Obtaining a complex mineral fertilizer from raw materials of varying degrees of purification from impurities

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Abstract. The article is devoted to the synthesis of a complex fertilizer magnesium-ammonium phosphate (MAP) from raw materials of varying degrees of purification, the effect of certain impurities on the MAP yield, as well as the choice of optimal conditions for obtaining this fertilizer. Phosphorus, as is known, is an irreplaceable element of plant nutrition, therefore the introduction of compounds containing phosphorus in one form or another is necessary for the normal development of plants during the growing season. Phosphoric acid, obtained by opening natural phosphates with mineral acids, in particular, sulfuric acid, is often used to obtain phosphoric fertilizers. One of the ways to purify the phosphoric acid obtained in this case is purification using various organic solvents. At the output, phosphoric acid is purified from most impurities, containing a small amount of impurity cations and anions, the main of which are fluorides and sulfates. We carried out the MAP synthesis on the basis of chemically pure phosphoric acid and using an acid purified with an organic solvent tributyl phosphate. It has been shown that the presence of sulfates and fluorides in purified phosphoric acid increases the MAP solubility in an aqueous solution by increasing the ionic strength of the solution and leads to a slight decrease in the yield of the synthesis product from 81% to 78%. The interfering effect of impurity anions can be reduced by conducting the process in an alkaline medium, pH 9-10, with the addition of an excess relative to the stoichiometric amount of an aqueous ammonia solution.

1 Introduction

The production of complex fertilizers in Russia was started in the 60s of the twentieth century, and by 1980 their share in the total amount of fertilizers for growing crops was 20.2% with a predominance of ammophos. If we talk about three-component fertilizers, in which the molar ratio of nutrients is 1:1:1, then preference is given to the use of nitrophoska and nitroammophoska. Gradually, the range of complex fertilizers expanded due to the use of polyphosphoric acids, as well as due to the enrichment of fertilizers with trace elements, magnesium, and other plant nutrition components. In particular, magnesium-ammonium

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phosphate (MAF) has become widespread, the production of which is the subject of this work.

MAP has high efficiency as a fertilizer [1, 2]. It combines elements necessary for plant growth - nitrogen in ammonium form, phosphorus in the form of phosphate and magnesium, which makes it an indispensable component for increasing soil fertility and improving the quality of plant development at all stages [3]. MAP has moderate solubility in a neutral environment, does not wash out into groundwater during heavy rains, but remains in the root zone of plants, which provides them with nutrition for a long time. Due to its low solubility, its use is relevant for soils with high moisture content, as well as for growing plants on hydroponics.

One of the main MAP advantages is its ability to provide plants with all the necessary nutrients. Magnesium in the fertilizer contributes to the formation of chlorophyll, affects the activity of enzymes and regulates metabolism, which leads to improved photosynthesis and increased yield. Ammonium and phosphates are the main sources of nitrogen and phosphorus for plants, which ensures their normal development.

In addition, MAP helps to improve the structure of the soil, promotes the penetration of moisture and air to the roots of plants. This, in turn, contributes to a better absorption of nutrients by plants, which has a beneficial effect on their growth and yield.

In nature, magnesium-ammonium phosphate (MAP) occurs in the form of the struvite mineral. Struvite is a biogenic mineral, it can often be found in the decomposition products of organic compounds by microorganisms in a putrefactive environment, and therefore struvite has another name – guanite. It is often possible to find struvite in the composition of deposits on pipes diverting wastewater from livestock complexes [4]. There are many studies devoted to the methods of obtaining MAP [5, 6, 7, 8]. Methods of obtaining MAP from agro-industrial wastewater have been developed. In particular, scientists of Perm Polytechnic University propose to extract magnesium-ammonium phosphate from agro-industrial or household wastewater. The proposed method makes it possible to obtain MAP from agro-industrial wastewater in the form of a large easily filtered sediment, which can be used as a complex fertilizer. As a seed, it is proposed to use a filtrate of purified wastewater containing finely dispersed MAP [9].

Nevertheless, in its pure form, the mineral struvite is quite rare in nature. In this regard, MAF is synthesized from inorganic substances according to the following scheme:

$Mg^{2+} + HPO_4^{3-} + NH_4^+ + 6H_2O = MgNH_4HPO_4 \cdot 6H_2O$.

