uncompensated energy ($E_p = -E_{ne}$) [11].

Ceteris paribus, the higher the ionic charges and the smaller the distance between them (between adjacent flat grids in the lattice), the greater the value of $\sigma$. In addition, the value of the specific surface energy depends on the type of flat lattice used to cleave the crystal.

Under external loads approaching the limits of compressive, tensile, and bending strengths, the material to be crushed begins to cleave and cracks appear. The instantaneous cleavage of the crushed material into smaller pieces is unlikely, as it requires a large supply of energy from the outside to the material.

According to the Griffiths-Orován-Rebinder theory, the destruction of a solid begins at the points of crystal lattice disruption (near defects). The local stress concentration near these defects under mechanical impact from the outside leads to the formation of nucleated microcracks, which, as they grow further, overlap each other and cause the crushed material to gradually fall to smaller pieces. Thus, a stepwise destruction of a solid is more likely to occur. The growth of microcracks during stepwise material destruction is no longer unambiguous. As long as the grain is subjected to stress, microcracks grow. After the load is temporarily removed (until the next impact by the grinding media), the microcracks can partially close (“heal”) due to the restoration of chemical bonds between the lattice nodes that have moved away from each other by a distance slightly exceeding the interplane distance $a$. Such self-healing of microcracks leads to the fact that during repeated impacts of the grinding bodies, the grain of the material to be ground has to again expend additional energy to cleave the healed microcrack areas [11].

The presence of a large number of broken (uncompensated) bonds at the surface lattice nodes in a finely dispersed system leads to involuntary aggregation of powder grains. The system tends to reduce its surface energy reserve due to the partial closure of broken bonds at the grain contact points. Additional portions of energy are spent on the destruction of aggregates throughout the grinding process.

The release of a large quantity of heat during milling (primarily due to $E_{upr}$ and $E_{tr}$) leads to the fact that in the heated material there is an increase in the thermal mobility of the structural elements of the lattice (especially the surface nodes in the grain friction zone). Thus, during dry milling in closed mills, the temperature of the ground material reaches 200 °C and above. This can cause a change in the orientation of the structural elements of the crystal in the near-surface layer – amorphization. With fine and ultrafine milling,
the thickness of the amorphized near-surface layer of grains can be, according to G.S. Khodakov, 15–16 nm [11].

The process of dispersing materials is greatly influenced by the background of the material to be ground and the grinding environment.

For example, it has been found in practice that pre-fired materials are crushed much more efficiently than materials that have not been heat treated. This might be due to:

- polymorphic transformations accompanied by a significant change in volume, which causes cracking;
- rapid, sharp cooling of materials after firing to normal temperature, which leads to the emergence of many macro- and microcracks in them.

In the current conditions of Ukraine, it is not always economically reasonable to carry out preliminary heat treatment of raw materials, but there are raw materials of technogenic origin in the country that have undergone certain heat treatment at the stage of obtaining the main product and, accordingly, can be used effectively in the future.

 Grinding (milling) of the material can be carried out in different environments, mainly in air – this is dry milling and in liquid – wet milling.

During dry milling, the high activity of the newly created surfaces (uncompensated broken bonds) causes them to affect gas molecules in the environment, which contributes to the adsorption of these molecules on the surface of the material being ground. The most easily adsorbed water molecules are \( \text{H}_2\text{O} \), as they have a large dipole moment. Adsorption of \( \text{H}_2\text{O} \) leads to surface interaction of water molecules with solid particles (electrostatic, orientational dispersion interaction, through hydrogen bonds), which causes partial compensation of broken bonds and a decrease in the level of surface energy [11].

Therefore, dry milling results in strong heating of the material to be ground (up to 200 °C and above), desorption of \( \text{H}_2\text{O} \) molecules from the grain surface, and amorphisation of the layers of near-surface grains (at a depth of 15–16 nm).

During wet milling, the picture is different. In the process of stepwise destruction of solids (development of microcracks), \( \text{H}_2\text{O} \) molecules, penetrating into microcracks, prevent the reverse closure (cohesion) of the bonds between the lattice nodes when the load is temporarily removed, thereby reducing the probability of self-healing of cracks and energy consumption for this unproductive activity (Fig. 2).

![Fig. 2](image)

Water forms fairly dense polymolecular shells up to 1–10 nm thick on the surface of the material to be ground. These shells have elastic properties that vary with their thickness. The water molecules in such shells are oriented to the grain surface. Such water has a high density (from 1.2 to 2.4 g/cm\(^2\)), a low heat capacity and freezes at -78 °C. As the water moves away from the grain surface, it gradually becomes ordinary free water, which determines the fluidity of the suspension [11].

The interaction of water with the surface nodes of the grains (adhesion) causes a decrease in the surface energy level from \( \sigma_0 \) (in a vacuum) to \( \sigma_{zh.} \) (in liquid) [11].

The presence of water shells around the grains sharply reduces the friction between the grains (water acts as a lubricant), grain aggregation, and thus its heating during milling.
The amorphisation of the surface areas of the grains also decreases (according to G.S. Khodakov, the thickness of the amorphised layer in this case is 1.6−2.0 nm). This means that during wet milling, the deformation of the lattice and its cleavage account for a larger proportion of the energy supplied to the solid than during dry milling, which makes it possible to increase the efficiency of the grinding process several times and reduce the specific energy consumption for milling.

