OTIMIZAÇÃO DA TECNOLOGIA DE PRODUÇÃO DE FERTILIZANTES NPK

OPTIMIZATION OF AN NPK-FERTILIZER PRODUCTION TECHNOLOGY

ОПТИМИЗАЦИЯ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ NPK-УДОБРЕНИЯ

KYDYRALIYEVA, Aziza D.^{1*}; BESTEREKOV, Uilesbek²; BOLYSBEK, Aidarbek A.³; YESKENDIROVA, Marina M.⁴; URAKOV, Kinis N.⁵;

^{1,2,3,4,5} M. Auezov South Kazakhstan State University, The Higher School of Chemical Engineering and Biotechnology, Department of Chemical Technology of Inorganic Substances, Shymkent – Republic of Kazakhstan

* Correspondence author

e-mail: aziza_kydyralieva@mail.ru

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RESUMO

O nitrato de amônio é o fertilizante de nitrogênio mais comum e eficaz do mundo. No entanto, o nitrato de amônio tem uma desvantagem muito séria – o risco de incêndio e o risco de explosão, o que causa certas dificuldades e limitações tanto para seus consumidores quanto para seus fabricantes. O objetivo deste trabalho foi estudar a possibilidade de produzir os fertilizantes NPK com propriedades agroquímicas melhoradas e com uma proporção controlada de nutrientes N/P₂O₅/K₂O, obtidos com base em uma solução de nitrato de amônio, rocha fosfática moída e cloreto de potássio. Os experimentos laboratoriais e industriais foram realizados usando um método de planejamento rotativo – o método de modelagem de segunda ordem Box-Hunter. O artigo apresenta os resultados de estudos sobre a regulação da proporção de nutrientes (N/(P₂O₅ + K₂O)) em fertilizantes contendo NPK, obtidos com base em uma solução de nitrato de amônio, rocha fosfática moída e cloreto de potássio. Foi estudada a influência de variáveis independentes – consumo específico de nitrato de amônio, fósforo moído e cloreto de potássio. Foi obtida uma equação de regressão adequada da influência desses fatores na proporção N/(P₂O₅ + K₂O) nos produtos finais. Os valores-limite do consumo específico de nitrato de amônio, fósforo moído e cloreto de potássio nas misturas iniciais foram encontrados, nos quais o conteúdo total de nutrientes nos produtos-alvo é de 30% a 33%, e o coeficiente N/(P₂O₅ + K₂O) possui um valor ótimo (1,14 - 3,50).

Palavras-chave: *nitrato de amônio, farinha fosfórica, cloreto de potássio, nutrientes, composição química.*

ABSTRACT

Ammoniac saltpeter is the most widespread in the world and effective nitric fertilizer. However, ammonia saltpeter has a severe disadvantage – fire risk and explosion hazard that causes some difficulties and restrictions of both its consumers and its manufacturers. The purpose of the present work consisted in the studying the possibility of production of NPK-fertilizers with improved agrochemical properties and a controlled ratio of nutrients N/P₂O₅/K₂O produced based on an ammonia saltpeter solution, ground phosphate rock, and potassium chloride. The laboratory and industrial experiments were continued using a rotatable planning method – the Box-Hunter second-order modeling technique. The article contains the research results on the regulation of nutritious elements (N/(P₂O₅+K₂O)) ratios in the NPK-containing fertilizers produced based on an ammonia saltpeter solution, a ground phosphate rock, and potassium chloride. The effect of independent variables – specific consumptions of ammonia saltpeter, a ground phosphate rock, and potassium chloride – was studied. The adequate regression equation of influence of these factors on an N/(P₂O₅+K₂O) ratio in the end products was obtained. Boundary values of the ammonia saltpeter, a ground phosphate rock and potassium chloride specific consumptions in the initial mixtures were found at which the total content of nutritious elements in the target products is from 30% to 33% and the N/(P₂O₅+K₂O) ratio has the optimum value (1.14 - 3.50).

