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IMPROVEMENT OF THE MASS TRANSFER PROCESSES EFFICIENCY BY MEANS OF MECHANICAL ACTIVATION OF HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

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Abstract

In this paper, the ways of intensification of technological processes by means of powerful short pulses of energy in activation machines in solid phase and water systems are considered. The mechanism of accumulation and relaxation of energy for the substances subjected to mechanical activation is shown.

Keywords: intensification, mechanical activation, rotary apparatus, cavitation, accumulation of energy, relaxation.

Streszczenie

W pracy omówione zostały metody intensyfikacji procesów technologicznych w ciałach stałych i cieczach przy użyciu krótkotrwałych impulsów energetycznych. Przedstawiono mechanizmy akumulacji i relaksacji energii w substancjach poddanych mechanicznej aktywacji.

Słowa kluczowe: intensyfikacja, mechaniczna aktywacja, maszyny wirnikowe, kawitacja, akumulacja energii, relaksacja.

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Changes of the physico-chemical properties of solid materials under the influence of mechanical strain had attracted the interest of many researchers from various countries, even at the beginning of the last century.

However, in the sixties and seventies of the last century, a new branch of science – mechanochemistry, appeared, the fundamentals of which were formulated by V. V. Boldyrev, Director of the Novosibirsk Institute of Solid State Chemistry and Mechanochemistry of the Russian Academy of Sciences [1], and by P.U.Butyagin (The Institute of IHF of RAS) [3, 4].

Previously, the tribochemistry concept, developed by P.Tissen and G. Hajnike, preceded the science of "Mechanochemistry" [2].

In the works of P. U. Butyagin and V. V. Boldyrev, it was demonstrated that the new surface formation, when the hard crystalline substances are destructed, is accompanied by a range of physico-chemical phenomena [1, 3, 4], such as:

a) electronic emission of various intensity;
b) luminescence;
c) formation of excess surface energy on the new surfaces and emerging of electric charges and fields due to the bombardment of the surfaces by high-energy electrons;
g) generation of radio waves and x-rays emission;
d) thermo-radiation and accumulation of energy in the form of the elevated temperature of a solid;
e) formation of free radicals on the surface, especially on polymeric materials [10].

It has been previously noted [1, 5, 6, 7] that, as any grinding apparatus or machine is a kind of mechanoactivator, then in order to apply the activated substances for intensifying a particular technology, it is necessary for the amount of accumulated energy in it (before application) to be greater than the energy released in the course of the relaxation process.

Naturally, the greatest effect is achieved when the technological process is carried out in the activating machine.

The list of chemical reactions being carried out in the mills of small dimensions (ball, vibration, ring and centrifugal planetary ones) covers different classes of reactions, which have been studied.

The solid – gas reaction includes synthesis of nitrides, hydrides, and carbonyls [6].

Gases (nitrogen, hydrogen, carbon monoxide) react with metals and oxides.

In the system of Solid 1 + Solid 2, carbides, borides, silicides were synthesised, and a reduction of metals oxides was performed; synthesis of ferrites, catalysts of superconducting ceramics, of new composite construction materials [5, 6, 7] was carried out. Experiments on the mechanochemical process of carbonate decomposition, which stayed for quite a long time in the centrifugal planetary mill, were performed [5].

It should be noted that mechanochemical synthesis was carried out mainly in laboratory high-energy centrifugal planetary ball mills, in which the ratio of centrifugal forces to the

force of gravity was: $\Phi = \dfrac{\omega^2 \cdot r}{g} > 80$

A way for project solution scaling for this types of mills is extremely complex due to large stresses at the machine nodes ($\sigma_{max} > [\sigma]$) when the productivity is $Y_m > 100$ kg/h. So, despite studies relating to the early 70-s of the 20th century, no industrial technology with

their application has yet been implemented, besides of the manufacture of small batches of some products.

In this context, a study of the influence of the strain rate on the intensity of mechanical activation of solids, aimed at further application of the continuously operated machines (mills) with a high speed impact loading, excluding the balls, their grinding and housing fretting, is of great interest. Under these conditions, the activated particles obtain multiple pulse loading, in which the occurring maximum voltages are greater than σ – beyond the limit of their strength.