Table 1

Methods of activation for binder and concrete (soluble) mixtures

<table>
<thead>
<tr>
<th>№ п/п</th>
<th>Method</th>
<th>Technological characteristics</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chemical additives</td>
<td>Modification of compositions</td>
<td>A wide range of modifiable compositions</td>
<td>High cost</td>
</tr>
<tr>
<td>2</td>
<td>Introduction of surfactants [16; 17]</td>
<td>Formation of additional crystallisation centres and stimulation of secondary formation growth</td>
<td>Densification of the cement stone structure</td>
<td>Limited range of application</td>
</tr>
<tr>
<td>3</td>
<td>Grinding of binder in a mill [18−21]</td>
<td>Different types of mills − ball, vibration, vario-planetary, etc.</td>
<td>Simplicity</td>
<td>High energy consumption</td>
</tr>
<tr>
<td>4</td>
<td>Liquid-phase mechano-activation</td>
<td>Mechanical influence produced in the rotary-pulsation apparatus</td>
<td>The hydration process is more complete, and rheological characteristics are improved</td>
<td>Minimum volume of mixture loading per cycle</td>
</tr>
<tr>
<td>5</td>
<td>Magnetic activation of kneading water</td>
<td>Magnetic treatment of water</td>
<td>Energy efficiency</td>
<td>Expensive equipment</td>
</tr>
<tr>
<td>6</td>
<td>Hydrodynamic activation [22; 23]</td>
<td>Synergistic effect of physical and chemical processes occurring in the flow of moving water, such as aeration, cavitation (cold boiling), collapse and coagulation</td>
<td>Converting water-dissolved substances into insoluble ones with their subsequent removal</td>
<td>Relatively low efficiency</td>
</tr>
<tr>
<td>7</td>
<td>Treatment with high-voltage electric discharges [24; 25]</td>
<td>Applying a constant field of high voltage to water-cement systems leads to the phenomena of water electrolysis and electrophoresis</td>
<td>Significant change in the ionic composition of the suspension and the appearance of polarized groups in water</td>
<td>Technological complexity</td>
</tr>
<tr>
<td>8</td>
<td>Electro-physical activation</td>
<td>Electromagnetic action (sometimes followed by steaming)</td>
<td>Significant improvement in the elastic strength of concrete</td>
<td>High costs</td>
</tr>
<tr>
<td>9</td>
<td>Microwave (dielectric) heating</td>
<td>Absorption of energy of electromagnetic fields of the microwave (HF or UHF) range by the material and conversion of this energy into thermal</td>
<td>High speed of the technological process</td>
<td>Expensive equipment</td>
</tr>
<tr>
<td>10</td>
<td>Thermal activation</td>
<td>Heating followed by cooling according to various schemes</td>
<td>Relatively simple and effective method</td>
<td>High costs</td>
</tr>
<tr>
<td>11</td>
<td>Ultrasonic treatment [15; 26; 27]</td>
<td>The effect of cavitation, solid-phase grinding, formation of microdefects in crystals is caused</td>
<td>Intensification of cement hydration processes</td>
<td>High energy consumption</td>
</tr>
<tr>
<td>12</td>
<td>Thermo-acoustic activation</td>
<td>The dough is pretreated in an aerosodynamic activator, then mixed with aggregates and heated to a temperature of 60-65°C before placing</td>
<td>Strength increases by 1.5 times</td>
<td>Processing complexity</td>
</tr>
</tbody>
</table>

The grinding of materials is even more efficient in the presence of surfactants, which are organic substances that can selectively adsorb to the surface of solid grains, displacing the previously bound water adhesive film. Such surfactants are fatty acids with rather large hydrocarbon radicals, fatty acid salts (soaps), sulfonic acids and their salts, alcohols, amines,
etc. During the adsorption of these molecules, the surface energy of the solid particles decreases more than during the adsorption of water molecules.

It is considered that surfactants used as additives in small quantities can serve as regulators of the properties of concentrated mineral dispersions.

The use of surfactants can reduce the milling duration. Surfactants, displacing bound water from the surface of solid particles and converting it into free water, increase the fluidity of the suspension and allow reducing the moisture content of the latter by 3−5 % while maintaining the required fluidity of the system [11].

K.K. Strelov and P.S. Mamykin call such substances hardening reducers (substances that facilitate deformation and mechanical destruction of solids) [12]. During the milling of materials in the presence of hardness reducers, two processes occur simultaneously: first, hardness reducers, adsorbing on solid particles, cause a decrease in the elasticity, yield strength and strength limits and thus facilitate milling; second, the liquid, penetrating into the microcracks of the pre-crushing zone, unwinds the pressure on the crack walls (capillary phenomena of the 2nd type). Hardness reducing agents – surfactants – can be aqueous solutions of many mineral salts: sodium chloride, calcium, magnesium and aluminium chloride salts, silicates or organic surfactants in the form of true or colloidal solutions, for example, soap in alkaline solution, etc [12].

One of the most effective methods of regulating the structural and mechanical properties of mineral dispersions is their chemical activation, which consists in introducing acids, alkalis, surfactants, or water-soluble polymers into the dispersed system [13–15].

The methods of activation for binder and concrete mixtures are structured in Table 1.

It should be mentioned that not all of these methods are currently implemented on an industrial level. This is due to various reasons. In particular, methods such as microwave heating, ultrasonic treatment and thermoacoustic activation are not yet sufficiently investigated and, consequently, industrial activators are not yet available. Methods such as electrophysical activation and heat treatment are quite energy-consuming, so manufacturers are in no hurry to implement them. It can be concluded that the main activation method used on an industrial level is mechanochemical activation in various types of mills.

Conclusions

Methods of influencing the system, the ultimate goal of which is to destruct the natural structure of the material, can be divided as mechanical, physical, chemical, biological and complex. The changing the energy state of a substance is called activation.

During the destruction of solids, the formation of new cleavage surfaces is accompanied by the breakdown of bonds between the structural elements of the substance and the transition of the potential binding energy into surface energy.

The specific surface energy $\sigma$ of a solid is considered as the total energy reserve of uncompensated bonds of surface nodes $E$ per unit area of the grain surface:

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