Keywords: *ammonium nitrate, phosphorus flour, potassium chloride, nutrients, chemical composition.*

АННОТАЦИЯ

Аммиачная селитра является наиболее распространенным в мире и эффективным азотным

удобрением. Однако аммиачная селитра имеет очень серьезный недостаток – риск возникновения пожара и опасность взрыва, что вызывает определенные трудности и ограничения как у ее потребителей, так и у ее производителей. Цель настоящей работы состояла в изучении возможности получения NPK-удобрений с улучшенными агрохимическими свойствами и контролируемым соотношением питательных веществ $N/P_2O_5/K_2O$, получаемых на основе раствора аммиачной селитры, измельченной фосфоритовой породы и хлорида калия. Лабораторные и промышленные эксперименты были проведены с использованием вращающегося метода планирования – метода моделирования второго порядка Box-Hunter. В статье приведены результаты исследований по регулированию соотношений питательных элементов ($N/(P_2O_5 + K_2O)$) в NPK-содержащих удобрениях, полученных на основе раствора аммиачной селитры, измельченной фосфатной породы и хлорида калия. Было изучено влияние независимых переменных – удельного расхода аммиачной селитры, молотого фосфорита и хлорида калия. Получено адекватное регрессионное уравнение влияния этих факторов на отношение $N/(P_2O_5 + K_2O)$ в конечных продуктах. Найдены граничные значения удельных расходов аммиачной селитры, молотого фосфорита и хлорида калия в исходных смесях, при которых общее содержание питательных элементов в целевых продуктах составляет от 30% до 33%, а $N/(P_2O_5 + K_2O)$ коэффициент имеет оптимальное значение (1,14 - 3,50).

Ключевые слова: аммиачная селитра, фосфорная мука, хлорид калия, питательные вещества, химический состав.

1. INTRODUCTION:

Ammoniac saltpeter is the most widespread in the world and effective nitric fertilizer (Ivanov *et al.*, 1990; Chernyshev *et al.*, 2009). It is used in agriculture for all kinds of crops and any types of soils (Maltas *et al.*, 2018; Besterekov *et al.*, 2019). However, ammonia saltpeter has a severe disadvantage – fire risk and explosion hazard that causes some difficulties and restrictions of both its consumers and its manufacturers (Oxley *et al.*, 2002; Dechy *et al.*, 2004; Lavrov and Shedov, 2004; Sinditskii *et al.*, 2005). For this reason, to obtain rich and qualitative harvests, it is necessary to apply balanced mineral fertilizers, i.e., containing nitrogen, phosphorus, potassium and other nutrients in reasonable ratios (Skydanenko *et al.*, 2017; Daitx *et al.*, 2019; Ramadhani *et al.*, 2019). These are so-called complex fertilizers whose major characteristic is their high agrochemical value (Abramov *et al.*, 2002; Levin and Sokolov, 2004; Pavlova, 2007; Ovchinnikov *et al.*, 2008; Akhmad *et al.*, 2018).

At present, there is a great demand for the fertilizers containing nitrogen, phosphorus and potassium that promotes numerous researches on introduction of phosphorus and potassium-containing components, be it natural minerals, the products obtained at their industrial processing or technogenic phosphorus and potassium-containing waste, in ammonia saltpeter melt (Belova and Ryabtseva, 2007; Dmitrieva and Ovchinnikov, 2007; Botirov and Beglov, 2008; Kiiski, 2009; Reymov *et al.*, 2013; Taran and Taran, 2016; Tugalukov *et al.*, 2017; Zhang *et al.*, 2018; Hirzel *et al.*, 2019; Yan *et al.*, 2019).