At ISUCT (Department of Machines and Apparatuses of Chemical Productions), Bobkov S. P. and Blinichev V. N. [11] performed studies on grinding various materials in mills with different constructive designs. The share of energy spent on the formation of a new surface, for releasing thermal energy and for accumulating energy of a grinded body, was measured. These studies revealed that while being ground, the solids accumulate in them significantly greater amount of energy in comparison with the energy spent on the formation of a new surface.

The greatest amount of the accumulated energy (up to 40% of the fed one) was observed in polymer materials, in particular, made of Teflon: the thermal energy was not taken into account – it was measured and then deducted from the total amount of energy absorbed by a solid.

Precise measurement of the surface particles before and after grinding allowed to determine the energy value for a newly formed surface, if the specific surface energy is known (for certain substances). These studies have shown that for the majority of grinded substances (such as NaCl, limestone, Teflon), the value of the accumulated energy is ten times greater than the energy value of the newly formed surface.

It has been established that the amount of energy accumulated by a solid greatly depends on the rate of its strain and can be written as follows [11]:

$$\frac{dE_{\text{м}}}{dt} = \lambda \cdot \upsilon_{\varepsilon}^{2} \tag{1}$$

where:

$E_{\text{м}}$ – is the energy being absorbed;

υ_{ε} – rate of material strain;

λ – (constant) proportionality depending on the physical and mechanical properties of the activated material and on the ability to absorb the energy supplied.

From equation (1), it can be seen that the accumulated energy is proportional to the square of the strain rate.

The kinetics of the active state relaxation is proportional to the quantity of the energy accumulated:

$$\frac{dE_{\text{м}}}{dt} = -\text{const} E_{\text{м}} \tag{2}$$

With multiple pulse loading, such as impact loading, (in collaboration with Bobkov S. P., Padokhin V. A., and Zueva G. A.) the following stochastic equation was derived

by us, which takes into account both the processes of accumulation and dissipation of energy:

$$\frac{\mathrm{d}E(t)}{\mathrm{d}t} = \alpha_c \sum_{i=0}^{i=n} A_i \cdot \delta(t - t_i) + \alpha_c \cdot E(t) \tag{3}$$

where:

$E(t)$ – the accumulated energy;

α_c – a coefficient that depends on the physical and mechanical properties of the material;

t_i – the time of the i-th act of the pulse loading;

A_i – power provided by a single (individual) impact pulse (*amplitude*), which is considered as an independent random variable.

Solution of the differential equation (3), which takes into account the cumulative and relaxation processes occurring when initially provided that $E = E_0$ at $t = 0$, is as follows:

$$E(t) = \alpha_c \cdot \sum_{i=0}^{i=n} A_i \exp\left[-\alpha_c(t - t_1)\right] + E_0 \exp(-\alpha_c \cdot t) \tag{4}$$

The analysis of the given equation demonstrates that between Delta-pulses (i.e. the acts of the particle impact loading) the energy $E(t)$ smoothly exponentially decreases, and at the moment of impact loading with A_1 energy, it rises abruptly at the value of A_i $\alpha_c \cdot A_i$.

Considering a short time lapse between the high-speed impact loadings in multi-staged mills (stress rate is very high, impact loadings are numerous, and the particles stay in a machine for $3.5 \div 5$ seconds), the quantity of the energy accumulated in these types of mills appeared to be the greatest, despite the fact that the time of staying them in a ball, vibration and centrifugal-planetary mills was 20 minutes.

Therefore, while grinding hard materials, not only an external new active surface is created, but also active centres within the particles in the form of micro- and macrodefects as well as concentration energy centres around them. The latter significantly increase the reactivity of the subsequent relaxation processes.

Given the heavy dependence of the accumulated energy on the stress rate, we performed all the researches on mechanical activation of solids in the installations with multiple impact loading rates ranging from 75 to 180 m/s, depending on the physico-mechanical properties of the activated material, with the productivity of solid material of more than 250 kg/h.