The task of our work was to select the conditions for the synthesis of MAP based on phosphoric acid of various degrees of purification from impurities. Chemically pure phosphoric acid and phosphoric acid obtained by purification using an organic extractant tributyl phosphate were used for synthesis. It should be noted that due to the changed geopolitical situation at the end of the twentieth century, the production of pure (thermal) phosphoric acid turned out to be outside the Russian Federation. In this regard, the purification of extraction phosphoric acid (EPA), formed after the sulfuric acid opening of natural phosphorites, using organic solvent extractants has become widespread. This method makes it possible to obtain purified acid of high quality, suitable for the production of feed, technical, and food phosphates. According to this method, EPA is first mixed with an organic solvent (extractant), while most of the phosphoric acid and a small part of impurities of various nature are extracted into the organic phase. The aqueous phase, raffinate, contains a certain amount of phosphoric acid and most *of* the impurities and can be used for the production of mineral fertilizers. From the organic phase, the extract, phosphoric acid is re-extracted with water or aqueous solutions of alkalis [10]. The acid (or its salts) obtained in this way differs from the initial EFC by a much higher degree of purity and can be used to produce food and feed phosphates, as well as for the production of chemically pure complex fertilizers.

By the method of extraction purification, we obtained phosphoric acid, which contained a certain amount of sulfuric and hydrofluoric acids. The objective of the experiment was to compare the synthesis yield of the complex fertilizer magnesium-ammonium phosphate from phosphoric acid of varying degrees of purification, namely, from chemically pure acid and from the obtained in the process of purification using an organic solvent. The synthesized complex fertilizer is then planned to be used in the vegetative experiment for growing vegetable crops.

2 Materials and Methods

Purification of EPA with tributyl phosphate. Extraction phosphoric acid obtained by sulfuric acid dissection of apatites and the past stage of preliminary purification from sulfates, of the following composition (%), was used as the starting material:

H_3PO_4 – 70 ÷ 80 (P_2O_5 – 50,5 ÷ 58,0)
SO_4^{2-} – 0,7 ÷ 1,1
F^- – max 0,2
$Fe_2O_3 + Al_2O_3$ – max 1,5
CaO – max 0,05
MgO – max 0,2
Solid suspensions – max 0.5.

The preparation of purified phosphoric acid was carried out as follows: the aqueous and organic phase (100% tributyl phosphate) was brought into contact and emulsified using a magnetic stirrer MM-5 (rotation speed 400-450 rpm). The contact time of the phases was 15 min, which corresponds to the achievement of equilibrium in the extraction process. In this case, most *of* the phosphoric acid and a small amount of impurities pass into the extract. Basically, these impurities are sulfates and fluorides. Cationic impurities are poorly soluble in the organic phase. The reextraction was carried out with distilled water. Then the resulting reextract was evaporated, reducing the concentration of fluorides and organic solvent in it. The reextract composition after evaporation, %:

H_3PO_4 – 68 ÷ 71 (P_2O_5 – 49,3 ÷ 51,5)
SO_4^{2-} – max 0,10
F^- – max 0,025
$Fe_2O_3 + Al_2O_3$ – max 0,005%

The resulting phosphoric acid was used for MAP synthesis.

Obtaining magnesium-ammonium phosphate. As already mentioned, MAP was obtained from phosphoric acid of various purification degrees – chemically pure and obtained as a result of purification with an organic extractant – tributyl phosphate.

The method of obtaining crystalline MAP is based on the reaction between solutions of magnesium chloride $MgCl_2$ and ammonium hydrophosphate $(NH_4)_2HPO_4$ in accordance with the reaction equation, that is, in a molar ratio of 1:1:

$$MgCl_2 + (NH_4)_2HPO_4 = NH_4MgPO_4 + NH_4Cl + HCl$$

NH_4^+-ammonium cations were introduced into the solution in excess relative to the calculated amount according to the stoichiometry of the reaction, since pH 9-10 is optimal for the deposition of NH_4MgPO_4. That is, a deliberately excessive volume of an aqueous ammonia solution was injected into the solution, controlling the pH in the reaction mixture. Ammonium hydrophosphate was prepared by adding an ammonia solution to phosphoric acid in a molar ratio of 2:1. The synthesis was carried out at room temperature. The deposition time was 3-4 hours. To obtain larger crystals, a seed can be introduced in the form of finely dispersed magnesium-ammonium phosphate. The resulting precipitate was washed with distilled water, transferred to a filter, dried in air and weighed on technochemical scales with an accuracy of 0.01 g. Calculations were carried out to determine the practical yield of the synthesis of magnesium-ammonium phosphate.

3 Results and Discussion

As a result of the work done with multiple repetition, we have obtained the following results:

1. The use of phosphoric acid containing impurities for the synthesis of MAP slightly reduces the yield of the final product from an average of 81-78%.
2. The use of acid with impurities did not affect the quality of the crystals obtained and the deposition time of MAP.