The only manufacturer of ammonia

saltpeter in the Republic of Kazakhstan is “KazAzot” JSC (Aktau, Kazakhstan). To solve the above-mentioned problem on the improvement of ammonia saltpeter agrochemical value and consumer properties, the own phosphate ores of the Republic of Kazakhstan can be successfully applied (Directory of deposits..., 2014). According to a draft proposal of the “KazAzot” JSC concerning to determination of new possibilities of improvement of agrochemical and consumer properties of ammonia saltpeter, the scientific personnel of the chair “Chemical technology of inorganic substances” of M. Auezov South Kazakhstan State University (Shymkent, Kazakhstan) (Official site..., 2019) has implemented the research on production of new NPK fertilizers on the basis of the following initial components: the ammonia saltpeter solution produced by “KazAzot” JSC, State Standard 2-2013; the ground phosphate rock of FM-2 grade (TS 930640000252-01-2011, 17% of P_2O_5), produced by “Temir-service” LP (Aktyubinsk, Kazakhstan) from the Chilisay phosphorite (The mining company..., 2014); potassium chloride – the most available potassium salt – meeting to technical requirements 2184-048-00203944-2014. Under the agreement with the customer, the 64-71 % ammonia saltpeter solution obtained in accordance with the traditional ammonia saltpeter technology at the first evaporation stage was applied as the initial component. The agreed content of nitrogen, phosphorus pentoxide and potassium oxide in the end products were 10-28%, 2.5-10%, and 2.5-10%, respectively.

The purpose of the present work consisted in the studying the possibility of production of NPK-fertilizers with improved agrochemical properties and a controlled ratio of nutrients $N/P_2O_5/K_2O$ produced based on an ammonia saltpeter

solution, ground phosphate rock and potassium chloride.

2. MATERIALS AND METHODS:

The research was carried out under the laboratory conditions of M. Auezov SKSU. The experimental results were tested at a trial plot of the operating ammonia saltpeter manufacture of "KazAzot" JSC. During the experiments, the individual volumes of 64-71% ammonia saltpeter solution with temperature of 110-130°C were mixed with calculated weights of the ground phosphate rock and potassium chloride (Dier *et al.*, 2018; Galliou *et al.*, 2018; Sigurnjak *et al.*, 2019). Insignificant quantities of a modifying mineral additive were also added in the mixture. The obtained suspension was carefully agitated and fed at the temperature of 120-130°C in sprayers of a granulating drum where the mixture was sprayed and dried by a direct-flow drying agent and granulated at the observance of technological parameters of the operating ammonia saltpeter manufacture (Ivanov *et al.*, 1990; Technological regulations..., 2012; Artyukhov and Ivaniia, 2017; Boyandin *et al.*, 2017; Gorbovskiy *et al.*, 2017; Lombardo *et al.*, 2017; Churov *et al.*, 2018; Rus *et al.*, 2019).

The analysis of composition and properties of the initial components and the obtained NPK-fertilizer samples was implemented according to the methods given in the standard documentation on the fertilizers:

- the total nitrogen content in the obtained NPK fertilizer according to State Standard 30181;
- the total and assimilable phosphorus pentoxide content (P_2O_5 total, P_2O_5 assim.) – in accordance with State Standard 20851.2-75;
- the potassium chloride mass fraction – in accordance with State Standard 20851;
- moisture content – in accordance with State Standard 20851.4;
- strength of the fertilizer granules on a device IPG-1M;
- pH on a device I-160 MI (Raposo *et al.*, 2017; Gezerman and Çorbacioğlu, 2017; Bamatov *et al.*, 2019; Macholdt *et al.*, 2019).

3. RESULTS AND DISCUSSION:

Tables 1 and 2 contain the results of the experimental research carried out at the laboratory and industrial conditions. Specific consumptions of the ammonia saltpeter, ground phosphate rock,

and potassium chloride were calculated in terms of 1 tonne of the target product.

First of all, the influence of specific consumptions of ammonia saltpeter, ground phosphate rock and potassium chloride, and also content of nutritious elements in them on the ratio of $N/(P_2O_5+K_2O)$ in the target products was studied. The results of the research are represented in Figures 1-3.

As follows from the obtained results, the change of the $N/(P_2O_5+K_2O)$ ratio in the products depends on two opposite processes: its growth at the increase in the nitrogen content, i.e. the specific ammonia saltpeter consumption, and its decrease at the increase in the phosphorus and potassium content, i.e., specific consumptions of the phosphorite and potassium chloride. In this connection, the further research was performed using a rotatable second-order experiment's planning technique (the Box-Hunter method) (Akhazarova and Kafarov, 1985; Zečević *et al.*, 2017; Silver *et al.*, 2018; Jameel and Al-Tai, 2017; Bijarniya *et al.*, 2019). The ratio of $N/(P_2O_5+K_2O)$ in the product was the optimization parameter. Table 3 contains the information about domains of variation of the independent variables calculated based on data of Table 1. The experiments' planning matrix and results are represented in Table 4.

