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DEVELOPMENT OF SUPERPHOSPHATE BASED SHELLS FOR THE PRODUCTION OF CAPSULATED ENVIRONMENTALLY SAFE FERTILIZERS

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Abstract. The perspectivity of attracting ammoniated superphosphate based on phosphorites with content of P_2O_5 is not less than 19 % as the main phosphate shell component for the encapsulation of urea have been substantiated. The peculiarities of the kinetics of phosphorus decomposition with the formation of ammoniated superphosphate have been established. Examples of its use as a phosphate shell are given. The ecological feasibility of using it as a phosphate shell is shown.

Key words: phosphate concentrate, superphosphate, encapsulation, phosphate shell, mineral fertilizer.

1. Introduction

The main type of phosphate raw materials for the production of phosphorus and complex fertilizers at domestic enterprises remains apatite and phosphate concentrates. Analysis of business proposals for obtaining of domestic apatite concentrates shows their perspectivity only with extraction and enrichment simultaneously with a titanium-containing concentrate and requires significant capital investments [1]. Currently, phosphate deposits are the only available source of phosphate raw materials in Ukraine [2]. However, the enrichment of these phosphates to the content of P_2O_5 over 20 % is not inexpedient because of significant losses of useful substances and a large amount of waste, which increases the environmental hazard of technology [3]. Due to the changing approach in recent years to the development of formulations of new types of fertilizers, Ukrainian phosphorous concentrates can be involved in the production of encapsulated mineral and organo-mineral fertilizers as part of the phosphate shell, despite the low content of active substances, which is confirmed by the previous agrochemicals research [4]. A significant positive argument regarding the use of domestic phosphorous concentrates is their environmental safety by indicators such as cadmium, plumbum, arsenic and natural activity of radionuclides [5].

The aim of the research is the development of environmentally safe organo-mineral fertilizers based on domestic phosphate raw materials and peat. The application of the development is aimed at reducing the man-made environmental load.

2. Experimental part

In the conduct of experimental studies in the laboratory, the methodological framework was the production technology for obtaining the ammonized superphosphate by the flow method, which is the closest analogue of the developed technology.

As a model substance, phosphorous concentrate of the Verchne-Kamskyj deposit was used. Physico-chemical parameters of the concentrate are presented in Table 1.

As given Table 1 testify, content of $P_2O_{5\ tot}$ in phosphorus concentrate sample accounts for 22.3 %. The share of assimilated forms of $P_2O_{5\ ass}$, which is determined by the content of P_2O_5 dissolved in trilon B, is high. It should be noted that the percentage of assimilated phosphates from the total content of P_2O_5 is more than in phosphate concentrates in Northern Africa and the Middle East, where it is declared at least 60 %. Impurities of the type Fe_2O_3 and Al_2O_3, which in some

cases are defective indicators of phosphate raw materials, are contained in this glauconite concentrate. It is known that the value of mass attitude 100 R_2O_3 : P_2O_5 < 12 phosphate raw materials can be applied for the production of phosphoric acid [6]. In presented sample this correlation accounts for 100 R_2O_3: $P_2O_5 \approx 33.1 > 12$, which indicates the inadvisability of bringing this concentrate to the production of phosphatic acid. At the same time, the high value of this correlation requires an individual study of the possibility of using phosphoric concentrate of the Verchne-Kamsky deposit in the production of superphosphate.

Table 1

Physical and chemical parameters of phosphate concentrate of Verkhne-Kamskyi deposit

Name of the indicator and unit of measurement	The result of the analysis
Mass fraction of total phosphates in terms of $P_2O_{5\,tot}$, %	22.3
Mass fraction of assimilable phosphates in terms of $P_2O_{5\,ass}$, %	21.9
Mass fraction CaO, %	36.15
Mass fraction of fluorine F, %	2.18
Indicator of activity of hydrogen ions, pH (10 % suspension)	7.2
Mass fraction of CO_2, %	5.5
Mass fraction of Fe_2O_3, %	3.6
Mass fraction of Al_2O_3, %	2.0
Mass fraction of water, %	2.02
Effective specific activity of natural radionuclides, Bq / kg	366

The concentration of sulfate acid, quantity and dosage amount of phosphorous concentrate, the nature of the temperature change of the suspension during the decomposition was determined during the development of test experiments of the technology for obtaining ammoniated superphosphate. The sulfate acid consumption for the decomposition stage was calculated in view of the conditions of linkage with sulfate anion of CaO of minerals of phosphate raw materials. The peculiarity of calculating the stoichiometric requirement in sulfate acid is the incomplete involvement of calcium compounds in the decomposition reaction, which accounts for from 90 to 95 % of total CaO contained in phosphorite [5].

