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METHODS OF OBTAINING SOME PHOSPHORUS FERTILIZERS

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Abstract
The article shows the importance of phosphate fertilizers. The most popular fertilizers for plants based on phosphorus are considered. The properties of phosphorus and methods for obtaining phosphorus fertilizers were studied.

Keywords: amorphous, superphosphate, precipitate, phosphate rock, Thomasslag, Diammonium Phosphate

Introduction

Phosphorus is a very important element that is necessary for the development of all plants. With its deficiency, gardeners and gardeners apply phosphate fertilizers. We will tell you what types they are and how to use them correctly on the site. Phosphorus controls the metabolic processes occurring in the plant and is a source of energy. This element is part of the cell nucleus and many substances that play a major role in the life of the flora [1-7]. And besides, in mineral form, phosphorus is involved in the synthesis of carbohydrates. Therefore, only with a sufficient amount of phosphorites, do plants develop correctly, grow quickly and bear fruit well.

The Main Part

Phosphorus fertilizers promote the growth of the root system of the plant and increase yields, so they are especially important for vegetable, grain, berry and fruit crops. As you can see, the importance of phosphate fertilizers is difficult to overestimate. The peculiarity of the use of such dressings is that you can not be afraid to "overfeed" the plants with phosphorus. An excess of this element in the

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soil will not harm green pets, since they absorb it in the amount that the plant needs for proper development. Of course, this does not mean that you can feed the plants without measuring, but you should not worry if you applied more fertilizer to the soil than was indicated in the instructions [8-11].

Types of Phosphate Fertilizers and Their Production

All phosphate fertilizers are recommended to be applied in the fall for digging, and not just scattered over the soil surface. The fact is that phosphorus is contained in them in a form that is difficult to digest, and during the winter these substances spread into the soil layers and in late spring-early summer are already well absorbed by plant roots. But some fertilizers (usually liquid), in which phosphorus is present in an easily digestible form, are also applied in the spring and during the growing season. Consider the most popular phosphorus-based plant fertilizers. Simple phosphorus fertilizers are subdivided into soluble (single-substituted), poorly soluble (disubstituted) and insoluble (trisubstituted) phosphates. Calcium salts and less often magnesium salts are used as fertilizers. Simple phosphate fertilizers are obtained from apatites and phosphorites [12-16]. The general formula of apatites.

$$\{Ca_3(P0_4)_2\}_{2/,,} \bullet CaX_2;$$

where X — are the Ions F^-, CI, OH' etc.

The formula of phosphorite is $Ca_3(P0_4)_2$. Consider some simple phosphate fertilizers.

Superphosphates are the simplest and most commonly used phosphate fertilizers. They are easily soluble in water, which facilitates the absorption of phosphorus by plants. This type of fertilizer can be used on any type of soil and in all types of cultivation, as well as in meadows and pastures, which is why they are called universal fertilizers. They should be applied before sowing, best in combination with potassium salts, in the presence of which they work most effectively. Phosphorus is one of the main nutrients for plants, and its deficiency is manifested by its stiffness and tendency to brittleness, lack of lustre, and red spots on the leaves may also appear. It should be remembered that phosphate fertilizers mainly affect the quality of the crop and not its abundance [17-22].

Simple superphosphate- a mixture of 1 mol of dihydrogen phosphate and 2 mol of calcium sulfate; water not listed. It is obtained by the interaction of phosphorite (apatite) and concentrated sulfuric acid in a molar ratio of 1: 2:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca_3(H_2PO_4)_2 Ca_2SO_4$$

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When obtaining it from phosphorite, it is necessary to ensure that HF and HC1 gases, which are toxic to living matter, do not enter the environment. Simple superphosphate - a greyish-white substance, slightly soluble in water (due to the presence of calcium sulfate in it), is used in granular form; has the effect of gypsum, therefore, contributes to the chemical reclamation of soils; the disadvantage is the relatively low content of the nutrient, which increases the cost of transportation [23-28].

