

# Technology for the Production of Organomineral Fertilizers Based on Organic Resources of Plant Origin and Off-Grade Phosphorites

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**Annotation:** The study investigates the process of producing fertilizers through the processing of substandard phosphorites (SP) using oxidation products of plant residues (PR) in various proportions. The following experimental conditions were examined: H<sub>2</sub>O<sub>2</sub> concentration – 10%, PR:H<sub>2</sub>O<sub>2</sub> ratio = 1:0.1, H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> molar ratio = 1:0.1–0.5, and phosphate raw material (PRM):PR weight ratio = 100:40–200. It was found that the treatment of phosphate raw material with oxidation products leads to a significant increase in the proportion of available (assimilable) P<sub>2</sub>O<sub>5</sub> forms. The optimal conditions were determined as H<sub>2</sub>O<sub>2</sub> concentration 10%, PR:H<sub>2</sub>O<sub>2</sub> ratio = 1:0.1, H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> molar ratio = 1:0.5, and PRM:PR weight ratio = 100:150. The commercial properties of the resulting fertilizers—hygroscopicity, moisture capacity, caking tendency, and granule strength—were evaluated, and

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X-ray diffraction analysis was performed. Based on the results, a technological process was proposed and a material balance for the production of fertilizers using oxidized PR in the presence of sulfuric acid was calculated.

**Keywords:** organomineral fertilizers, plant residues, low-grade phosphorites, oxidation, hydrogen peroxide, humic substances, soil fertility, phosphorus solubility, sulfuric acid, agricultural waste recycling, eco-friendly fertilizer production.

## INTRODUCTION

Currently, all over the world, organic substances of humic nature are widely used as ameliorating agents and fertilizers to optimize the ecological condition of soils. Excessive use of mineral fertilizers in agriculture has become one of the major causes of severe soil pollution and degradation. Therefore, research aimed at creating environmentally friendly, resource-efficient, and biologically active fertilizers based on local raw materials, such as substandard phosphorites and oxidized organic residues, is of high scientific and practical importance for sustainable agricultural development.

An essential condition for ensuring the food security of a country is the sustainable development of domestic agriculture, which can only be achieved through the preservation of soil fertility and the justified replenishment of nutrients removed by agricultural crops via the effective use of fertilizers. In this regard, the combined application of mineral and organic fertilizers is considered the most rational approach. The analysis of long-term field experiments conducted both abroad and under local conditions shows that obtaining high and high-quality yields requires the simultaneous use of organic and mineral fertilizers. This helps avoid excessive salt concentration in spring while providing sufficient nutrient reserves for the second half of the growing season. To achieve this, it is crucial to supply agriculture with high-quality fertilizers and expand their range.

In this context, the development of fertilizer production technologies based on plant residues (PR) and low-grade phosphorites is of great importance. Such fertilizers can be effectively used to combat soil degradation, increase humus content, and enhance soil fertility.

The utilization of waste materials is one of the most urgent problems of modern society, encompassing household, industrial, and agricultural wastes. Among them, agricultural waste has a high potential for effective recycling and can be used in various sectors of production [1]. In recent years, worldwide attention has been focused on the production of fertilizers containing humic substances, plant growth and development stimulants, and humic-based ameliorants obtained from organic resources, as well as their application in agriculture, due to the decreasing humus content in soils.

During agricultural production, as land is cultivated, part of the soil humus gradually mineralizes, releasing nitrogen and other nutrients that become available for plant uptake. However, the annual humus loss can reach 0.6–0.7 tons per hectare. Under high-yield conditions for cereal crops, the soil loses about 0.5–1.0 tons/ha of humus annually, and for row crops, the loss increases to 1.5–3.0 tons/ha. It has been established that a 1% decrease in soil humus content leads

to a reduction in crop yield by approximately 5 centners of grain units per hectare [2, 3].

This emphasizes the need for scientifically grounded approaches to restoring humus balance through the use of organic and organo-mineral fertilizers, especially those derived from local waste materials such as plant residues and low-grade phosphorites.

