




OBTAINING OF COMPLEX MINERAL FERTILIZER BY PHOSPHOGYPSUM CONVERSION WITH AMMONIUM NITRATE

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Abstract. The paper proposes an environmentally friendly method for phosphogypsum processing into N,Ca,S,P-fertilizers. The liquid complex mineral fertilizer was obtained by treating phosphogypsum with an ammonium nitrate solution. The dependence of the content of Ca^{2+} , SO_4^{2-} , NO_3^- ions in the temperature range of 20-80°C at the ratio $\text{CaSO}_4:\text{NH}_4\text{NO}_3=1:0.5$ was studied. The optimal temperature for the fertilizer obtaining was established at 60°C. It was obtained a complex liquid N,Ca,S,P-fertilizer with the content of nutrients (wt. %) N:Ca:S:P= 56:26:12:6 in the dry product, and 16.8:3.6:7.8:1.8 in the liquid phase. The obtained fertilizer increased the yield of radish by 7.16% compared to the control. The advantage of the proposed method is reducing the cost of the fertilizer, increasing its nutritional value, and obtaining useful products from the waste.

Keywords: phosphogypsum, ammonium nitrate, complex mineral fertilizer, wet conversion.

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Introduction

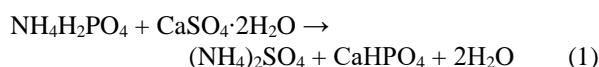
Phosphogypsum (PG) is a large-scale waste from the production of extractive phosphoric acid (EPA) and phosphorus fertilizers [1,2]. PG is formed during the processing of apatite and phosphorite raw materials and, depending on the technology used, it can be presented in the form of di- or hemihydrate of calcium sulphate [3]. For one ton of phosphorus pentoxide in EPA, about 7.5 tons of PG are formed [4]. Annually, the world volume of PG accumulation reaches 120–130 million tons, while its re-used share does not exceed 10–15% [5]. About 90 million tons of PG already have been stockpiled in Ukraine. These dumps are the source of environmental pollution in the regions where mineral fertilizer production is located, e.g., Sumy, Rivne, Armyansk, Vinnytsia, and Kamianske [6].

PG can be used in agriculture as a Ca,S-fertilizer on soils with a lack of calcium and sulphur, as an additive in the production of organo-mineral fertilizers by composting, or as an ameliorant for alkaline and acidic soils [7]. In the course of numerous studies in various climatic zones, it has been established that the ameliorative effect of natural gypsum and PG is equivalent [8]. The amount of PG introduced depends on the soil itself and agronomic conditions of climatic zones and ranges from 2.5 to 15 t/ha. The consequences

of land reclamation can last 7–20 years, after which chemical land reclamation is required again. The use of PG in agriculture reduces the technogenic impact on the environment by cutting down the volume of mining (gypsum and anhydrite) and the amount of stored waste. A comparison of crop yields on different soils showed that PG can be successfully used as an analog of natural gypsum, provided that these are applied in equivalent amounts in terms of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ content [9]. The average increase in the yield of grain crops when applying 5–10 tons of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ per 1 ha of steppe and meadow-steppe solonchic soils was 1.6–4.0 centners/ha, corn – 90–127 centners/ha, perennial grasses (wheatgrass, hay) – 2–10 centners/ha [9].

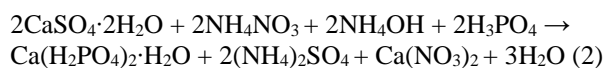
Another effective path of PG utilization is in the ammonium carbonate conversion to obtain ammonium sulphate and calcium carbonate, which seems highly promising [10,11]. However, it should assume the availability of large-scale production of carbon dioxide and ammonia nearby. An alternative method of utilization of PG is the thermal processing into sulphuric acid and lime [12]. The production of sulphuric acid is an energy-intensive technology as well as the thermal decomposition of PG [13]. So, this technique is considered unprofitable, especially given the complexity of the decomposition process itself. In

a recent study, an attempt was made to convert gypsum from phosphoric acid pulp to ammonium sulphate and calcium phosphate; the process can be described by Eq.(1) [14].