For the processing of 1 ton of phosphorus concentrate, the composition of which is given in Table 1, the stoichiometric requirement for sulfate acid is calculated by the formula:

$$G = 10 \times K \times [CaO] \times 98/56 = 597.83 \text{ kg in terms of 100 \% } H_2SO_4\text{/t phosphorite,} \quad (1)$$

where K = 0.945 – degree of the involvement of CaO in calcium sulfate; [CaO] = 36.15 % – mass fraction of CaO in phosphorite; 98 and 56 are the molar masses, respectively, H_2SO_4 and CaO, kg/mol.

The amount of ammonia water was also determined for charge ammonization and the quality parameters of the superphosphate sample were estimated. The chemical analysis of powdered ammoniated superphosphate, obtained in the test mode, is given in Table 2.

Table 2

Chemical analysis of powdered superphosphate ammoniated

Name of the indicator and unit of measurement	The result of the analysis
Mass fraction of total phosphates in terms of $P_2O_{5\,tot}$, %	14.32
Mass fraction of assimilable phosphates in terms of $P_2O_{5\,ass}$, %	14.00
Mass fraction of water-soluble phosphates in terms of $P_2O_{5\,w.s.}$, %	7.44
Mass fraction of free phosphates in terms of $P_2O_{5\,free}$, %	1.3
Mass fraction of ammonized nitrogen in terms of N_{ammon}, %	0.76
Mass fraction of water H_2O, %	2.03
Mass fraction of fluorine F, %	1.27

During the complex laboratory investigations, the phosphorite decomposition was carried out in a thermostatically controlled reactor at a fixed temperature using various sulfuric acid norms. The acid was mixed with water prior to introduction into the reactor and adjusted up to concentrations of 65 %, 60 %, 55 %, 50 %, 45 % of H_2SO_4. Then, discretely, the dosage of the phosphate concentrate was performed by mixing the suspension. The mixture was matured at 80 °C. After one hour, the charge was unloaded from the capacity and then was rubbed. The resulting charge was neutralized with ammonia water to a predetermined pH, while evaluating ammonia water consumption, and then dried at 105 °C. Drying was conducted to a humidity of less than 3 %. The density and a series of specifications of the ammoniated pulp were analyzed. The dried product was grinded and evaluated by its main parameters: $P_2O_{5\,tot}$, $P_2O_{5\,ass}$, $P_2O_{5\,w.s.}$, $P_2O_{5\,free}$. The obtained research results are presented in Table 3.

Table 3

Chemical analysis of the finished product at different rates of sulfate acid

Norm of H_2SO_4	The result of the analysis			
	$P_2O_{5\,tot}$, %	$P_2O_{5\,ass}$, %	$P_2O_{5\,w.s.}$, %	$P_2O_{5\,free}$, %
65	14.67	14.52	9.1	2.6
60	15.10	15.00	8.63	1.36
55	15.71	15.08	8.58	2.21
50	16.41	15.46	7.71	1.51
45	16.43	15.58	7.16	1.21

In the course of the research, the ratio of the values of $P_2O_{5\,ass}$ and $P_2O_{5\,tot}$, in the finished product at different norms of sulfate acid was also determined (Fig. 1).

The analysis of the dependencies presented in Figure 1 shows that the calculated sulfate acid norm for the decomposition of phosphate concentrates of the Verchne-Kamskoye field is confirmed by the results of laboratory tests and may be recommended for the ammonized superphosphate production with high content of P_2O_5.

According to the results of laboratory studies for obtaining superphosphate ammonized from phosphate-glauconite concentrate, an experimental batch of capsulated fertilizers was developed, where the superphosphate was ammonized as the basis of the shell and the calcium humate was used as a plasticizer [7].

