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Effect of Mechanical Activation Frequency on the Reactivity of Phosphate Rock Mixtures in an Impact Mill

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Abstract: This article presents the results of an experimental investigation into the mechanical activation of a phosphate rock mixture using a single-rotor impact activator. The key indicators used to assess the effectiveness of activation were the content of water-soluble P_2O_5 and the heat of dissolution of phosphorite in hydrochloric acid. The obtained graphical data illustrate a clear improvement in these parameters with increasing rotational speed and frequency of mechanical impacts on the material particles. Analysis of the results revealed that both the content of accessible P_2O_5 and the heat of phosphorite dissolution increased by approximately 15-20% when the intensity of mechanical activation was enhanced under the specified grinding conditions.

Keywords: phosphate rock, mechanical activation, impact grinding, sustainable agriculture, resource efficiency, green technology, fertilizer quality, heat of dissolution.

1. Introduction

To increase the productivity of agricultural lands, it is necessary to apply high rates of phosphorus fertilizers and widely use phosphate rock as an ameliorative agent, especially on acidic and phosphorus-depleted soils [1].

Phosphorus rock is the cheapest, but relatively ineffective fertilizer, since its form of P_2O_5 is difficult for plants to absorb. For use as fertilizer, the predominant part of apatites and phosphorites is converted into soluble compounds using thermal enrichment or the interaction of phosphate ores with mineral acids. In connection with the search for new methods of processing phosphorus raw materials into fertilizers, cheaper than its acid and thermal decomposition, several works related to its mechanical processing have recently appeared.

Intensive mechanical processing of phosphates in high-energy devices enables to increase their reactivity. This is the essence of mechanical activation, which leads to the modification of materials using mechanical energy to change the structure and properties of the material [2, 3, 4]. Phosphates can be solubilized in an alkaline solution of ammonium nitrate, depending on the conditions and intensity of mechanical processing, and become fertilizers that are much better absorbed by plants.

Compared with the traditional acid method used to activate phosphate rock mixture, mechanical and chemical activation treatment is characterized by greater environmental friendliness, since chemicals aren't used within the process and there

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is no liquid waste [5]. This improves the reactivity of phosphate ores [5, 6]. Therefore, many researchers have paid attention to mechanical and chemical activation for the direct treatment of medium and low purity phosphate ores [5, 6, 7, 8].

Mechanical activation is indicated to be an effective and environmentally friendly method for processing medium and low quality phosphorite ore for fertilizer [9]. Phosphorite ore after processing in a ball mill had improved solubility of phosphorus in citric acid. The mechanism of phosphorus solubility after mechanical and chemical activation of phosphate ore and its ability to release phosphorus was actively studied. Experiments on the content of extractable phosphorus and the solubility rate were carried out at different grinding times.

Similar findings have also been confirmed by other researchers [10, 11, 12]. Phosphorite powder was processed in a grinder for different periods of time from 5 to 150 minutes. This increased the specific surface area of the powder particles, leading to higher phosphorus solubility in citric acid [10]. The procedure of grinding phosphorite in a planetary high-speed (up to 1500 rpm) mill for 30 min significantly improved the solubility of phosphorus in citric acid [11].

The studies conducted [12] confirm the sufficiently high efficiency of the mechanical activation of fine phosphorite ore and the mechanical and chemical activation of phosphorite-containing mixtures, which make it possible to significantly increase the content of accessible P2O5 phosphorus pentoxide in composite fertilizers containing phosphorus. During mechanical activation, an amorphous layer is formed on the surface of dispersed phosphorite particles and the density of the phosphate substance decreases, which significantly increases its reactivity and solubility. As a result of mechanical activation of finely dispersed phosphorite ore in a planetary mill, the relative content of the citrate-soluble form P_2O_5 in the activated phosphorite increases more than threefold from 17.63% to 53.18%. The mechanical activation time is within 5–10 minutes.

In study [13], it was shown that in the process of mechanical activation of phosphorites the content of accessible forms of P_2O_5 depends on the grinding time and reaches maximum values at 10 minutes of the mechanical activation process.

