Intensification of the process of producing phosphorus-containing fertilizers using industrial waste

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Abstract. A study was conducted to study the possibility of intensifying the process of phosphorus-containing fertilizer, in particular superphosphate, using industrial waste. Based on retrospective analyzes of literature data on known methods for producing phosphorus-containing fertilizers, experimental studies were carried out using silicon-containing gel, danburite mineral , and organic acids. Based on theoretical and experimental data, the conditions and parameters that allow the intensification of this process are determined.

1 Introduction

Mineral fertilizers share mainly macro- and microelements containing. Macroelements include nitrogen, phosphorus, potassium, and microelements include boron, molybdenum, manganese, zinc and others. Among phosphorus-containing fertilizers, the most famous and cheapest is simple granular superphosphate [1].

Granular simple superphosphate, compared to other phosphorus-containing fertilizers, contains a relatively low content of digestible P_2O_5 (20 ± 1%). Therefore, there is an opinion about reducing or reducing its production of simple superphosphate, as well as the complexity of its production technology.

However, according to the majority of scientists and specialists, even if the use of superphosphate as a phosphorus fertilizer for agricultural crops is abandoned, it retains its valuable qualities and - the possibility of introducing its composition into various types of compounds of macro and microelements, as well as components in the production of complex mixed fertilizers [2].

Taking into account the above, research has been carried out on the production of phosphorus-containing fertilizers, in particular simple superphosphate, with the introduction of various nutrients into its composition, including industrial waste containing microelements, to improve its quality indicators and agrochemical efficiency [2].

The production of simple superphosphate involves the decomposition of phosphate raw materials (apatite or phosphorite) with sulfuric acid, followed by chamber and warehouse

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aging (with shoveling three times in the warehouse), neutralization with neutralizing additives, granulation by moistening in a drum granulator , drying, classification and cooling [4].

2 Materials and methods

In order to intensify the technology for producing simple superphosphate, various raw materials and additives are being carried out and introduced, including microelement-containing substances **.** Since pure salts of microelements are expensive and scarce, the intensification of the process using various industrial wastes seems to be an urgent task. Such industrial waste is potassium metaphosphate, liquid glass, organic acids and silicon-containing ash at a certain ratio. At the same time, potassium metaphosphate and liquid glass meet the requirements of existing standards, and silicon-containing ash is a production waste for the extraction of polysaccharides and proteins from ribbed red algae of the Black Sea, using the following composition, in %: SiO_2 - 40.13; CaO - 32.44; Al_2O_3 -5.83; Fe_2O_3 - 3.69; MgO - 3.30; Na_2O -3.5; MnO -1.65; P_2O_5 -1.47; B -1.115; K_2O -0.83; TiO_2 - 0.74; Zn -0.5; Pb, Cu, Cr, Ni, Ag <0.1; V, Sn, Co, Nb, Mo, Sr, Br <0.01 [5].

3 Results and Discussion

The experiments were carried out according to the method [6] as follows: in a laboratory condition, an 800 ml porcelain glass was placed with 140 ml of sulfuric acid with a concentration of 64% and heated to 65-70 ^{0}C. Then, with vigorous stirring, 200 g of apatite concentrate and 4 g of a mixture of potassium metaphosphate, liquid glass and silicon-containing ash at a mass ratio of 0.6:1 (1.5-2.5), respectively, stirring was continued for another 5-7 minutes and the resulting mass was placed in a thermostat or drying cabinet at 105-115 ^{0} C for one hour. After this, the reaction mass is unloaded from the laboratory beaker, then cooled, and the following indicators are analyzed: P_2O_5 free (st. P_2O_5), digestible P_2O_5 (st. P_2O_5) and total P_2O_5 (tot. P_2O_5). After 24 hours, superphosphate is neutralized with ground and dried limestone with a content of St. P_2O_5 up to 2.0-2.5%, granulated in a drum granulator, dried, cooled and classified according to a generally accepted technological scheme [7]. Qualitative indicators and selected ratios of components are shown in Table 1.

Table 1. Analytical indicators of fertilizer obtained using potassium metaphosphate, liquid glass and silicon-containing ash in their ratio.

Examples	Potassium metaphosphate: liquid glass: siliceous ash.	Superphosphate composition								
		1st. day		2nd day						
		P_2O_5 usv.	P_2O_5 total.	P_2O_5 st.	P_2O_5 usv.	P_2O_5 total	K_r	hygroscopicity, %	chamber aging time, min.	m mechanical strength of the granule, kgf/cm^2
1	0.6:1:1.0	19.3	20.9	2.4	20.0	20.6	97.08	75	57	22
2	0.6:1:1.5	19.7	20.4	2.2	20.2	20.4	99.01	80	52	26
3	0.6:1:2.0	20.2	20.5	2.3	20.8	21.0	99.04	85	46	27
4	0.6:1:2.5	21.0	20.8	2.1	21.4	21.4	99.5 0	90	39	29
5	0.6:1:3.0	21.0	20.8	2.2	21.4	21.5	99.53	85	39	29

From Table 1 it can be seen that the use of potassium metaphosphate, liquid glass and silicon-containing ash in the production of superphosphate at a certain ratio increases the content of hydrocarbons. P_2O_5 , the degree of decomposition and mechanical strength of the granules, while simultaneously reducing hygroscopicity and chamber ripening time. Similar experiments with the aim of reducing chamber aging time and increasing the degree of

decomposition of phosphate raw materials were carried out using active organic compounds and bone meal. As an organic compound, a mixture of organic acids and their mixtures is used at a mass ratio of 1:1.