In collaboration with Fedosov S. V., by applying high strain rates, we managed to realise a combined process: grinding and drying of large PVC sintered particles, in a 3-speed mill of impact-radiant type with the following initial parameters: initial humidity – 38%, the terminal one – less than 0.5%; the initial size of the sintered particles – $10 \div 50$ mm, the final one – 250 microns, the time of staying particles in the mill – 10 seconds, the productivity of a machine in the workshop for PVC production is 250 kg/h.

Our joint studies with Ladaev N. M, aimed at removal of moisture from capillary-porous single particles by the impact with different strain rate, revealed that when the rate of impact loading is more than 45 m/s with a single impact of the particles with a diameter

of 5 mm, and initial humidity is 40%, the particle loses up to 30% per cent of its humidity, even without its destruction, due to inertial forces and waves of the elastic strain.

All these results prove that in cases when it is necessary to obtain dry and fine powder, it is necessary to combine the process of drying and milling, as $70 \div 98$ % of the supplied energy is converted into thermal energy (internal pulse heat source), and inner diffusion moisture turns into surface moisture, which evaporates easily.

Another example of energy accumulation in polymers in the process of their milling is mechanochemical synthesis of fluorine rubber when Teflon and rubber are jointly milled in our multi-staged impact radiant mill implemented at Saint-Petersburg "Giproplast" plant with the productivity of 250 kg/h.

Totally inert to many PTFE systems, Teflon forms, in the process of joint milling, chemical bonds with rubber due to the energy accumulated in it as microdefects and radicals if a good mixing of the components and multiple impact loadings are provided. Thus, fluorine rubbers were synthesised, which otherwise could not be obtained.

High efficient mechanical activation of solids was achieved by means of their multiple high-rate impact loading in the multi-staged mills of continuous action (Fig. 1) at the Department of "Machines and Apparatuses of Chemical Productions" at ISUCT (with an average time of staying in the mill of less than 10 c) when the process of manufacturing new composite materials based on Teflon and coke was performed, the productivity of the raw materials mixture being $300 \div 350$ kg/h. Both components were continuously supplied as doses into the mill in the predetermined ratios of fluorine (initial average size of the particles – 1 mm) and coke (average size – 0.25 mm), the ratio of PTFE being: coke – 70:30, 60:40.
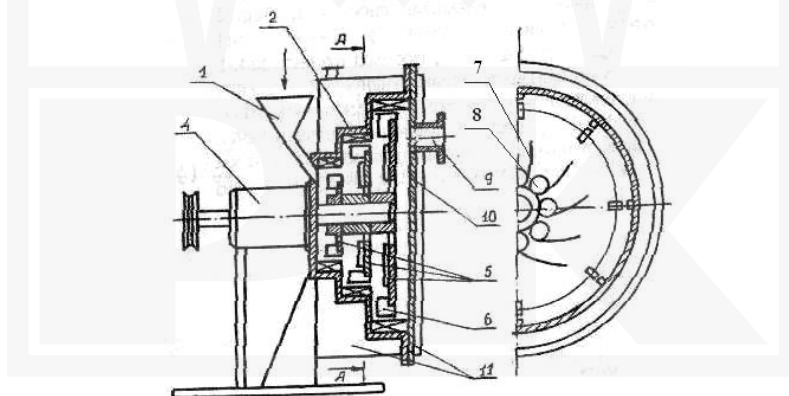

Fig. 1. Multistage continuous mill
1 – loading fitting; 2 – mill housing ; 3 – baffle plates; 4 – shaft; 5 – rotor; 6 – beater; 7 – blades;
8 – holes; 9 – unloading choke; 10 – flange; 11 – cooling jacket

A number of combined processes was carried out in the mill: mixing in powerful turbulent whirlwinds, which were created by the rotor blades and stator bumpers (of a mill housing); the additional pulse milling and mechanical activation of the components. Sintered compositions enabled to create new antifriction materials (FC-30 and FC-40), advantageously differing from the source material (Teflon).

The strength of the new composite materials has increased more than three times (compared with FC-20, which was obtained by means of conventional mixing of powders). Friction coefficient decreased by 2.5 times, and the cost dropped proportionally to the coke content as a cheap raw material.