One of the non-traditional sources for replenishing humic substances (HS) in irrigated soils can be plant residues (PR). The rational use of plant residues in agriculture is one of the key factors in maintaining and increasing soil fertility. The application of plant residues from agricultural crops as fertilizers contributes to an increase in the soil content of humus and nutrients.

The modern agricultural system actively promotes the use of plant residues as organic or organo-mineral fertilizers. Along with organic matter, plant residues also contain nitrogen, the concentration of which ranges from 0.5 to 0.7%, and in the case of pea residues, it can reach 1.6%. The highest potassium content is observed in oat straw (1.6%), while in other crops it varies within 0.8–1.0%. The phosphorus content in agricultural plant residues averages 0.2–0.3% [4].

Plant residues represent a complex of diverse chemical substances. It has been established that plant residues of different types contain essentially the same components, though in varying proportions. The main ones are cellulose, hemicellulose, and lignin, which form the cell wall and account for 90–95% of the mass of absolutely dry plant material. The remaining 5–10% are classified as extractive substances, i.e., compounds that can be extracted by various solvents without significant alteration of their structure. Under the conditions of a negative humus balance in agriculture and the annual organic matter deficit, the incorporation of processed plant residues of agricultural crops into the soil serves as an effective means of replenishment. The use of plant residues for producing organic and organo-mineral fertilizers is a promising direction [5].

The raw materials for obtaining humic substances (HS) include manure, peat, lignin, sapropel, brown coal, and other organic-mineral raw products (OMRP) [6–8]. One of the on-site methods for processing phosphogypsum (PG) is its conversion into sulfuric acid, which can be reused in the production of extraction phosphoric acid. However, this method of sulfuric acid production requires significant economic costs compared to traditional technologies [9].

The results of research [10] describe a conversion process for phosphogypsum into ammonium sulfate and calcium carbonate. It was shown that based on phosphomel, an innovative multifunctional product, calcium hydrocarbon aluminate ( $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot n\text{CO}_2\cdot 11\text{H}_2\text{O}$ ), can be synthesized. The study also outlines possible applications of calcium hydrocarbon aluminate in various sectors of the economy.

Based on the above, the objective of this study is to evaluate the possibility of converting plant residues into valuable chemical products through oxidation.

The object of research is coarsely ground plant residues (PR). The PR samples were dried to an air-dry state and then milled to a particle size of 0.25 mm. After grinding, an average representative sample was prepared with the following composition (wt.%): moisture – 6.86; ash – 10.74; organic matter – 82.4; extractive substances extracted with 1% NaOH solution – 4.37; extractive substances extracted with water – 1.22.

Table 1 presents the results of mass spectrometric analysis (ICP–MS) of the ash obtained from the PR samples. According to the data, plant residues contain a wide range of microelements essential for plant growth and development, confirming their potential use as a valuable raw material for fertilizer production.

**Table 1 – Results of Mass Spectrometric Analysis (ICP–MS) of Plant Residue Ash**

<b>Mg</b> 2,77	<b>Si</b> 2.08	<b>P</b> 3,88	<b>S</b> 0.405	<b>K</b> 28,4	<b>Ca</b> 9,47	<b>Mn</b> 0,06	<b>Fe</b> 0,429
<b>Zn</b> 0,041	<b>Br</b> 0.0011	<b>Rb</b> 0.0243	<b>Sr</b> 0.0270	<b>Ti</b> 0,0411	<b>Zr</b> 0.145	<b>Sn</b> 0.0013	<b>Re</b> 0.0041

To increase the content of extractive substances (ES)—that is, to convert plant residues (PR) into humic acids, fulvic acids, and other organic acids—the oxidation process of PR with hydrogen peroxide ( $H_2O_2$ ) in the presence of sulfuric acid ( $H_2SO_4$ ) was investigated.

The oxidation process was carried out using a 10% hydrogen peroxide solution at a temperature of 60°C for 120 minutes, with a weight ratio of PR: $H_2O_2$  = 1:0.025–1:0.2. The ratio refers to the organic portion of PR to monohydrate  $H_2O_2$ . Experiments were performed in a cylindrical reactor equipped with a thermostatic jacket and a mechanical stirrer. The oxidizing agent and acid were added to the reactor, the temperature was stabilized, the stirrer activated, and the ground PR sample loaded.