Using the data of Table 4 and (Inkov *et al.*, 2000) we obtained the regression equations of influence of ammonia saltpeter, phosphorite and potassium chloride amounts in the initial mixture on the $N/(P_2O_5+K_2O)$ ratios in the coded and natural kinds (Equations. 1-2):

Determination of the coefficients in regression equation (2) was carried out using the Student's test, and the adequacy of the equation – using the Fisher's test. In our case, the Fisher's test tabular value makes 5.10, and its calculated value taking into account a 5% error of the experiment is 5.00. As $F_{tab} > F_{cal}$, the obtained regression equation is adequate. The experimental and calculated according to (2) values of $N/(P_2O_5+K_2O)$ ratios in the NPK fertilizers produced are represented in Table 5.

On the basis of equation (2) using the MathCAD program (Ochkov, 2007) the 3D images of response surfaces of $N/(P_2O_5+K_2O)_{nat} = f(AS, GPR \text{ at } KCl = \text{const} = 0.097; 0.063; 0.131; 0.154; 0.352 \text{ (according to data of Table 4)})$ and their horizontal sections were constructed (Figures 4-8).

Besides the $N/(P_2O_5+K_2O)$ ratio, modern

fertilizers should meet the following requirements: the size of fertilizer's granules – 2-4 mm, their mass fraction – not less than 83-89%, the granules' strength – not more than 60 N/g. As follows from Table 2 data, these requirements are fulfilled if the $N/(P_2O_5+K_2O)$ ratio ≥ 1.14 . Figures 1-5 show the areas *mnpj*, *xyzh*, *abcd*, *qwvf*, *rusk*, for which this ratio is 1,14-3.50.

Table 6 contains the information about the boundary values of optimization parameters and variable factors for $N/(P_2O_5+K_2O) \geq 1.14$.

As follows from Figures 1-5 and table 6, the least value of the optimization parameter – the $N/(P_2O_5+K_2O)$ ratio – is characteristic for the technological area *rusk*. Therefore, the optimization of the process studied should be carried out within the *rusk* area. The values of technological parameters in the *rusk* area are represented in Table 7.

Judging by the data of Figure 5 and Table 7, the optimum values of ammonia saltpeter and ground phosphate rock specific consumptions at the maximum allowed particular potassium consumption chloride equal to 0.154 t and the $N/(P_2O_5 + K_2O)$ ratio in the NPK-fertilizer obtained within 1.14-1.73 are situated on lines *ks* (ammonia saltpeter) and *su* (phosphorite). That is the specific consumption of ammonia saltpeter can change from 0.47 t to 0.71 t, and for the phosphorite – from 0.23 t to 0.47 t.

4. CONCLUSIONS:

Based on the results obtained at the modeling the influence of ammonia saltpeter, ground phosphate rock and potassium chloride specific consumptions on the nutrients ($N/(P_2O_5 + K_2O)$) ratio in the NPK-containing products it is possible to draw the following conclusions:

- the change of the $N/(P_2O_5+K_2O)$ ratio in the target products depends on two opposite processes: its growth at the increase in the nitrogen content, i.e., the specific ammonia saltpeter consumption, and its decrease at the increase in the phosphorus and potassium content, i.e., specific consumptions of the phosphorite and potassium chloride;

- to produce the NPK-containing fertilizers of required quality and with the $N/(P_2O_5 + K_2O)$ ratio within 1.14-3.50 based on the 64-71% ammonia saltpeter solution (State Standard 2-2013), the Chilisay ground phosphate rock of FM-2 grade (TS 930640000252-01-2011, 17% of P_2O_5) and potassium chloride meeting to technical requirements 2184-048-00203944-2014, the

consumptions of the components should be maintained in the following limits: ammonia saltpeter – 0.4-0.71 t, Chilisay ground phosphate rock – 0.23-0.47 t, potassium chloride – 0.040-0.131 t. At the maximum allowed potassium chloride rate (0.154 t), the corresponding consumptions of ammonia saltpeter and Chilisay phosphorite are in the limits of 0.47-0.71 t and 0.23-0.47 t, respectively. In this case, it is possible to produce many nitrogen, phosphorus, and potassium-containing fertilizers in which the total content of nutritious elements will make: 33%; 32%; 31%; 30%; that convincingly enough prove their high agrochemical value.