In research [14] low-grade phosphorites were subjected to mechanical activation in a mill for 60 minutes. It resulted improved reactivity and solubility of the activated samples.

In the studies [15], the morphology of particles, crystallinity, specific surface area and free surface energy of grinding products were studied at different grinding times, up to 180 min. The specific surface area and free surface energy of phosphate ore positively correlate with the solubility coefficient of the enthalpy of phosphorus ore in citric acid, and the solubility coefficient of phosphorus ore in citric acid significantly increases from 9.14% to 61.68%. The presented research results are of certain importance for the enrichment of phosphorite ore powder activated by ultrafine grinding.

Most previous studies have focused on the mechanical activation of phosphate rock mixtures, primarily examining how the content of the accessible form of P_2O_5 and the solubility of phosphorite particles depend on grinding time. In contrast, this study aims to investigate how these critical indicators are influenced by the number and speed of mechanical impacts.

2. Experimental Materials and Methods

A multi-stage experimental setup was developed to investigate the influence of impact velocity and loading frequency on the physicochemical properties of dispersed materials subjected to mechanical activation. This setup also enables the assessment of how repeated impacts affect changes in the structural and chemical characteristics of the processed materials. Figure 1 presents the schematic diagram of the single-rotor laboratory-scale impact activator. The system comprises the impact activator unit (1), a screw feeder (2), a cyclone separator (3), an electric drive motor (4), and two sensors (5, 6) for process monitoring and control.

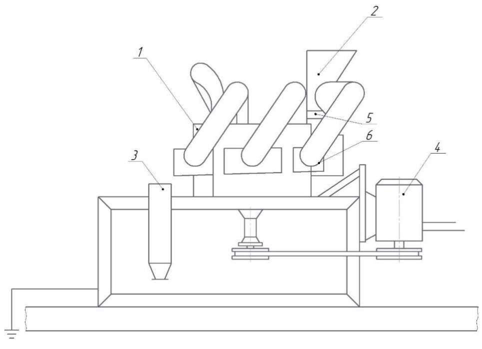

Figure 1: Basic diagram of a single-rotor impact activator.

The general layout of the impact activator is presented in Figure 2. The grinding unit consists of a cylindrical housing (1) with external n-spiral channels (2) connected to additional feed pipes (3) via slots (4). Inside the housing, a rotor is installed, comprising a shaft (5) and a disk (6) equipped with accelerating blades (7) containing slots (8) for the entry of material from the external spiral channels. A main feed pipe (9) is mounted on the top cover of the housing, while the tangential outlet pipe (10) is used for discharge. An adjustable air intake (11) regulates airflow.

During operation, the material enters the grinding chamber through the main feed pipe (9) and is impacted by the accelerating blades (7), which direct it into the external spiral channel (2). The air stream then returns the material via the additional feed pipes (3) back under the blades. This recirculation continues until the desired number of impacts is achieved, after which the material is discharged through the tangential outlet (10).

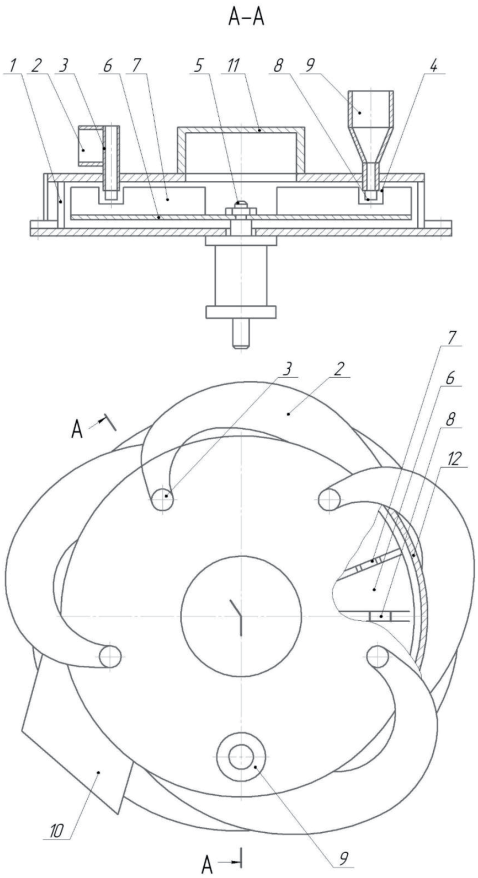

Figure 2: Single-rotor impact activator.