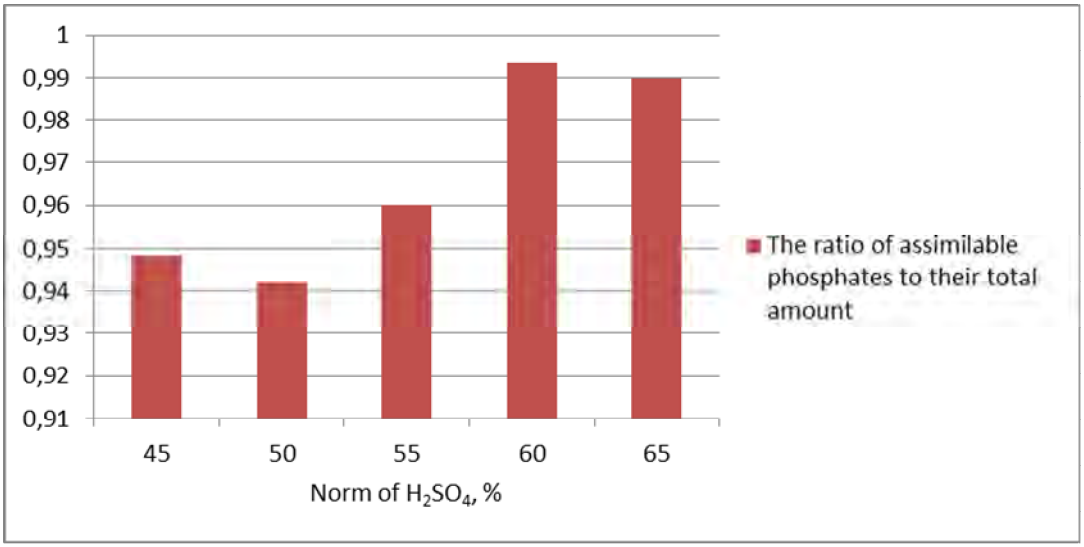

Fig. 1. The ratio of the values of $P_2O_{5\,ass}$ and $P_2O_{5\,tot}$ at different norms of sulfate acid

The results of chemical analysis of phosphate-glauconite concentrate are given in Table 4.

Table 4

Physico-chemical indicators of phosphate-glauconite concentrate

Name of the indicator and unit of measurement	The result of the analysis
1 Mass fraction of total phosphates (amount of fast and slow acting forms of P_2O_5), %, not less	19.7
2 Mass fraction of assimilable phosphates in terms of $P_2O_{5\,ass}$, %, not less	16.48
3 Mass fraction of total potassium in terms of K_2O, %, not less	2.2
4 Mass fraction of water, %, not more	0.62
5 Mass fraction of cadmium, mg/kg, not more	4
6 Mass fraction of plumbum, mg/kg, not more	2
7 Mass fraction of arsenic, mg/kg, not more	1
8 Residue on sieve: – with grid №2K (GOST 6613), % – with grid № 02K (GOST 6613), %, not more	 0 37
9 Effective specific activity of natural radionuclides, Bq/kg, not more	370

In accordance with the data of Table 4, the content in these phosphorites ecologically normalized indicators of cadmium, plumbum, arsenic and the effective specific activity of natural radionuclides is significantly less than the indicators laid down in the technical conditions TU U 24.1-14005076-065-2003 “Foreign phosphorites” (Cadmium – 30 mg/kg, Plumbum – 25 mg/kg, Arsen – 14 mg/kg), that allows to consider these phosphates as one of the environmentally safe types of raw materials.

The chemical composition of the manufactured capsular mineral fertilizers is presented in Table 5.

Table 5

Chemical composition of encapsulated mineral fertilizers

Name of fertilizer	Indicators				
	N_{tot}	$P_2O_{5\,tot}$	$P_2O_{5\,w.s.}$	H_2O	pH
	%				
1. Carbamide	46.2	–	–	–	–
2. Carbamide, coated with superphosphate, plasticizer calcium humate	24.10	6.80	3.9	1.97	2.4

The use effectiveness of a new type of fertilizer with coating was investigated by conducting a laboratory-model experiment on barley plant growth compared to control (without fertilizers) and introducing a mixture of carbamide with superphosphate. The fertilizer was applied to the sand by mixing it with the whole sand mass. Experiments were carried out in glasses of 0.7 kg of sand. Threefold repetition was held. Test culture of barley, grade "Pepper". The mentioned approach to the research was regulated by the fact that in the laboratory-model experiments the influence of the climatic factor (hydrothermal conditions, activity of the soil biota, micro variegatedness of soil cover, agrotechnical measures, etc.) is leveled out and the research period is significantly reduced in comparison with, for example, field studies [8].

The data of the laboratory-model experiment are presented in Table 6.

