preparation of phosphorus-potassium-nitrogen containing liquid suspension fertilizers with insecticidal activity

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ABSTRACT

The principal possibility for a rational technology of liquid and suspended complex fertilizers with insecticidal activity of general-purpose action on the basis of Central Kyzylkum phosphorite has been shown in this study. The fertilizers should be used for root and for leaf-feeding, as effective fertilizer and insecticide, exterminating spider mites and sucking plant pests. In order to obtain the optimal ratios of nutrients to the nitrophosphate pulp are added necessary amounts of potassium chloride and solution of ammonium nitrate, for improving the rheological properties of the latter, during the vegetation period. The proposed suspended nitrogen-phosphorus-potassium containing complex fertilizers are characterized by a simple scheme as compared to standard solid fertilizers and meet exhaustively all requirements of agriculture.

Keywords: liquid fertilizers, high-calcareous phosphorite, nitrophosphate pulp, potassium chloride and ammonium nitrate.

INTRODUCTION

It is well known, that mineral fertilizers are a basic factor for raising the level of crop yield and the quality of crops. Their wide applications open the way for intensification of the agricultural production. It is necessary to use the latest advantages in chemistry and chemical technology in full to increase crop capacity, as well as to provide an adequate meeting of the country’s needs for high-quality agricultural products, and the industry needs for raw materials.

The “Chemicalization of agriculture” requires broad and varied usage of chemical products as fertilizers, pesticides and plant diseases, for treatment of seeds, for chemical weed control, etc. [1].

Most organic compounds in plants contain carbon, hydrogen, oxygen, nitrogen, sulfur and phosphorus. In addition, there are important elements in the cellular, such as calcium, potassium and phosphorus, playing an important role in the growing of a plant. Besides them, there are in small amounts (less than 0.001 %) micronutrients - boron, copper, zinc, manganese, molybdenum, iron, and others, which are also required for the normal functioning of plants.

Reserves of nutrients require increasing many time their contents in the soil than the needs of plants. However, most of them are inaccessible compounds for plants. Their transformation into acceptable compounds under the influence of the microorganisms’ activity and other reactions is usually slow. The total content of nutrients in the topsoil from different soils is uneven [2].

The lack of nutrients in the soil should be covered by fertilizers, as a rule, containing elements for nutrition of the plants by available form.

With mineral fertilizers in abundance, we can control productivity, and achieve its increase by several times.

Recently, in our country’s basic efforts for the production of solid fertilizers were started. Several studies
[3 - 5] were devoted to production of nitrocalcium phosphate and ammophosphate fertilizers. The main drawbacks of the developed technologies are the following: high energy intensity and high hygroscopicity of produced fertilizers, especially of the nitrocalcium phosphate fertilizer.

It is known that the efficiency of a liquid and suspended complex is higher than that of solid fertilizers for leaf-feeding of plants. The application of the suspension not only improves crop yields, but also improves the quality of the products, as well as contributes to the vitality of the plants to adverse environmental conditions.

In [6, 7] the obtaining of the liquid fertilizers based on dolomite, nitric acid and ammonia, was studied.

At present in our country there is no technology for a complex preparation with universal action for the root and for leaf-feeding as an effective fertilizer and insecticide, exterminating spider mites and other sucking plant pests, although [8] was devoted to the production of liquid and complex fertilizers, based on the phosphorite from the Central Kyzylkum.

Thus, the development of a scientifically based and intensive resource-saving technology with the existing equipment operating for manufacture of liquid and suspended complex fertilizer with insecticidal activity from the low-grade and high-calcareous phosphorite from the Central Kyzylkum is an actual problem.

**EXPERIMENTAL**

**Materials**

For the experiments the used high-calcareous phosphorite had the following chemical composition (mass %): P2O5 - 17.55; CaO - 43.68; CO2 - 14.83; R2O3 - 2.47; MgO - 1.68; SO3 - 1.01; F - 2.17; 3.80 - insoluble residue (i.r.). 58.50 % nitric acid, technical sulfuric acid and potassium chloride produced in the Dehkanabad potash plant (Qashqadarya region), containing in recalculation K2O 60 %, were the other materials used.