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$$N/(P_2O_5+K_2O)_{\text{cod}} = 4.449 \cdot Z_1^2 - 0.3251 \cdot Z_1 \cdot Z_2 - 26.631 \cdot Z_1 \cdot Z_3 + 1.362 \cdot Z_1 - 2.189 \cdot Z_2^2 + 8.07 \cdot Z_2 \cdot Z_3 - 0.722 \cdot Z_2 + 47.803 \cdot Z_3^2 - 7.214 \cdot Z_3 + 1.462 \quad (\text{Eq. 1})$$

$$N/(P_2O_5+K_2O)_{\text{nat}} = 1.462 + 1.362 \cdot AC - 0.722 \cdot \Phi M - 7.214 \cdot KCl + 4.449 \cdot AC^2 - 2.189 \cdot \Phi M^2 + 47.803 \cdot KCl^2 - 0.3251 \cdot AC \cdot \Phi M - 26.631 \cdot AC \cdot KCl + 8.07 \cdot \Phi M \cdot KCl \quad (\text{Eq. 2})$$

Table 1. Specific consumptions of the initial components, contents and ratios of nutrients in the end products

Fertilizer sample	Specific consumption, tonne			Content of a nutrient (N, P ₂ O ₅ , K ₂ O) in the end product, %	Ratio of the nutrients (N/P ₂ O ₅ /K ₂ O) in the end product
	Ammonia saltpeter, t (AS)	Ground phosphate rock, t(GPR)	Potassium chloride, t (KCl)		
1	0.814	0.146	0.040	28.0/2.5/2.5	11.2/1/1
2	0.639	0.283	0.078	22.0/5.0/5.0	4.4/1/1
3	0.553	0.351	0.096	19.0/6.0/6.0	3.1/1/1
4	0.466	0.412	0.113	16.0/7.0/7.0	2.28/1/1
5	0.437	0.442	0.121	15.0/7.5/7.5	2.00/1/1
6	0.290	0.557	0.153	10.0/10.0/10.0	1.05/1/1

Table 2. Basic physical and chemical properties of the fertilizers obtained

Fertilizer sample	pH of the 10 % solution	Humidity of the product, %	Strength of the fertilizer granules, N/g	The ratio in the end product		Mass fraction of 2-4 mm granules in the end product, mass %
				N:P ₂ O ₅ :K ₂ O	N/(P ₂ O ₅ +K ₂ O)	
1	6.38	0.17	50.58	11.2:1:1	5.60	85-95
2	6.40	0.17	55.70	4.4:1:1	2.20	85-94
3	6.47	0.17	58.68	3.1:1:1	1.50	84-89
4	6.50	0.15	60.65	2.28:1:1	1.14	83-89
5	6.55	0.16	62.47	2.00:1:1	1.00	81-88
6	6.65	0.15	66.15	1.05:1:1	0.52	78-80

Table 3. Variation intervals of the variables

Variation interval	Variables			
	Code kind X _i	Natural kind		
		Ammonia saltpeter consumption, tonne	Ground phosphate rock consumption, tonne	KCl consumption, tonne
Basic level	0	0.552	0.352	0.097
Variation interval	Δ	0.156	0.123	0.034
Upper level	+1	0.708	0.475	0.131
Lower level	-1	0.396	0.229	0.063
Upper star arm	+1.68	0.814	0.557	0.153
Lower star arm	-1.68	0.290	0.146	0.040

Table 4. The planning matrix and results of studying the effect of ammonia saltpeter, ground phosphate rock and potassium chloride in the initial mixture on the nutrients' ratio in the end products