Effective on soils requiring gypsum. Obtaining simple superphosphate by the action of sulfuric acid on fluorapatite is a complex and multi-stage process. The reaction itself proceeds mainly in a diffuse medium. The first stage is the preparation of phosphorites, which consists in grinding their grains to a size of less than 0.16 mm. Parallel to this process, dilution (to a concentration of about 68%) and cooling of sulfuric acid can be carried out. Depending on the type of raw material used, H_2SO_4 is used at different temperatures. As a rule, it is about 30-40 °C in the case of phosphorites and about 60-70 ℃ in the case of apatites. The crushed raw material is transported to the scales and poured into a continuous mixer. Then add sulfuric acid. The next step in obtaining simple superphosphate is to mix it, i.e. mechanical mixing of all components. Already at this moment, the initial decomposition of phosphorites is initiated [29-33]. After mixing, the contents from the mixer enter the continuous reaction chamber, where the solidification and hardening processes take place. At a further stage, the superphosphate is crushed and then stored at a temperature of about 35-40 ℃. Thus prepared mass "ripens" for about 2-3 weeks and at this time the reaction of decomposition of phosphorins is completed. During the maturation cycle, the content of free phosphoric acid in SSP decreases and the amount of P_2O_5 increases, which is very well absorbed by plants. Stirring superphosphate during storage, additionally, accelerates the ongoing processes

Double superphosphate consists mainly of calcium dihydrogen phosphate

$$Ca(H_2P0_4)_2.$$

It is called double because, unlike simple superphosphate, it is obtained in two stages, while the phosphorus content in it is twice as high as in simple superphosphate:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4$$

Phosphoric acid is separated and reacted with phosphorite:

$$Ca_3(PO_4)_2 + 4H_3\,PO_4 = 3Ca(H_2PO_4)_2$$

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Double superphosphate (after amorphous) is the most valuable phosphate fertilizer used on any soil. The disadvantage is the high cost compared to simple superphosphate. Economical in transportation (why?). It looks like simple superphosphate but is more soluble than the latter.

In Russia, the flow method is mainly used: decomposition of raw materials, followed by granulation and drying of the resulting pulp in a drum granulator-dryer. Commercial double superphosphate from the surface is neutralized with chalk or NH_3 to obtain a standard product. A certain amount of double superphosphate is produced in a chamber way. Phosphorus-containing components are basically the same as in simple superphosphate, but in larger quantities, and the content of $CaSO_4$ is 3-5%. When heated above 135-140 ℃ double superphosphate begins to decompose and melt in the water of crystallization, after cooling it becomes porous and brittle. At 280–320 ℃, orthophosphates are converted into meta, pyroandpolyphosphates, which are in digestible and partially water-soluble forms. It melts at 980°C, turning after cooling into a glassy product in which 60-70% of the metaphosphates are citrate-soluble. Double Superphosphate contains 43-49% of assimilable phosphoric anhydride (phosphorus pentoxide) P_2O_5 (37-43% water-soluble), 3.5-6.5% free phosphoric acid

H_3PO_4 (2.5-4.6% P_2O_5):Ca3(PO4)2 + 2H2SO4= Ca(H2PO4)2 + 2CaSO4

There is also a method for the decomposition of phosphorus-containing raw materials phosphoric acid: [2,3,4]

$$Ca_5(PO_4)_3F + 7H_3PO_4 = 5Ca(H_2PO_4)_2 + HF$$

Precipitate- concentrated phosphate fertilizer composition $CaHPO_4 \bullet 2H_2O$. As a fertilizer, it has the following advantages: the high concentration of P_2O_5, good efficiency on all types of soil and for all crops, and reduced soil acidity. There are two grades of precipitate: the 1st contains at least 31% P_2O_5, the 2nd - 27% P_2O_5 Precipitate $CaHP0_4 \bullet 2H_2O$, calcium hydrogen phosphate dihydrate; obtained by the reaction between slaked lime and phosphoric acid in a 1:1 molar ratio:

Obtained by neutralizing phosphoric acid with a solution of calcium hydroxide at a temperature of 50 ℃:

$$H_3PO_4 + Ca(OH)_2 = CaHPO_4 \bullet 2H_2O$$

Or (also at 50 ℃):

$$H_3PO_4 + CaCO_3 + H_2O = CaHPO_4 \bullet 2H_2O + CO_2\uparrow$$

It can also be obtained by interaction with calcium carbonate (limestone or chalk): [5,6]

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$$CaCO_3 + H_3PO_4 + H_2O = CaHPO_4 \cdot 2H_2O + CO_2\uparrow$$

A greyish substance, slightly soluble in water, is used as the main fertilizer on any soil, more effective on acidic soils. phosphate rock – mineral phosphate fertilizer. Phosphorite flour is obtained by fine grinding phosphorites- sedimentary rocks formed mainly minerals groups apatite.