The formulas of calculations

The mass of nitric acid for its various norms according to Ca5(P2O7)3F in the initial phosphorite we determined by the formula:

\[
m_{\text{HNO}_3} = \frac{m_{\text{in phosph}} \cdot w(Ca_5(PO_4)_3F) \cdot 0.875 \cdot N_{\text{HNO}_3}}{58.50}
\]  

where \(m_{\text{in phosph}}\) is the mass of the initial phosphorite; \(N_{\text{HNO}_3}\) is the norm of HNO3 and 58.50 is the concentration of HNO3;

\(0.875\) is the ratio of molar mass of HNO3 and Ca5(PO4)3F in the reaction:

\[
2Ca_5(PO_4)_3F + 14HNO_3 = Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF
\]  

The mass of nitric acid for its various norms according to CaCO3 in the initial phosphorite we determined by the formula:

\[
m_{\text{HNO}_3} = \frac{m_{\text{in phosph}} \cdot w(CaCO_3) \cdot 1.26 \cdot N_{\text{HNO}_3}}{58.50}
\]  

where \(m_{\text{in phosph}}\) is the mass of the initial phosphorite; \(w(CaCO_3)\) is the mass fraction of CaCO3 in the initial phosphorite; \(N_{\text{HNO}_3}\) is the norm of HNO3 and 58.50 is the concentration of HNO3;

\(1.26\) is the ratio of molar mass of HNO3 and CaCO3 in the reaction:

\[
CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + CO_2 \uparrow + H_2O
\]  

The norm of nitric acid was taken in amount of 20 - 70 from stoichiometry for Ca5(PO4)3F and for CaCO3.

The decomposition coefficient of the phosphorite was determined in accordance with:

\[
K_{\text{de}} = \frac{P_{2O_5, \text{accept.}}}{P_{2O_5, \text{t.}}} \times 100 \%
\]

where \(P_{2O_5, \text{accept.}}\) by 0.1N HCl; \(P_{2O_5, \text{t.}}\) - total content of P2O5.

**EXPERIMENTAL PROCEDURE**

In order to obtain samples of the sulfur containing compounded fertilizer we calculated the amount of the mixture prepared by thorough mixing of phosphate raw material (PRM) and sulfur at a ratio of 9:1. The interaction process of the mixture with nitric acid was performed at 35 - 40°C in a glass reactor, equipped with a stirrer. The stoichiometry norm of nitric acid was 20 - 70 %.

The reactor was charged with nitric acid and a suit-
able amount (25 g) of the mixture. The interaction of sulfur-containing PRM with the acid occurred in the “solid-phase mode”, without foam, for 15 - 20 minutes. In order to improve the quality and properties of the liquid fertilizer, a calculated amount of ammonium nitrate solution, obtained by neutralization of 58.5 % nitric acid with gaseous ammonia, is added into the prepared sulfur-nitrogenous phosphoric pulp, under continuous stirring. After decomposition, the required amount of water was added, according to the calculation that the humidity of the pulp was 30 %, as provided in the technology of fertilizer.

Then the required amount of potassium chloride was added into the formed solution to obtain triple fertilizers. Viscosity was measured with a glass capillary viscometer (GCV-2) with a diameter of 0.77 mm, in the temperature range 20 - 60°C. The crystallization temperature of the liquid fertilizer was determined by the visual polythermal method [9]. Besides, we used the clarified part from the liquid fertilizer, as in the suspended liquid fertilizer it is impossible to determine the freezing point, due to the turbidity of solutions.

Methods for analysis

The obtaining of suspended and liquid fertilizer were subjected to chemical analysis as follows: all forms of P₂O₅ [total (t), acceptable by 0.1N HCl (ac.h.a.) and water solubility (w.s.)] were determined by the calorimetric method on the calorimeter CPhC-3 (λ = 440 nm) in the form of yellow phosphorovanadiomolybdenum complex compound [10]. The error of the results was ± 1 %. The N total (t) was determined by the method of Kjeldahl for nitrogen [11]. The sulfur content was determined by the gravimetric method with barium chloride [12]. The total (t) and water solubility (w.s.) forms of CaO were determined by volume complexometric titration with 0.02 N EDTA, in the presence of the indicators calcein or chrome navy-blue [13].

RESULTS AND DISCUSSION

The laboratory test results are shown in Table 1. It is seen that with increasing of the acid norm in all ratios N:P₂O₅:K₂O, increasing of the decomposition coefficient of phosphorite. For example, in N:P₂O₅:K₂O = 1:0.5:0.5 with increasing of the acid norm from 20 to 70 %, the phosphorite decomposition coefficient increased from 30.48 to 80.92 %, i.e. 2.65 times. The total content of nitrogen, phosphorus and potassium decreased insignificantly, from 10.51 to 10.39 % from 5.25 to 5.19 %, and from 5.25 to 5.19 %, i.e. only 0.12, 0.06 and 0.06 %, respectively.