If we talk about the effect of impurity anions SO_4^{2-} and F^- on the yield of the synthesis product, then it is different. Fluorides form MgF_2 precipitate with magnesium cation, the solubility of which is 0.0076 g/100 g of water or 1.23 $\times 10^{-3}$ mol/l, which is greater than the solubility of MAP, which is 8.1×10^{-4} mol/l in a neutral medium. The amount of fluoride impurities in the phosphoric acid used for synthesis is negligible (less than 0.025%), so the possible contamination of the magnesium-ammonium phosphate precipitate with magnesium fluoride will be minimal. Sulfates do not form a precipitate with magnesium cations, but contribute to increasing the solubility of the magnesium-ammonium phosphate precipitate by increasing the ionic strength of the solution, Fig.1.

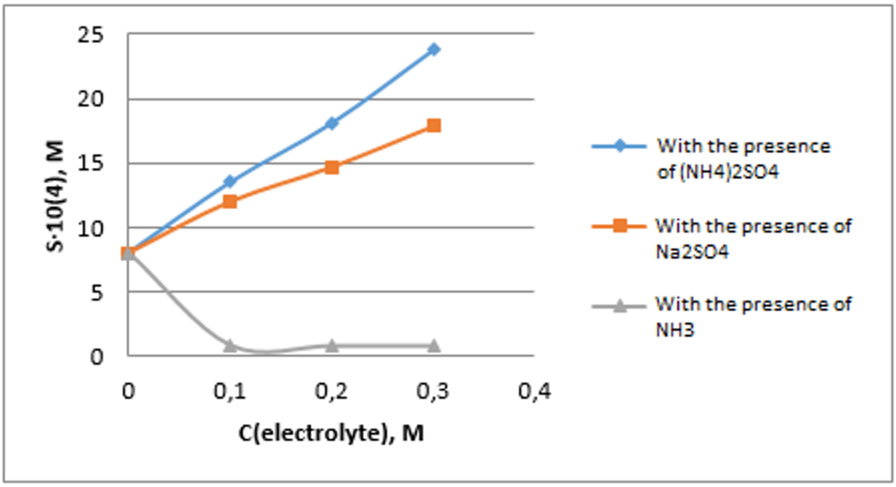

Fig. 1. Dependence of the magnesium-ammonium phosphate solubility on the concentration of electrolyte solutions

From the graphs shown in Figure 1, it can be seen that in the presence of sodium sulfate with a concentration of 0.1 M, the solubility of $MgNH_4PO_4$ increases to 12 $\times$ 10^{-4} mol/l, and in the presence of an ammonium sulfate solution of the same concentration, the solubility of MAP is already 13.5 $\times 10^{-4}$ mol/l. Ammonium sulfate, unlike neutral sodium sulfate, gives a slightly acidic medium in solution, which leads to an increase in the solubility of MAP, the value of which increases in an acidic medium. The graph also shows how sharply the MAP solubility decreases in the presence of ammonia.

The presence of cationic impurities (Fe^{3+}, Al^{3+}) does not interfere with the deposition of MAP.

Perhaps a slight decrease in the yield of the target product is due to the presence of a residual amount of organic solvent – tributyl phosphate. Note that the solubility of TBP in water is 0.39 g/l.

In any case, such a discrepancy of 3% between the yield values according to the experimental variants suggests the possibility of using phosphoric acid purified by extraction method for the synthesis of magnesium-ammonium phosphate.

Speaking about the use of magnesium-ammonium phosphate as a fertilizer, it should be noted that its use is recommended for cereals, legumes, root crops and other agricultural crops. The use of MAP in potato cultivation increases its yield and nutritional value. The same is noted when growing tomatoes and cucumbers. Since MAP has an alkaline environment, it is recommended to use it on acidic soils to neutralize the negative effect of increased acidity on plant development. In addition, in a slightly acidic environment, the solubility of MAP increases, and, consequently, the availability for plants of the nutritional components that it contains increases.

4 Conclusions

The experimental data obtained allow to talk about the possibility of synthesizing a compound complex fertilizer magnesium-ammonium phosphate not only from chemically pure phosphoric acid, but also from acid that has been purified with an organic solvent that does not mix with water. A slight decrease in the yield of the synthesis product is due to the presence of impurities in phosphoric acid, nevertheless, impurity ions did not affect the deposition time and the quality of the obtained MAP crystals.

To find out the effect of the obtained fertilizer on the growth and development of agricultural crops, it is planned to conduct a growing experiment on several vegetable crops.

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