The method consisted of a deep ammoniation (pH 7–8) of a mixture of phosphoric acid and PG, which allowed obtaining a solution of complex mineral fertilizer, consisting mainly of dicalcium phosphate and ammonium sulphate. The operating conditions of this method are still to be optimized.

“Dniprovskyy zavod mineral’nykh dobryv” (“Dnipro Mineral Fertilizer Plant” or “DZMD”) in Kamianske produces PG as an ameliorant according to national standard TUU 24.1-31980517-002:2005 [15]. Recently, the process of obtaining purified PG with the release of rare earth elements during the treatment of calcium sulphate with nitric and sulphuric acids has been studied. The results revealed the optimal indicators of rare earth elements allocation [16]. Consequently, it was the first successful attempt to use PG from “DZMD” to obtain a complex NSCa-fertilizer by Eq.(2).



The present study was primarily aimed at the elaboration of a feasible method for obtaining a nutrient-rich N,Ca,S,P-fertilizer by PG conversion using ammonium nitrate. Testing of the obtained fertilizer for intensification of radish growing was the secondary subject of investigation.

Experimental

Materials

The following reagents were used: NH_4NO_3 ; H_3PO_4 ; glycol; zinc powder; α -naphthylamine; sulphonic acid; sodium hydroxide; murexide indicator; Trilon B (all purchased from Merck, USA).

In the present study, two types of PG were used: the first was sampled at the “DZMD”, the second – at phosphoric acid production dumps at the “Prydniprovsky Chemical Plant” (“PChP”) in Kamianske. The parameters of each type of PG varied insignificantly and average values were as follows, %: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – 80.0; moisture – 26.0; total phosphates – 2.0; dissolved fluorine compounds (Na_2SiF_6 , K_2SiF_6) – up to 0.6. PG was subjected to acid treatment for purification, after which rare earth elements were isolated from the

obtained filtrate according to the previously described technique [16]. Purified PG was used in fertilizers production.

Methods

The raw materials and products were analysed to determine the content of P, Ca, NO_3^- , and SO_4^{2-} ions using the standard methods described in the literature [17] e.g., phosphorus, nitrate and sulphate ions – calorimetric; calcium – titrimetric method.

Thermogravimetric (TG) analysis of phosphogypsum was performed on a synchronous thermal analyser STA 409 PC (NETZSCH, Germany). The starting material was averaged by quartering and wiped through a sieve with a mesh cell of 0.1 mm. The powder was moistened and formed into a "tablet". The sample was dried at 100°C for 20 hours. Thermal analysis was performed on a piece that was chipped from it. The rate of heating is 10 degrees per min until the temperature of 300°C.

Synthesis of complex mineral fertilizer

The scheme of the laboratory installation is shown in Figure 1 [16]. Briefly, a volume of 500 mL of 80% ammonium nitrate solution was poured into a vessel with a stirrer, then 200 g of each sample of PG was added with continuous stirring after the isolation of rare earth elements, changing the temperature in the vessel from 20 to 80°C. The mass ratio of PG to ammonium nitrate was 1:0.5. After obtaining a homogeneous mass, 36 mL of 25% phosphoric acid was added, then the pH was adjusted to 7 by adding the appropriate volume of ammonium hydroxide solution. After the allotted time, the precipitate was filtered off using a “blue ribbon” paper filter, and a liquid phase – complex mineral fertilizer was tested in the growth of radish.

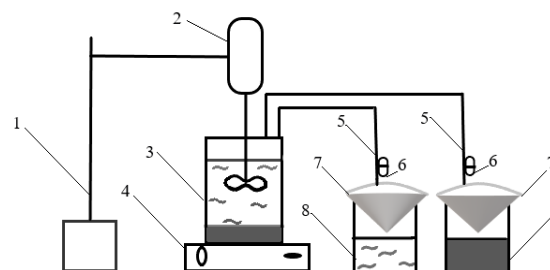


Figure 1. Laboratory installation for the phosphogypsum processing using ammonium nitrate [16].

(1 – tripod; 2 – stirrer; 3 – pulp container; 4 – furnace; 5 – tube; 6 – valve; 7 – paper filter; 8 – filtrate container).