In order to achieve the set goal [8-9] 61-62 parts by mass of 70% sulfuric acid are poured into a porcelain glass with a volume of 0.5 liters and heated to 65 ^{0} C. Then 1.0-1.3 parts by mass of a mixture of (sulfobenzoic and chlorosulfobenzoic) acids and bone meal are added to it, respectively. After this, 100 parts by weight of phosphate rock are added to the acid mixture with intensive movement and stirring continues for another 5-7 minutes. In this case, due to the exothermic reaction, the temperature of the reaction mass reaches 80-95 ^{0} C and then place a laboratory drying cabinet or thermostat at a temperature of 110-115 ^{0} C for one day.

The resulting product contains, in%: dry . R_2O_5 , -17.6; total R_2O_5 , -18.4; H_2O-6.8; K_p - 95.65.

The selected ratios of components and the results of other indicators are shown in Table 2.

Table 2. Indicators of phosphorus fertilizer using a mixture of acids and bone meal.

p/p	Acid mixtures: bone meal by weight	Superphosphate	Chamber aging time, min.	Kp, %
1	1.0:0.5	American in 3 days	66	92.29 92.94
2	1.0:1.0	American in 3 days	60	94.12 94.94
3	1.0:1.2	American in 3 days	54	95.00 95.65
4	1.0:1.3	American in 3 days	50	96.24 96.77
5	1.0:1.4	American in 3 days	50	95.25 96.78
6	Acid mixture: bone meal 1:(1.0:0.4)	American in 3 days	50-60	94.12-96.24

From Table 2 it can be seen that the use of a mixture of organic acids and bone meal when producing phosphate fertilizer reduces the ripening time of fertilizers and increases the degree of decomposition of phosphate raw materials.

Also, in order to intensify the process of enrichment of phosphorus fertilizer and enrichment with microelements [10-12], experiments were carried out using the mineral danburite and silicon-containing ash of the above chemical composition during the acid decomposition of phosphate raw materials.

The experiments were carried out according to the method [13] in the following way: 38 ml of 64% sulfuric acid was loaded into a laboratory reactor, heated to 60-65^0 With intensive stirring, 48 g of apatite of standard composition and 2 g of a mixture of phosphorite, danburite and silicon-containing ash are added to it with intensive stirring at their mass ratio of 1:0.6: (0.1-0.3), respectively. Silicon containing ash is similar to the above composition [5].

Stirring the reaction mass is continued for 5-7 minutes and a drying cabinet or thermostat is placed at 110-115 ^{0} C for one hour.

After time, the resulting product is unloaded, cooled, neutralized, granulated and analyzed. The fertilizer contains, in%: P_2O_5 St. 2.1-2.4; R_2O_5 acv. 20.4-207; R_2O_5 total. 20.8-20.9; Kr_- 94.2-99.5; F 0.34-0.50.

Variations in the ratio of components and the obtained indicators are shown in Table 3.

Table 3. Effect of the ratio of components of phosphorite, danburite and siliceous ash on the fluorine content in the product.

No.	Phosphate rock: danburite: siliceous ash	Fluorine release into the gas phase, %	P_2O_5, arb. %	Fluorine content in the product, %
1	1:0.6:0.05	53.0	20.1	0.54
2	1:0.6:0.1	58.1	20.4	0.50
3	1:0.6:0.2	61.4	20.6	0.43
4	1:0.6:0.3	68.2	20.7	0.34
5	1:0.6:0.4	68.3	20.7	0.34

Table 3 shows that the introduction of phosphate raw materials, danburite and silicon-containing ash into the decomposition process has a positive effect on the release of fluorine into the gas phase and, consequently, reducing its content in the product [14-17].

Reducing the fluorine content of phosphorus-containing fertilizers is a very important factor, since it has toxicological properties and negatively affects the quality of agricultural products. For example, when plants absorb phosphorus together with fluorine, fluorine accumulates in it and its use impairs the development of infants.

Considering that agriculture requires the use of fertilizers only in granular form, the resulting fertilizer according to tables 1, 2 and 3 was separately mixed, the acidity was neutralized to a content of no more than 2.5% with ground and dried limestone and subjected to the process of granulation, drying, classification and cooling [18-20] and analyzed using existing methods and standards [1-22].