Technology and equipment were implemented at the Kirovo-Chepetsk chemical plant.

Another example of a large accumulation of energy in repeated high-rate impact loading is ignition of the graphite milled in a multi-staged mill of an impact-radiant type [8].

While testing the optimal operating mode for the impact-radiant separation mill aimed at milling graphite from the Zaval′evsk deposits by means of an industrial machine, designed and constructed by us for Voskressensk Chemical Plant in order to maximise the number of particles of the product with the size less than 1 µm already at the stage of dry grinding, we managed to obtain the product with the particle content 25% less than 1 µm.

Having selected a probe for granulometric composition, we left 30 kg of the product in the cyclone hopper, the temperature in which reached 55^0 C. Within an hour, the product left in the hopper burnt down.

For industrial technology of fine graphite milling by means of CWC, we had to reduce the rate of impact loading in dry grinding mill and to obtain colloidal graphite product with 95% content of particles with dimensions of less than 1µm already in colloid-cavitational wet grinding mill [9], presented in Fig. 2.

Similarly mechanoactivation with pulse energy supply proceeds in liquid media, but only at greater velocity of relaxation processes.

In the works of several authors [12 ÷ 16] and in our works, it has been shown that the greatest effect is observed in water, suspensions and emulsions activation, when they are treated in rotary machines of various constructive design (see Fig. 2) in which a powerful pulse voltage arising because of the burst of cavitation bubbles overlaps with shear stress in a narrow annular gap between the rotor and the stator. Cavitation occurs in the fluid due to pressure pulsations and changes in the fluid flow rate.

Academician Dolynsky A. A. [17, 18], while studying fluid systems activation in rotary-pulsation apparatus, showed that periodic bursts of cavitation bubbles create powerful energetic discrete-pulse energy inputs in fluid systems in the nanoscale, and this process results in significant changes in their structure.

Studies on water and fluid systems activation were conducted by various authors on rotary machines, the basic schemes of which are presented in Fig. 2.

Despite somewhat different constructive features of rotary activators, for all of them, a major trigger factor is the discrete energy input in the form of *cumulative* flow when the cavitation bubbles burst. The frequency of bubbles occurring and bursting depends on constructive features of rotors and stators, as wells on rotors rotation frequency.

In our studies on water treatment of various origin (distilled, tap water and artesian) in rotary cavitators of types (a) and (b) (Fig. 2), it is shown that owing to the number of revolutions in the rotor cavitator and, accordingly, to the intensity of the cavitation impact, only the measured values of redox potential (ORP) increase significantly (Fig. 3); water pH increases insignificantly.

The value of ORP in relaxation process within a few days reduces; however, the level of steady-state values of the AFP remains higher compared to its initial value.
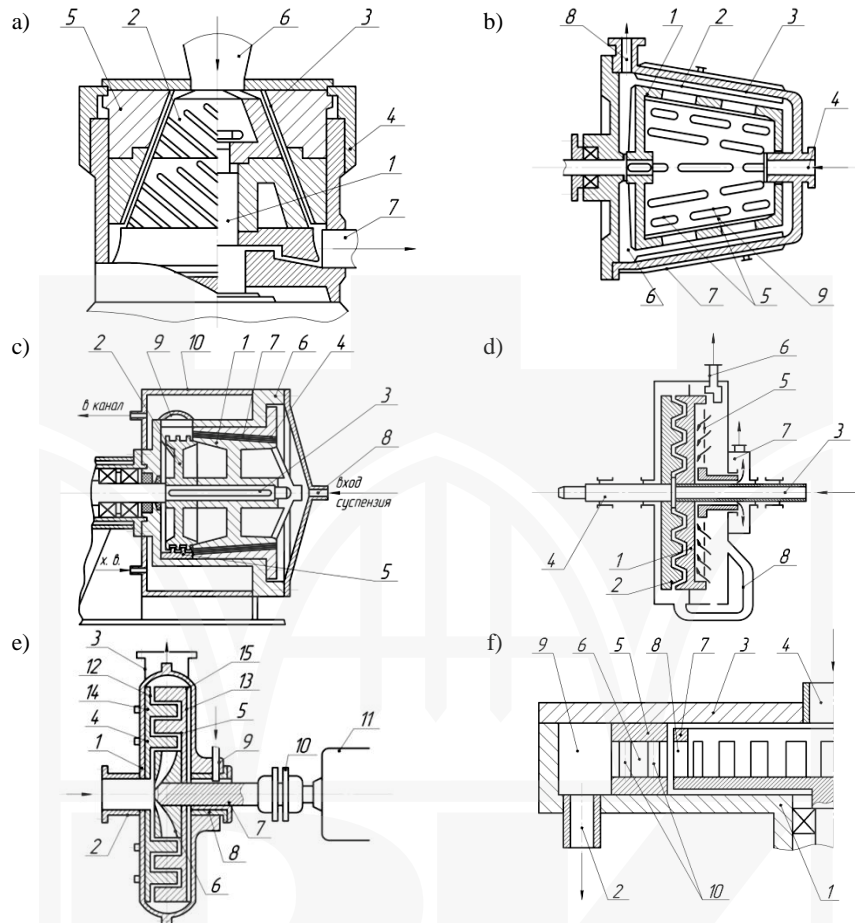
Fig. 2. Scheme of activators