An intense hydrodynamic mixing regime ($Re = 10^4$) was provided by a propeller stirrer (rotation speed 180 rpm). During ammonization the binding of water-soluble calcium compounds, which is contained in PG, occurred, which was accompanied by the appearance of a new solid phase, presented mainly by $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

Testing of the obtained fertilizers

The experiment was conducted in four variations: 1) solid complex mineral fertilizer “nitroammophoska” (marketable NPK-fertilizer); 2) liquid complex mineral fertilizer 1 (LCMF1) – based on “DZMD” PG; 3) liquid complex mineral fertilizer 2 (LCMF2) – based on “PChP” PG; 4) control – without fertilizers. The research was conducted during May-June 2021 on the local research field, using the radish variety “Sora”. Planting of radish was performed by the tape method; the depth of wrapping is 2–3 cm. The total area of the experimental plot was 6 m². Fertilization was carried out during the period of active vegetation of seedlings on the 14th day after sowing in the stage of appearance of 2–3 leaves. Solid fertilizer was dissolved in water in the ratio of 2–3 g of “nitroammophoska” per 1 L of water, LCMF samples were diluted in water in the ratio of 8 mL of fertilizer per 1 L of water.

Results and discussion

Differential thermal analysis of phosphogypsum

The thermogravimetric analysis of “DZMD” PG was carried out to study the phase transformations in raw material and to establish the dehydration temperature of raw $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Gypsum dihydrate gradually dehydrates as the

temperature rises and turns into an anhydrous state, turning into an insoluble compound. The thermal analysis makes it possible to determine the maximum heating temperature at which the process of chemical interaction of PG and an aqueous solution of ammonium nitrate can be carried out.

Thus, it was established that the maximum dehydration temperature of raw $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is 130°C (Figure 2). It is known from [16], that for “PChP” PG stored for more than 40 days after formation, the dehydration temperature can increase up to 200°C. It can be attributed to the emergence of new chemical bonds between PG crystals, which leads to their aggregation. Destruction of these crystals requires more energy than the dehydration of fresh PG. Increasing the storage time of PG raises the temperature of dehydration, so the processing of fresh PG becomes more energy-efficient. Thus, the “DZMD” PG was subjected to thermal analysis.

Original PG is a greyish-white mass with a moisture content of up to 40%, $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ content of 95–98%. The first endothermic process, which refers to the dehydration of gypsum to the hemihydrate $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, begins at a temperature of ~130°C, ends at 180°C, and is characterized by a mass loss of 15–18%. The maximum rate of mass loss is 4.5% per min. The next endothermic process (190–200°C) characterizes the complete dehydration of gypsum to CaSO_4 with a weight loss of ~3%. It occurs at a slower speed (1–2% per min) and ends at a temperature of 220°C.