The average analytical indicators obtained using the above methods for phosphorus-containing granular fertilizers are given in Table 4.

Table 4. Analytical indicators of granular phosphorus-containing fertilizers.

No.	P_2O_5, %		granulometric composition, mm, %				moisture, %	mechanical strength of granules, kgf/cm^2
	free	usv.	< 1	1-4	4-	> 6		
1	2.3	21.2	2	92	6	0	2.9	24
2	2.4	20.4	1	90	9	0	3.0	21
3	2.2	21.6	0	93	7	0	3.1	27

Note: example 1 shows the results of the fertilizer mixture in table 1, respectively, tables 1 and examples 2 and 3 of tables 1 and 2, respectively.

From table 1 it is clear that all indicators of phosphorus fertilizer have the properties of the current standard [22]. The analytical parameters of the resulting phosphorus-containing fertilizers were determined by standard chemical methods using a KFK-3 photocolorimeter, as well as ion-selective electrodes.

4 Conclusion

Thus, the above data shows that the use of phosphorus-containing fertilizers, in particular superphosphate, potassium metaphosphate and silicon-containing ash in the production of phosphorus-containing fertilizers, increases the degree of decomposition of phosphate raw materials, reduces chamber ripening time, and hygroscopicity. The use of by-products of organic acids accelerates the storage aging process, and a mixture of the natural mineral danburite and silicon-containing ash allows an increase in the release of fluorine into the gas phase and, accordingly, a decrease in its content in the product. At the same time, the

yield of the commercial fraction and the mechanical strength of phosphorus-containing fertilizer granules increases.

Thus, the above experiments and the data obtained show that the use of various minerals and industrial waste allows us to intensify the process of obtaining phosphorus-containing fertilizers and improves the quality of the product, as well as agrochemical efficiency and environmental protection.

References

1. A.A. Sokolovsky, T.P. Unonyants, A short guide to mineral fertilizers, M. Chemistry, 375 (1977)
2. D.B. Shirinova, G.V. Seyidova, S.N. Hasanov, Z.Q. Huseynov, M.O. Khumbatov, Patent AZ I 2009 00 61. Fertilizer based on powdered superphosphate (2009)
3. I.A. Filenko, Acid decomposition of natural phosphorites with the production of various forms of complex fertilizers 05.17.01, Technology of inorganic substances Dissertation for the degree of Candidate of Technical Sciences, Moscow (2019)
4. M.O. Gumbatov, Preparation of boron-enriched superphosphate molybdenum Scientific journal "Current problems of humanitarian and technical sciences" RF, **3** (2016)
5. M.O. Humbatov, Patent AZ I 2024 0013, Method of obtaining simple superphosphate (2024)
6. M.O. Humbatov, D.B. Shirinova, Y.Y. Huseynov, M.N. Huseynov, S.X. Khalilov, Patent AZ İ 2008 0084, Method of obtaining sal superphosphate (2008)
7. M.E. Pozin, Technology of mineral salts. M., Chemistry, **2**, 1555 (1974)
8. I.G. Grishayev, M.O. Humbatov, H.A. Sariyev, G.K. Bayramov, Patent AZ İ 2013 0017, Method of obtaining sal superphosphate (2013)
9. M.E. Pozin, Technology of mineral fertilizers, L. Chemistry, 352 (1989)
10. M.O. Humbatov, F.E. Mammadov, MM. Mustafayev, Patent AZ İ 2008 0060, Method of obtaining simple superphosphate (2008)
11. M.O. Humbatov, Patent AZ I 2024 0014, The method of obtaining sal superphosphate (2014)
12. M.E. Pozin, B.A. Kopylev, E.B. Belchenko, Guide to practical classes on the technology of inorganic substances, M. Chemistry, 252 (1989)
13. M.O. Gumbatov, I.I. Mustafaev, Element of creation and destruction, M. 2017, ZhGZ, Ministry of Emergency Situations, **8,** 52-53 (2017)
14. I.P. Galkin, V.A. Zaitsev, M.B. Seregin, Capture and processing of fluorinated gases, M., Atomizdat, 235 (1975)
15. P.V. Klassen, I.G. Grishaev, Fundamentals of granulation technology, M., Chemistry, 271 (1982)
16. M.O. Gumbatov, D.B. Shirinovd, S.Kh. Khalilov, Yu.Yu. Guseinov, Patent AZ I 2009 0071, Superphosphate granulation method (2009)
17. V.N. Kochetkov, Granulation of mineral fertilizers, M., Chemistry, 271 (1977)
18. Methods for analyzing phosphate raw materials, phosphorus and complex fertilizers, feed phosphates, M., Chemistry, 219 (1975)
19. GOST 5956-98 Granulated superphosphate from apatite concentrate without additives and with added microelements (1998)