Each material, depending on its dispersion and friction coefficient, has a certain angle of departure from the rotor. Taking this into account, the spiral flows are designed in such a way that 98-99% of the material after interaction with the impact elements gets into a strictly defined spiral flow. The gap between the rotor and the machine body is set at a minimum of 2 mm. To reduce the slippage of the material, a bumper 12 is located on the wall of the body immediately behind the spiral flow in the direction of rotation. The gap between the bumper and the rotor is 0.5 mm. The bumper is made of steel. This feature ensures the probability of the material getting into the desired spiral flow after interaction with the impact elements up to 98-99%. The design features listed above enable to achieve a single loading of the material on each spiral flow.

The number of loadings during the studies varied from 1 to 5 and the number of spiral flows was different. There are located sensors one at the input and the other at the output to determine the average time between material loadings on the first spiral flow, counting from the main loading pipe along the direction of rotation. In all experiments, the average time between two successive loadings was 10 s. The time between two successive loadings was adjusted by the flow rate of air sucked through the impact activator. The air flow was adjusted by changing the free cross-section of the air intake and averaged 50 m^3/hour.

The material was dosed by a screw feeder with its constant capacity of 2.5 kg/hour.

To determine the phosphorus content in the studied phosphorites, a differential photo-colorimetric method was employed [16]. The phosphorus content was evaluated in terms of P2O5 extracted with a 2% citric acid solution. Measurements were carried out using a microprocessor-based spectrophotometer Lasany LI-722 (Lasany International, India). The P_2O_5 content (wt%) was calculated using the following formula:

$$P_2O_5 = \frac{a \cdot 25}{g \cdot V}, \tag{1}$$

where a – the amount of P_2O_5 determined from the calibration curve, mg; g – the mass of the sample taken for analysis, g; V – the volume of the aliquot, ml.

3. Results

Phosphorite was processed in a single-rotor impact activator. The dependence of the content of citric soluble phosphorus on the number and speed of loading is shown in Fig. 3 and 4.

The content of citric soluble phosphorus in both the first and second cases increases with the number of loadings and its speed. The dependence of the content of citric soluble phosphorus on the number of loadings is linear, and on the speed of loading is polynomial. The conducted studies enabled to identify the dependence of the heat of phosphorite dissolution on the number of loadings and their speed. The experimental data are presented in Fig. 5 and 6, respectively.

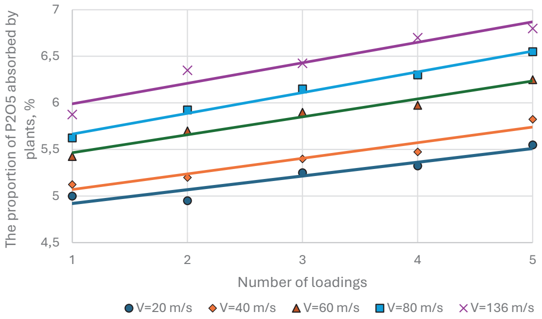

Figure 3: Content of P_2O_5 depending on the number of loadings.

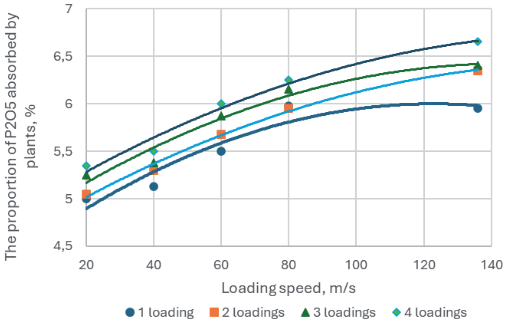

Figure 4: Content of P_2O_5 depending on the loading speed.