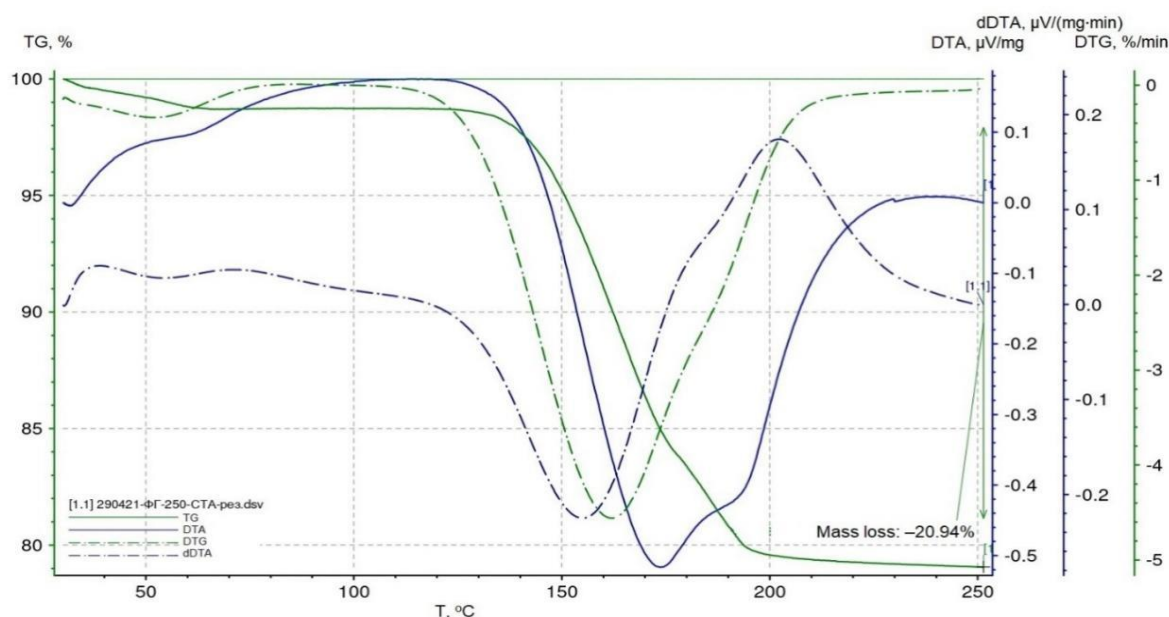


Figure 2. TG curves of the “DZMD” phosphogypsum.

Influence of conversion parameters on the content of nutrients in the liquid complex mineral fertilizer

The dependence of the temperature on the content of nutrients in the liquid fertilizer was studied, and the result is presented in Figure 3. The concentration of Ca^{2+} increases with temperature rise. An increase in the water-soluble form of calcium from 248 to 251.8 mg/L indicates the reaction of ammonium nitrate with calcium sulphate. Calcium enhances metabolism and maintains acid-base balance in plant organisms and affects the metabolism of carbohydrates and proteins, ensuring their better transport, improves chlorophyll synthesis, is part of pectin and some other organic compounds [18]. If applied to the soil in a digestible form, it is expected to increase the crop yield [19,20].

During the increase of temperature from 20 to 60°C in the samples of liquid fertilizers, there was an increase in the content of dissolved sulphates from 23.5 to 44.5 mg/L. Since the temperature of the beginning of crystallization of the liquid phase is 60°C, the anions SO_4^{2-} do not precipitate and remain in the dissolved state in the liquid phase of LCMF. When PG is treated with phosphoric acid and ammonia water at pH 6.8–7.2, a deep conversion occurs, which makes it possible to bind the phosphates present in PG (FePO_4 , $\text{Ca}_3(\text{PO}_4)_2$, Na_3PO_4) on one hand, on the other hand – to extract sulphates from PG. The presence of ammonia causes the complete conversion of the mixed components. At a pH over 7.5 ammonia losses increase, at $\text{pH} < 6.0$ dicalcium phosphate passes into double superphosphate, as stated in Eq.(2). In the mineral nutrition of plants, only sulphur, which is in the forms SO_4^{2-} and SO_3^{2-} , is important, as only ionic forms of sulphur can be absorbed by the plant [21].

With the increasing temperature in samples 1 and 2 (Figure 3), the concentration of NO_3^- ions decreases. It was found that the introduction of PG in a solution of NH_4NO_3 leads to a decrease in nitrogen content in the final product from 35 to 16.8%. At the same time, during the chemical interaction with calcium sulphate, the composition of ammonium nitrate is enriched with two macronutrients – sulphur and calcium, which are contained in PG. The decrease in the concentration of nitrogen in the liquid fertilizer is explained by the fact that part of the NO_3^- anions are utilized for the neutralization of PG. During the reaction between PG and ammonium nitrate, there is a decrease in the content of nitrogen because raw PG does not contain nitrogen [22].

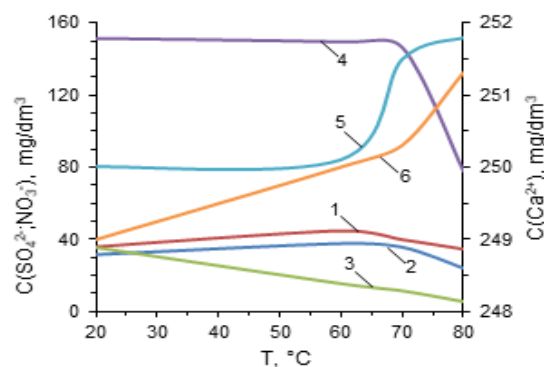


Figure 3. The dependence of the concentration of nutrients in the liquid fertilizer from the temperature: SO_4^{2-} (1); SO_4^{2-} (2); NO_3^- (3); NO_3^- (4); Ca^{2+} (5); Ca^{2+} (6); source of phosphogypsum: “DZMD” (1,4,5); “PChP” (2,3,6).