After the process, the reaction mass was dried to an air-dry state, and parameters such as ash content, moisture, organic matter, and yield of extractive substances (1% NaOH solution) were determined. Ash content was measured according to GOST 11022-95, moisture content according to GOST 11014-91, and organic matter was calculated by difference between 100% and the sum of ash and moisture percentages. The extractive substances in the initial and oxidized PR (with nitric acid) were determined by the method described in [11].

The results showed that the composition of oxidized PR varied depending on the concentration and dosage of  $H_2O_2$ . The amount of oxidized PR increased up to 104.3% relative to the organic portion of the initial PR. At a 10%  $H_2O_2$  concentration, a PR: $H_2O_2$  ratio of 1:0.2, 60°C temperature, and 2-hour duration, 31.56% of the initial PR remained unoxidized. The main goal of oxidation—increasing the content of water- and alkali-soluble organic acids—was successfully achieved: the content rose from 4.37% in the original PR to 69.36% in the oxidized PR.

Thus, the conducted study demonstrated that oxidation of PR with hydrogen peroxide in the presence of sulfuric acid significantly increases the content of extractive substances, which are valuable products for the production of organic and organo-mineral fertilizers and plant growth stimulants.

The technological process for producing humic fertilizers (HF) based on oxidized organic plant residues (OPR) with  $H_2O_2$  in the presence of  $H_2SO_4$  and low-grade phosphorites (LP) consists of the following main stages:

- Oxidation of PR with  $H_2O_2$  in the presence of  $H_2SO_4$ ;
- Processing of phosphate raw materials (PRM) with oxidation products of PR;
- Ammonization of the acidic product;
- Pelletizing the product in a drum granulator with return material;
- Drying;
- Crushing, sieving, and packaging.

For fertilizer production, low-grade phosphorites (LP) of the following composition (wt.%) were used: LP:  $P_2O_5$  – 11.67; CaO – 41.18;  $Al_2O_3$  – 1.82;  $Fe_2O_3$  – 1.40;  $CO_2$  – 20.94; CaO: $P_2O_5$  = 2.98. Mineral mixture (MM):  $P_2O_5$  – 14.43; CaO – 43.12;  $Al_2O_3$  – 1.16;  $Fe_2O_3$  – 1.34;  $CO_2$  – 14.76; CaO: $P_2O_5$  = 3.53.

Other components included  $H_2SO_4$  (92%), PR ground to 1.0 mm with the following composition (wt.%): moisture – 6.86; ash – 10.74; extractives (1% NaOH) – 4.37; water-soluble

extractives – 14.64; insoluble organics – 63.39; and H<sub>2</sub>O<sub>2</sub> (10%).

The oxidation of OPR with H<sub>2</sub>O<sub>2</sub> in the presence of H<sub>2</sub>SO<sub>4</sub> was carried out at ratios PR:H<sub>2</sub>O<sub>2</sub> = 1:0.1 and H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> (molar) = 1:0.5. Due to the exothermic nature of the reaction, the temperature of the reaction medium rose to 70°C, and simultaneously, the reaction heat caused partial moisture evaporation. After adding the final portion of PR, oxidation continued for 120 minutes.

As a result of oxidation, the product contained 37.17% extractives in 1% NaOH solution, 26.57% water-soluble organics, and 36.26% residual PR. This dense, moist oxidized mass was then used as a starting component for processing low-grade phosphorites.

The oxidation products containing sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were transferred into a stirred reactor, where the required amount of low-grade phosphorite (LP) was added in portions at a mass ratio of phosphate raw material (PRM) to oxidized plant residue (PR) = 100:150. The obtained suspension was stirred for 30 minutes and subsequently neutralized with 25% aqueous ammonia to reach a pH level of 4.0–4.5. The drying process was carried out at 80°C, while granulation occurred during ammoniation and drying by the pelletizing method. The chemical composition and mechanical strength of the granules were analyzed, showing that granules with a diameter of 2–3 mm had a compressive strength of 2.2–2.4 MPa, which confirms their structural stability. The experimental results are summarized in Table 2. Based on the conducted research, the optimal process conditions for treating phosphate raw materials and mineral mixtures were determined as follows: hydrogen peroxide concentration – 10%, ratio PR:H<sub>2</sub>O<sub>2</sub> = 1:0.1, molar ratio H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> = 1:0.5, and mass ratio PRM:PR = 100:150. A batch of 50 kg of the resulting fertilizer was prepared and sent for agrochemical field testing to assess its agronomic efficiency.