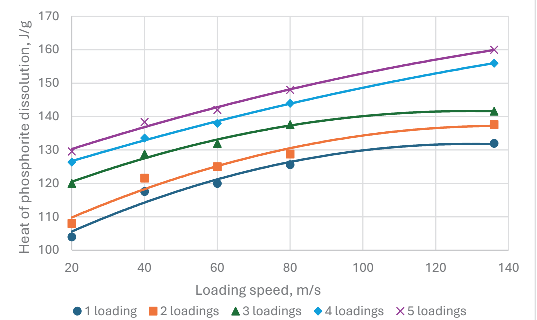

Figure 5: Heat of phosphorite dissolution depending on the loading rate.

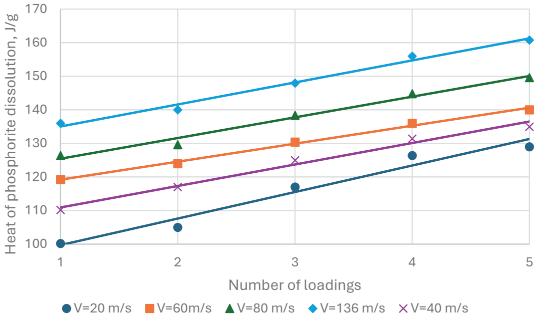

Figure 6: Heat of phosphorite dissolution depending on the loading number.

The content of citric-soluble phosphorus increases with both the number and speed of mechanical impacts. A linear relationship was observed between the phosphorus content and the number of impacts (Fig. 3), while a polynomial trend was established with respect to impact speed (Fig. 4). The dissolution of phosphorites in hydrochloric acid is accompanied by heat release. A consistent increase in the heat of dissolution was recorded with rising impact speed and frequency (Figs. 5, 6). The dependence on the number of impacts is linear (Fig. 5), whereas the dependence on speed follows a polynomial pattern (Fig. 6).

4. Discussion

The experimental data in Figures 3 and 4 demonstrate that at low impact velocities (20–40 m/s), even with two to three loading cycles, the proportion of plant-available P_2O_5 remains below the initial value. This effect can be attributed to a slight reduction in the specific surface area of the dispersed system. At such low velocities, the energy delivered to the particles is insufficient for their fragmentation. However, due to the formation, migration, and annihilation of structural defects induced by mechanical impact, the material's reactivity increases.

These structural defects tend to migrate toward the particle surface, enhancing its surface activity. The resulting increase in surface energy promotes the formation of stable agglomerates composed of the finest particles, which contribute significantly to the total surface area.

When the number of impacts is increased to five, even at low speeds (20–40 m/s), an observable increase in surface area occurs. This is likely due to the evolution of the defect structure, involving the formation and propagation of primary cracks within individual particles. Higher impact velocities further intensify defect formation, leading to additional surface development and improved material activity, as evidenced in Figures 3 and 4.

The moderate increase in heat of dissolution observed at intermediate impact speeds (40–60 m/s) and low numbers of impacts (n = 1–2) can be explained by the pre-existing defect structure of the material, stemming from its production process. Under low-intensity impact, some of the internal energy stored in the defect-rich solid is released through the fracture of particles containing large flaws. This process is accompanied by both the elimination and generation of new defects. However, at such low intensities, most of the supplied energy contributes to the destruction of existing major defects rather than forming new ones, which accounts for the slight decrease in dissolution heat.

When the impact velocity exceeds 80 m/s and the number of impacts increases, a consistent growth in the heat of dissolution is observed, reflecting the intensified defect formation and structural reorganization within the phosphorite particles.

5. Conclusions

The conducted study established a strong dependence of the physicochemical activation of phosphate rock mixtures on the regime parameters of mechanical treatment in a single-rotor impact activator. It was shown that both the number and the speed of mechanical loadings significantly influence the increase in the content of citric-soluble P2O5 and the heat of phosphorite dissolution in hydrochloric acid. These effects are associated with defect structure evolution, enhanced surface energy, and particle disintegration mechanisms. Quantitatively, the accessible phosphorus content and the dissolution enthalpy increased by 15–20% under optimized loading conditions. The findings support the feasibility of tailoring mechanical activation parameters to improve the reactivity of low-grade phosphate materials, thus contributing to sustainable fertilizer production and the advancement of green chemistry and circular economy strategies.

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