Table 6

Weight of barley seedlings in a laboratory-model experiment

Options	Weight of seedlings of barley, g/dishes	Increase	
		g/dishes	%
1. Control (without fertilizers)	1.10	–	–
2. Carbamide (N_{60}) + Superphosphate (P_{20})	1.27	0.17	15.5
3 Carbamide, coated with superphosphate, plasticizer calcium humate	1.43	0.33	30.0
HIP_{05}	0.08		

3. Results and discussion

It can be noted that the developed mark of the studied fertilizers with the coating provided the established growth of biomass of barley seedlings in comparison with absolute control. Better efficiency of carbamide coated with superphosphate with calcium humate plasticizer has been significantly improved, compared with a mixture of fertilizers. The obtained results confirm the conclusions of the authors [8], which assert that the capsulated fertilizers allow more fully utilize the mineral and organic components of the tufts. The advantage of such slow-acting fertilizers in comparison with traditional ones is the sustainable maintenance of plants by nutrients for a long time and, most importantly, increasing the fertilizer use rate. It has been established in the experiments that fertilizers with coatings in the form of membranes of various composition allow to improve the qualitative structure of the crop, to save the amount of tufts at introduction, and to protect the environment from chemogenic pollution by reducing or eliminating the migration of mineral substances from the fertilized soil areas [8].

The developed technical solution allows to make a reasonable assumption about the possibility of reducing the amount of fertilizers applied and to predict the significant ecological effect when applying such fertilizers in the country's agriculture.

In accordance with the methodology for determining environmental safety in the application of developed brands of fertilizers, which was stated earlier [7], the calculation of the environmental efficiency coefficient by the equation:

$$k_e = k_{a.l.}/k_n\,, \qquad (2)$$

where: k_e – coefficient of ecologically dangerous loading of polluting substances (mineral fertilizers) on land (crop area); $k_{a.l.}$ – an indicator of the actual loading of pollutants (mineral fertilizers) on land (crop area), kg/ha; k_n – an indicator of the standard loading of pollutants (mineral fertilizers) on land, which is taken at the level of 60 kg/ha.

If the coefficient of the ecologically safe loading of pollutants on land is less than 1, then the load of pollutants on land is considered environmentally safe. When $k_e = (1.0 - 2.5)$ is ecologically admissible, at $k_e = (2.6 - 4.0)$ – ecologically dangerous, and if $k_e > 4.0$ – critical.

Calculation of environmental factor for traditional fertilizers (according to the data of Table 5) shows that:

$$k_e = (60 + 20)/60 = 1.33\,, \qquad (3)$$

where in the numerator the amount of mechanical mixture nutrients of carbamide and superphosphate, which corresponds to the ecologically acceptable index of environmental safety.

As the data in Table 5 show, increasing barley yield by 30 % reduces the amount of fertilizer applied by 30 % to produce the same amount of crop. Thus for the developed fertilizer the calculation of the environmental factor is determined by:

$$k_e = [70\,\% \times (60 + 20)]/60 = 0.93\,. \qquad (4)$$

A value of k_e less than 1 indicates that the developed mark of encapsulated fertilizers can be attributed to environmentally safe fertilizers.

Conclusions

Consequently, we can conclude that it is expedient to attract Ukrainian phosphate concentrates with a low content of $P_2O_{5\ tot}$ as a component of new types of environmentally safe fertilizers for the cultivation of organic produce. This technical solution will provide a significant environmental effect.

1. According to the results of the conducted research, the possibility of encapsulating nitrogen

fertilizers with phosphate shells on the basis of domestic phosphate concentrates with an insignificant content of $P_2O_{5\ tot}$ was proved for a significant reduction of the technogenic loading on the environment.

2. The feature of obtaining superphosphate from phosphate concentrates with low content of $P_2O_{5\ tot}$ was investigated and technological features of its production were determined. The condition for obtaining superphosphate with high content of $P_2O_{5\ ass}$ is the consumption rate of sulphate acid value is 600 kg, based on 100 % H_2SO_4 / t phosphorite.

3. The results of agrochemical laboratory-model researches allow to conclude that it is expedient to attract Ukrainian phosphate concentrates with low content of P_2O_5 into processing as a component of new types of environmentally safe fertilizers for growing organically pure agricultural products. It has been experimentally proven that the use of carbamide with a superphosphate-based shell from phosphate concentrates with a P_2O_5 content of not more than 22 % compared with the mechanical mixture of carbamide and superphosphate allows increasing the barley yield from 15.5 % to 30 % according to the soil samples without fertilizers.

4. The proposed technical solution for encapsulating carbamide with phosphate shell on the basis of superphosphate allows to obtain a significant economic effect by reducing the amount of introduction of a new fertilizer brand by 30 % to obtain the same yield increment. The use of smaller doses of new encapsulated organo-mineral fertilizers will reduce the technogenic load on the environment and will have a significant ecological effect, which is confirmed by the calculation of the environmental factor, which makes it possible to attribute this organo-mineral fertilizer to environmentally safe one.

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