The nitrate form of nitrogen increased from 5.78 to 7.01 %, i.e. 1.21 times. Moreover, the sulfate content of sulfur increased from 0.62 to 1.62 %, i.e. the coefficient of converting elementary sulfur into sulfate raised from 18.24 to 48.36 %. Similar trends are observed in other ratios of N:P₂O₅:K₂O. With increasing ratios of N:P₂O₅:K₂O from 1:0.5:0.5 to 1:1:1 at the same norm of the acid: the total nitrogen content decreased while the quantity of phosphorus and potassium increased. For example, at norm of the acid 40 % the total content of nitrogen reduced from 10.45 to 6.64 %, the total phosphorus and potassium content increased equally from 5.22 to 6.64 %.

The nitrate form of nitrogen and ammonia decreased from 6.26 to 4.64 %, and 4.18 to 1.99 %, respectively. The decomposition coefficient of the phosphorite is decreased insignificantly from 52.87 to 51.05 %. The coefficient of conversion of elementary sulfur into sulfate is reduced slightly from 40.06 to 39.81 %.

The above products were used for technological studies of processes for new types of liquid and suspended complex fertilizers with insecticidal activity.

The liquid phase of the phosphorus-potassium-nitrogen containing liquid and the suspended fertilizers (PPNLSF) generally consist of water soluble salts - calcium nitrate, ammonium nitrate and potassium chloride, slightly monobasic calcium phosphate and in the solid phase - dicalcium phosphate, elemental sulfur, gypsum, insoluble residue, undecomposed phosphorite. The latter is in an activated condition.

So, increasing the norm of the nitric acid promotes raising of the acceptable form of phosphorus, but there is no purpose to increase it, as higher consumption of nitric acid is observed (Fig. 1). The figure shows the change in the nitrate content of (a) ammonia and (b) nitrogen as dependences on the norm of nitric acid. It is seen that increasing the norm of nitric acid for all ratios of N:P₂O₅:K₂O leads to raising of the nitrate form of nitrogen and vice versa - decreases the ammonium form of nitrogen.

In further research we studied the viscosity and freezing point of PPNLSF. The data are shown in the form of a volume graph (Fig. 2). It is seen (Fig. 2a) that
Table 1. Chemical composition of the suspension fertilizers.

<table>
<thead>
<tr>
<th>N(_2)P(_2)O(_5)K(_2)O</th>
<th>N(_2)</th>
<th>P(_2)O(_5)</th>
<th>CaO (%)</th>
<th>K(_2)O (%)</th>
<th>S (%)</th>
<th>H(_2)O</th>
<th>K(_{ac})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)P(_2)O(_5)K(_2)O</td>
<td>1:0.5:0.5</td>
<td>10.51</td>
<td>5.25</td>
<td>1.60</td>
<td>-</td>
<td>13.09</td>
<td>5.25</td>
</tr>
<tr>
<td>N(_2)P(_2)O(_5)K(_2)O</td>
<td>1:0.6:0.5</td>
<td>9.51</td>
<td>5.61</td>
<td>1.68</td>
<td>-</td>
<td>13.98</td>
<td>5.71</td>
</tr>
<tr>
<td>N(_2)P(_2)O(_5)K(_2)O</td>
<td>1:0.7:0.5</td>
<td>8.56</td>
<td>5.99</td>
<td>1.77</td>
<td>-</td>
<td>14.92</td>
<td>5.99</td>
</tr>
<tr>
<td>N(_2)P(_2)O(_5)K(_2)O</td>
<td>1:0.85:0.85</td>
<td>7.61</td>
<td>6.33</td>
<td>1.84</td>
<td>-</td>
<td>15.76</td>
<td>6.46</td>
</tr>
<tr>
<td>N(_2)P(_2)O(_5)K(_2)O</td>
<td>1:1:1</td>
<td>6.69</td>
<td>6.69</td>
<td>1.90</td>
<td>-</td>
<td>16.67</td>
<td>6.69</td>
</tr>
</tbody>
</table>

with increasing of temperature, the viscosity of the liquid fertilizers decreased in all ratios N: P\(_2\)O\(_5\):K\(_2\)O and norms of nitric acid.

For example, in the ratio N: P\(_2\)O\(_5\):K\(_2\)O = 1:0.5:0.5 and on the norm of HNO\(_3\) 20 %, the viscosity of the solutions of PPNLSF decreased from 11.85 to 4.12 centipoises, i.e. 2.88 times for increasing temperature from 10 to 50°C. Similar trends are observed at the same of norms HNO\(_3\) and in all ratios of N: P\(_2\)O\(_5\):K\(_2\)O.

With increasing the ratios of N: P\(_2\)O\(_5\):K\(_2\)O and the norm of HNO\(_3\) for the same temperatures increasing of the viscosity of the solutions of PPNLSF is observed. For example, at temperature 10°C and norm of HNO\(_3\) 20 % with increasing ratios N: P\(_2\)O\(_5\):K\(_2\)O from 1:0.5:0.5 to 1:1:1, the viscosity of the solutions of PPNLSF increased from 4.12 to 6.38 centipoises, i.e. 1.55 times.