As a result of the conversion, three salts are formed with a clear phase separation: in the precipitate, a poorly soluble salt of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ double superphosphate, and in the liquid phase, salts of ammonium sulfate and calcium nitrate, which have good solubility. Double superphosphate can be used as a ready-made fertilizer that is used for the pre-sowing application for all crops on all types of cultivated and uncultivated soils. Ammonium sulfate and calcium nitrate obtained in the liquid phase can be used as liquid fertilizers with N:Ca:S:P in the dry product – 56:26:12:6 wt.%, in a liquid phase – 16.8:3.6:7.8:1.8 wt.%. Theoretical consumption coefficients for the production of one ton of liquid fertilizer are as follows: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – 220 kg; NH_4NO_3 – 100 kg; 25% H_3PO_4 – 500 kg; 25% NH_4OH – 180 kg.

The technical result in the industrial implementation of this conversion method is an increase in nutritional value and a decrease in the cost of fertilizer due to the production of liquid fertilizer containing ammonium sulfate and calcium nitrate. Due to the re-use of PG in the production of complex mineral fertilizers, a high environmental effect could be achieved, stopping the environmental pollution by fluoride, phosphorus, and sulphur compounds contained in dumps.

Testing the efficiency of the liquid complex mineral fertilizers

During radish growth, the crops looked almost uniform. Even after the introduction of LCMF the plant body was not damaged. The highest average mass of root was 27.9 g and the length of the top 28 cm was observed with the introduction of LCMF2 (Table 1), and the total yield was significantly higher compared to other variants.

Table 1

The comparative efficiency of the liquid complex mineral fertilizers.

Fertilizer type	Tops length, cm	Root length, cm	Root mass, g	Radish head diameter, cm
“Nitroammophoska”	25	6.8	22.5	11.6
Liquid complex mineral fertilizer based on “DZMD” phosphogypsum (LCMF1)	26.5	5.5	23.8	13
Liquid complex mineral fertilizer based on “PChP” phosphogypsum (LCMF2)	28	5	27.9	12
Control (without fertilizer)	24	4.5	20	11

The lowest average weight of root (20 g) was observed in the first variant with the application of “nitroammophoska”, but the length of the crop (6.8 cm) was the maximal. After the application of LCMF1, the average mass of the root was 23.8 g, which is lower by 4.1 g after the application of LCMF2, but higher than options 1 and 4. In the control version, all indicators were significantly lower. The yield structure of the studied radish is shown in Table 1.

Thus, the highest yield and mass of radish root were obtained by applying LCMF2. The research results indicate the high agronomic efficiency of obtained liquid complex mineral fertilizers for radish cultivation. This enables using LCMF1 and LCMF2 when growing other important crops.

Conclusions

The possibility of obtaining a liquid multicomponent fertilizer by the exchange reaction of PG with ammonium nitrate has been experimentally proved. During the interaction of PG with ammonium nitrate with the addition of ammonium and phosphoric acid, a clear phase separation was noted: a slightly soluble $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the precipitate, and well-soluble salts of $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$ in the liquid phase. The fertilizer can be obtained at a mild temperature of 60°C.

An increase in temperature from 20 to 60°C leads to the increase of the content of dissolved sulphates from 23.5 to 44.5 mg/dm³ in the liquid fertilizer. Since the temperature of the beginning of crystallization is 60°C, the anions SO_4^{2-} do not precipitate as double superphosphate remain dissolved in the liquid phase. The introduction of PG into NH_4NO_3 solution leads to nitrates decrease from 253 to 228 mg/L, which is explained by the fact that part of the NO_3^- anions are used for PG neutralisation. At the same time, during the chemical interaction with calcium sulphate, the

composition of the fertilizer is enriched with two macronutrients, S and Ca, which are contained in PG.

The obtained complex liquid fertilizer with the content of nutrients N:Ca:S= 24:8:12 increases the yield of radish by 7.16% compared to the control. In the industrial implementation of the proposed method, it is possible to obtain a multicomponent fertilizer, which application may compensate for the loss of nitrogen, calcium, and phosphorus from the soil, and solve the problem of PG storage.

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