a) Cone Colloid Mill Activator (1 – shaft; 2 – rotor; 3 – ribs; 4 – housing; 5 – stator; 6 – suspension inlet);

b) Colloid Mill Activator with the Perforated Rotor (1 – rotor; 2 – baffles; 3 – housing; 4 – suspension inlet; 5 – perforations; 6 – suspension unloading zone; 7 – jacket ; 8 – suspension outlet);

c) Cavitation-Colloid Mill Activator (1 – rotor; 2 – impact device; 3 – shaft; 4 – stator; 5 – counterbaffles; 6 – housing; 7 – grooves; 8 – suspension inlet; 9 – suspension outlet; 10 – cooling jacket);

d) Colloid Activator with Two Rotating Rotors and Separation of the Activated Solid Phase (1 – rotating hollow shaft rotor; 2 – rotating rotor; 3 – hollow shaft; 4 – shaft; 5 – separator; 6 –outlet of coarse particles; 7 – fine particles outlet);

e) Rotary Hydraulic Mill (1 – housing; 2 – inlet fitting; 3 – suspension outlet fitting; 4 – fixed disc; 5 – movable disc; 6 – rotor; 7 – shaft; 10 – shaft coupling; 11 – coupling drive; 12, 13 – grooves; 14, 15 – protrusions);

f) Rotary RPA Apparatus (1 – housing; 2 – suspension outlet fitting; 3 – cover; 4 – inlet fitting; 5 – stator; 6 – stator channels; 7 – rotor; 8 – rotor channels; 9 – voice camera; 10 – rods).
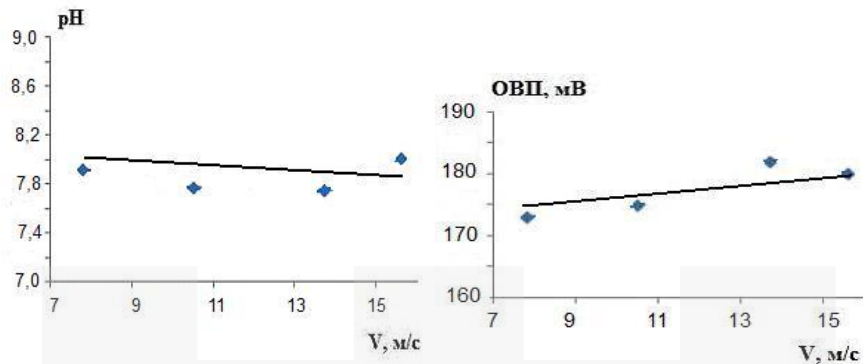
Fig. 3. Dependence of pH and ORP on the linear speed of rotor in the activator

In order to prove that cavitation bubbles do arise and burst in the cavitators, sensors were attached to the housing of the rotor. They allowed to register housing vibration when cavitation bubbles "exploded". Firstly, the housing vibrations of the idle activator operation were registered, and then those in the working mode (see Fig. 4).