Similar trends are observed at the same temperatures in other ratios of N: P\(_2\)O\(_5\):K\(_2\)O and norms of HNO\(_3\). The crystallization temperature of the sample solutions of PPNSLF decreased with increasing the ratios of N: P\(_2\)O\(_5\):K\(_2\)O and the norms of HNO\(_3\). For example, for N: P\(_2\)O\(_5\):K\(_2\)O = 1:0.5:0.5 and norm of HNO\(_3\) 20 % the crystallization temperature of the sample is -4.3°C (Fig. 2b) and at ratio of N: P\(_2\)O\(_5\):K\(_2\)O = 7:0°C. Similar trends are observed at other temperatures and norms of HNO\(_3\). The results obtained have allowed to determine the optimal conditions for obtaining of PPNLSF: norm of HNO\(_3\) 40 %, mass ratio of N: P\(_2\)O\(_5\):K\(_2\)O = 1:1:1.

The X-ray diffraction analysis data of fertilizer, obtained at norm 40 % HNO\(_3\) and at mass ratio of
Fig. 1. Change of nitrate nitrogen (a) and ammonia nitrogen (b) content in dependence on the norm of HNO$_3$ in ratios N:P$_2$O$_5$:K$_2$O: 1) - 1:0,5:0,5; 2) - 1:0,6:0,6; 3) - 1:0,7:0,7; 4) - 1:0,85:0,85 and 5) - 1:1:1.

Fig. 2. Influence of the ratios of N:P$_2$O$_5$:K$_2$O and the norm of HN0$_3$ on the viscosity (a) and the crystallization temperature (b) of the solutions of LSPPNSN with temperatures: 1 - 10°C, 2 - 20°C, 3 - 30°C, 4 - 40°C, 5 - 50°C.
N:P₂O₅:K₂O = 1:1:1, pure KCl, NH₄NO₃, S and phosphorite flour are given in Fig. 3.

The interpretation of the diffraction analyses was done according to [14]. In the X-ray diffraction analyses of potassium chloride can be seen diffraction fringes, such as 1.57; 1.82; 2.01; 2.24; 2.52; 2.86; 3.17 Å. From X-ray diffraction analyses of ammonium nitrate are seen diffraction fringes, such as 1.30; 1.45; 1.61; 2.69; 4.87 Å.

From X-ray diffraction analyses of phosphorite flour, the diffraction fringes, such as 1.84; 1.90; 2.73; 2.96 Å are for fluorine apatite, 1.88; 1.90; 2.06; 3.09 Å and 2.13; 3.35 Å belong to calcite and silicon dioxide, respectively.
The diffraction fringes 1.61; 1.71; 2.09; 2.81; 3.07; 3.39; 3.79; 3.99, 5.64 Å, are typical for sulfur. On the X-ray diffraction analyses of the fertilizer obtained, there are diffraction fringes 1.84; 1.90; 2.73; 2.96 Å for fluorine apatite, 1.88; 1.90; 2.06; 3.09 Å for calcite and 2.13; 3.35 Å for silicon dioxide but they are reduced significantly. Besides that, diffraction fringes, such as 2.57; 3.21; 3.66; 3.71; 4.37; 4.44; 5.68 Å for Ca(H₂PO₄)₂, 2.94; 4.23; 4.25 Å for CaHPO₄ and 2.01; 2.03; 2.04; 5.15; 5.22; 6.07; 6.12; 6.14 Å for Ca(NO₃)₂ appear.

CONCLUSIONS

The fundamental possibility for obtaining a rational technology of liquid and suspended compound fertilizers with wide action, on the basis of Central Kyzyl Kum’s phosphorite, both for root and for leaf-feeding, which are effective fertilizer and insecticide, exterminating spider mites and sucking plant pests are shown for the first time. In order to obtain the optimal proportions of nutrients during the vegetation period of the plants and improve the rheological properties of the pulp, the necessary amounts of potassium chloride and ammonium nitrate solution, obtained by neutralizing nitric acid with ammonia gas are added into nitrophosphate pulp.

On the basis of experimental data it is established, that the addition of potassium chloride to the solutions of PPNLSF, containing 30 % H₂O, improves the rheological properties of these fertilizers and increases the digestibility coefficient of nutrients.

The proposed phosphorus-potassium-nitrogen containing liquid and the suspended fertilizers as compared with standard solid fertilizers, have a simple process scheme and meet all requirements of agriculture.

REFERENCES