**Table 2**

**Composition of organomineral fertilizers obtained from oxidized organic substances of plant origin and off-grade phosphorites**

Ratio phosphorite : PR	Влага, %	P <sub>2</sub> O <sub>5</sub> total, %	P <sub>2</sub> O <sub>5</sub> ass., %	P <sub>2</sub> O <sub>5</sub> ass. Tr.B, %	CaO total, %	$\frac{P_2O_{5,Tr-B}}{P_2O_{5tot.}}$ , %	SO <sub>3</sub> total, %	N total, %	Organic matter, %	Humic acids, %
Oxidation product: H <sub>2</sub> O <sub>2</sub> concentration 10%, ratio PR : H <sub>2</sub> O <sub>2</sub> = 1 : 0.1 (molar ratio H <sub>2</sub> O <sub>2</sub> : H <sub>2</sub> SO <sub>4</sub> = 1 : 0.5), <i>sludge phosphorite</i>										
100 : 100	3,54	4,64	3,52	3,01	16,51	64,87	4,23	1,34	42,84	9,35
100 : 150	4,37	3,52	2,84	2,48	12,53	70,45	4,66	1,48	50,16	12,84
100 : 200	4,58	2,95	2,67	2,34	9,81	79,32	4,77	1,58	54,54	16,19
Oxidation product: H <sub>2</sub> O <sub>2</sub> concentration 10%, ratio PR : H <sub>2</sub> O <sub>2</sub> = 1 : 0.1 (molar ratio H <sub>2</sub> O <sub>2</sub> : H <sub>2</sub> SO <sub>4</sub> = 1 : 0.5), <i>mineralized mass</i>										
100 : 100	3,47	5,61	3,86	3,28	17,88	58,47	5,36	1,46	42,61	9,61
100 : 150	3,83	4,22	3,68	3,06	13,87	72,51	5,63	2,16	49,94	13,18
100 : 200	4,12	3,52	3,24	3,05	11,11	86,65	5,97	2,76	54,43	16,67

Thus, the process of obtaining fertilizers by processing low-grade phosphorites (LP) using oxidation products of plant residues (PR) in various proportions was studied. The experiments

were carried out under the following conditions:  $\text{H}_2\text{O}_2$  concentration of 10%, PR :  $\text{H}_2\text{O}_2 = 1 : 0.1$ , molar ratio  $\text{H}_2\text{O}_2 : \text{H}_2\text{SO}_4 = 1 : 0.1-0.5$ , and mass ratios of phosphate rock : PR = 100 : 40–200. It was found that the treatment of phosphate raw materials with oxidation products of PR led to a significant increase in the relative content of assimilable forms of  $\text{P}_2\text{O}_5$ . The optimal conditions were determined as follows:  $\text{H}_2\text{O}_2$  concentration = 10%, PR :  $\text{H}_2\text{O}_2 = 1 : 0.1$ , molar ratio  $\text{H}_2\text{O}_2 : \text{H}_2\text{SO}_4 = 1 : 0.5$ , and phosphate rock : PR = 100 : 150. The physical and chemical properties of the obtained fertilizers—such as hygroscopicity, moisture-holding capacity, caking tendency, and granule strength—were determined, and X-ray diffraction analysis of the samples was performed. In addition, the technological regime and material balance for fertilizer production using PR oxidized with hydrogen peroxide in the presence of sulfuric acid were developed. The proposed method provides an efficient approach for producing high-value organo-mineral fertilizers through the combined use of organic and mineral raw materials, contributing to improving the fertility and ecological condition of agricultural soils.

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