Contains 19-30% P_2O_5 as $Ca3(PO_4)_2$. Since calcium phosphate is poorly soluble in water, phosphate rock can be absorbed by plants only on acidic soils- podzolic and peaty, in which $Ca_3(PO_4)_2$ gradually turns into dihydrogen phosphate $Ca(H_2PO_4)_2 \cdot H_2O$ available to plants. The assimilation of phosphate rock is favoured by the fineness of grinding, as well as its introduction into the soil together with acidic fertilizers, for example, with $(NH_4)_2SO_4$ or manure. It is also used for the preparation of manure and peat compost [28-31].

Phosphorite rock consists mainly of calcium phosphate $Ca_3(P0_4)_2$ It is a finely ground natural phosphorite. Insoluble substance; use only on acidic soils, since a reaction is possible, ionic equation

Which $Ca_3(PO_4)_2 + 4H^+ = 3Ca^{2+} + 2H_2PO_4$

The bone meal consists mainly of calcium phosphate. Obtained by grinding burnt bones; it is used similarly to phosphate rock (its use is interesting as a way to dispose of waste from animal husbandry and the food industry).

Thomasslag (approximately $Ca_3(P04)_2$ 2CaO) is the product of the interaction of phosphorus oxide P_2O_5 with lime CaO. It turns out in the formed slag at thomasing cast iron- removal from it phosphorus according to the converter method of S. Thomas. Thomasslag is a valuable mineral fertilizer.

It is a waste of metallurgical production. It is formed during processing cast iron with great content of phosphorus in the technical iron Thomasian way. Different from normal calcium phosphate the fact that it contains an excess of CaO, due to which it is strongly alkaline. Thomasslag is used in the form of a finely ground powder for highly acidic soils(for example, peaty and swampy), where it neutralizes excess acids and at the same time enriches the soil with phosphorus [29-34].

Thomasslag— shredded waste of steel production by the converter method, contains calcium phosphate; it is used in the same way as phosphate rock (its use is interesting as a way to dispose of production waste).

Ammaphos. Obtained by neutralization phosphoric acid ammonia

$$2H_3PO_4 + 3NH_3 = NH_4H_2PO_4 + (NH_4)_2HPO_4$$

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Amorphous is a concentrated granular complex phosphorus-nitrogen fertilizer obtained by neutralizing phosphoric acid with ammonia. Amorphous is based on mono ammonium phosphate $NH_4H_2PO_4$and partially diammonium phosphate $NH_4H_2PO_4$.

Amorphous, which is produced in the form of two grades - "A" and "B", contains 9-11% N and 42-50% P_2O_5, i.e. the ratio of N, P_2O_5 in the fertilizer is excessively wide, equal to 1: 4 (nitrogen contains 4 times less than phosphorus). This is a highly concentrated fertilizer containing nitrogen and phosphorus in a form that is well absorbed by plants. 1 centner of amorphous replaces at least 2.5 centners of simple superphosphate and 0.35 centners of ammonium nitrate.

The most common fertilizer formula is 11-52-0. Solubility at 20 ℃ is 370 g/l, and the pH of the solution is 4-4.5. It is recommended to use it at the beginning of the season when the need for the root system for phosphorus is especially high. The fertilizer is low hygroscopic and belongs to the group of water-soluble phosphate fertilizers. These are compounds that are highly soluble in water.

In the presence of moisture in the soil, it quickly decomposes into $NH_4^+$and $H_2PO_4^-$, ions that are well absorbed by plants. The reaction of the soil solution changes to slightly acidic, so amorphous is a good choice for neutral and alkaline soils. Granular amorphous is applied by spreading over the soil surface with subsequent incorporation or by banding. Monoammonium phosphate in the soil can be placed close to germinating seeds without the risk of damaging them with ammonia. The lack of nitrogen is compensated by the introduction of nitrogen fertilizers into the top dressing.

Amorphous can also be used directly as a sowing (row) fertilizer for cotton, potatoes and grain crops [6-17].