From the plot (3) (Fig. 4,) it is clearly seen that when water passes through the activator, high frequency spectrum of additional pressure pulses from the cavitation bubbles bursts appear.
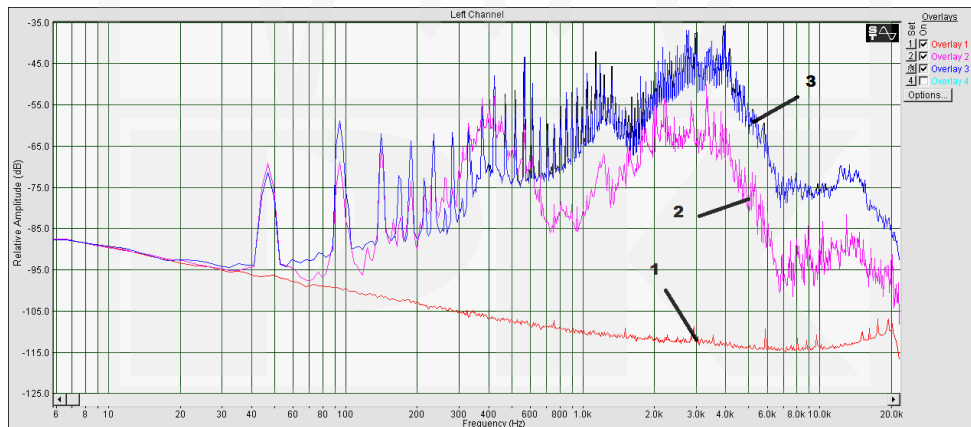

Fig. 4. Fourier spectrum in water treatment (water consumption is 1.44 m^3/h)
1 – background noise, 2 – spectrum of idle mode, 3 – spectrum of fluctuations in operating mode

The same phenomenon is observed when suspension passes through the cavitation device. In earlier works, it has been shown that if the fluid contains solid phase particles, the cavitation bubbles are formed and burst exactly on the moving hard particles.

A powerful pulse of energy, supplied to the hard particles when a bubble bursts, is the very "hammer" which destroys even small particles of solid materials. It is known that the

strength of many materials depends on the particle size, and when the latter reaches a monocrystal size, it increases by two orders of magnitude.

Therefore, when designing the construction of cavitation colloid mill for superfine milling of graphite (95% of the particles should have dimensions less than 1 micron), we have tested about a dozen of different machines constructions with a view of elaborating a cavitator, which would provide the conditions for forming and bursting the maximum number of cavitation bubbles.

The researches that we have jointly conducted with the staff of the Ivanovo Medical Academy and aimed at activation of two licensed drugs for treating diseases of joints (*Tomed and Tomed-Aqua*) in rotary cavitators of type (a) (Fig. 2), showed that death intensity of the various types of bacteria increases significantly, and efficiency of drugs application for treating these diseases (according to medical clinics data for the last 2 years) is growing.

Under the supervision of S. V. Fedosov, T. E. Slizneva (Ivanovo State Polytechnic University) undertook the studies of activation process in rotary-pulsation apparatus in a magnetic field of water solutions of electrolytes [19, 20]. It was shown that their mechano-magnetic treatment contributes to the enhancement of frost resistance of fine-grained concrete for $40 \div 50$ cycles and provides the increase of the rate of curing at the early stages of hardening and elongation of beginning of setting along with reduction of its finishing, as well as results in enhancing the strength by $15 \div 22\%$ compared to the concrete obtained by means of traditional technology. Application of mechano-magnetic activation of liquid mixing allows to save up to 10% of cement.

Mechano-magnetic activation of tempered water containing organic plasticising and water-reducing organic additives promotes mobility of the concrete mixture by up to 100% during $1,5 \div 2$ hours, i.e. $1.2 \div 2.4$ times more in comparison with not activated water systems.

Taking into consideration the above-mentioned information, we can conclude that impact pulse loading with a larger momentum energy of solids and water systems allows to intensify significantly many of the heat- and mass-transfer processes, including chemical reactions.

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