Diammonium Phosphate- nitrogen-phosphorus complex complex fertilizer. Does not contain nitrates and chlorine. It is applied to all types of soils, under all cultures. Obtained in a single technological process by neutralizing phosphoric acid with an excess of ammonium. Diammonium phosphate, like amorphous, is obtained by neutralizing phosphoric acid with ammonia.

$$H_3PO_4 + 2NH_3 \rightarrow (NH_4)_2H_2PO_4$$

The acquisition is carried out in two stages. After the neutralization reaction at the first stage, the pulp is cooled and enters the second stage reaction, where the evaporated solution is additionally saturated with ammonia. Then - for crystallization, centrifugation and drying.

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Stronger crystals of diammonium phosphate are obtained by crystallization in the presence of inorganic additives - chlorides and sulfates.

Azofoska (nitroammophoska)- complex, solid, complex, granular nitrogen-phosphorus-potassium fertilizer. Contains phosphorus in a completely water-soluble form. It is used for pre-sowing (main) and pre-sowing (landing) applications, as well as for top dressing regardless of soil types.

The technology for obtaining nitroammophosphates consists of joint or separate neutralization of H_3PO_4 and HNO_3 ammonia. Methods for the production of nitroammophosphates are based on the processing of melts or solutions. In the first case, the mixture is neutralized to pH 3.2-2.8, the resulting solution is evaporated to humidity1.5% in a single case evaporator and granulate melt in special. apparatus - tower; dignity granulation floats-lack of external return (part of the finished product returned to the system); disadvantages of the process - limited brands produced fertilizer due to the impossibility of obtaining diammonium forms and the difficulty of introducing potassium-containing components into the system. In the second case, to-you are neutralized separately (mass ratio NH_3/H_3PO_4 approx. 0.7) to obtain a melt of NH_4NO_3, mixed with pulp ammonium phosphates, NH3 and KCl in the ammonizer-granulator; further granular. the product is dried, classified, cooled and conditioned; during pulp, ammoniation phosphates up to NH3/H3PO4 approx. 1.0 and 1.8 receive respectively. nitroammophoska and nitrodiammophoska; The advantage of this multi-recycle process is the possibility of obtaining fertilizer in a wide range on installations of large unit capacity.

When obtaining phosphorus fertilizers by decomposition of Central Kyzylkum phosphorites with nitric acid, the efficiency of phosphorus fertilizers was increased, and a precipitate was also obtained [14,15]. The phase composition of the products obtained from the treatment of Kyzylkum phosphorites with nitrogen salts was studied by the X-ray method. It has been established that nitrogen-phosphorus fertilizers consist of dicalcium phosphate, undecomposed fluorine and hydroxyapatite, ammonium and calcium nitrate, and phosphorus fertilizers consist of various forms of calcium phosphates, as well as undecomposed fluorohydroxyapatite, calcium and ammonium nitrate salts [12,19]. When decomposed with nitric acid, mineral phosphorites are completely decomposed, and the following reaction produces phosphoric acid, calcium nitrate salt and hydrogen fluoride gas:

$$Ca_5(PO_4)_3F+10HNO_3=3H_3PO_4+5Ca(NO_3)_2+HF$$

Due to the splitting of fluorapatite with nitric acid, monocalcium phosphate and dicalcium phosphate are formed:

$$2Ca_5(PO_4)_3F + 14HNO_3 = 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF$$

$$Ca_5(PO_4)_3F + 4HNO_3 = 3CaHPO_4 + 2Ca(NO_3)_2 + HF$$

Carbonate minerals and trivalent metal oxides also react with nitric acid to form nitrogen salts.

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + CO_2 + H_2O$$

$$MgCO_3 + 2HNO_3 = Mg(NO_3)_2 + CO_2 + H_2O$$

$$R_2O_3 + 6HNO_3 = 2R(NO_3)_3 + 3H_2O$$

The resulting gaseous hydrogen fluoride is converted into silicon hydrofluoric acid [15,16,17].

$$HF + SiO_2 = SiF_4 + 2H_2O$$

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O$$

$$2HF + SiF_4 = H_2SiF_6$$

$$3SiF_6 + 2H_2O = 2H_2SiF_6\ H_2O + SiO_2.$$

The process of enrichment of Kyzylkum phosphorites by decomposition at different norms of nitric acid has been studied. This is because the calcium minerals in phosphorite react much more strongly than other minerals. Therefore, nitric acid first interacts with fluorapatite, and then with carbonate minerals to form phosphorite.

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