No.	Variables						N/(P ₂ O ₅ +K ₂ O) ratio in the fertilizer
	Code kind			Code kind			
	X ₁	X ₂	X ₃	AS, tonne	GPR, tonne	KCl, tonne	
1	+1	+1	+1	0.708	0.475	0.131	1.50
2	-1	+1	+1	0.396	0.475	0.131	0.84
3	+1	-1	+1	0.708	0.229	0.131	2.00
4	-1	-1	+1	0.396	0.229	0.131	1.18
5	+1	+1	-1	0.708	0.475	0.063	2.50
6	-1	+1	-1	0.396	0.475	0.063	1.14
7	+1	-1	-1	0.708	0.229	0.063	3.00
8	-1	-1	-1	0.396	0.229	0.063	1.75
9	+1.68	0	0	0.814	0.352	0.097	2.90
10	-1.68	0	0	0.290	0.352	0.097	0.80
11	0	+1.68	0	0.552	0.557	0.097	1.20
12	0	-1.68	0	0.552	0.146	0.097	1.70
13	0	0	+1.68	0.552	0.352	0.153	1.20
14	0	0	-1.68	0.552	0.352	0.040	2.20
15	0	0	0	0.552	0.352	0.097	1.58
16	0	0	0	0.552	0.352	0.097	1.68
17	0	0	0	0.552	0.352	0.097	1.65
18	0	0	0	0.552	0.352	0.097	1.55
19	0	0	0	0.552	0.352	0.097	1.53
20	0	0	0	0.552	0.352	0.097	1.52

Table 5. Comparative data of experimental and calculated values of nutrients ratios in the NPK-fertilizers

No.	N/(P ₂ O ₅ +K ₂ O) experimental	N/(P ₂ O ₅ +K ₂ O) calculated	Error, %
1	1.50	1.62	-7.87
2	0.84	0.79	5.09
3	2.00	1.97	1.42
4	1.18	1.12	4.59
5	2.50	2.49	0.02
6	1.14	1.11	2.32
7	3.00	2.99	0.40
8	1.75	1.58	9.88
9	2.90	2.83	2.57
10	0.80	0.95	-18.62
11	1.20	1.14	4.70
12	1.70	1.83	-7.69
13	1.20	1.18	1.93
14	2.20	2.29	-4.44
15	1.58	1.58	-0.06
16	1.68	1.58	5.90
17	1.65	1.58	4.19
18	1.55	1.58	-2.00
19	1.53	1.58	-3.33
20	1.52	1.58	-4.01

Table 6. Boundary values of optimization parameters and variable factors

Technological area	AS specific consumption, t	Phosphorite specific consumption, t	KCl specific consumption, t	Optimization parameter N/(P ₂ O ₅ +K ₂ O)
mpj	0.4-0.71	0.23-0.47	0.040	1.30-3.50
xyzh	0.4-0.71	0.23-0.47	0.063	1.15-3.00
abcd	0.4-0.71	0.34-0.47	0.097	1.14-2.43
qwvf	0.41-0.71	0.23-0.47	0.131	1.14-1.95
rusk	0.47-0.71	0.23-0.47	0.154	1.14-1.73

Table 7. Ranges of technological parameters in the rusk area (Figure 5)

Points in Figure 5	Ammonia saltpeter specific consumption, t	Ground phosphate rock specific consumption, t	KCl specific consumption, t	N/(P ₂ O ₅ + K ₂ O) ratio in the end product
r	0.61	0.47	0.154	1.14
u	0.71	0.47	0.154	1.40
s	0.71	0.23	0.154	1.73
k	0.47	0.23	0.154	1.14

Figure 1. Change of the ratio of $N/(P_2O_5+K_2O)$ in the end product depending on the nitrogen content and specific consumption of ammonia salt peter

Figure 2. Change of the ratio of $N/(P_2O_5+K_2O)$ in the end product depending on the phosphorus pentoxide content and specific consumption of ground phosphate rock

Figure 3. Change of the ratio of $N/(P_2O_5+K_2O)$ in the end product depending on the potassium oxide content and specific consumption of potassium chloride

Figure 4. Influence of the ammonia salt peter and ground phosphate rock rates on the $N/(P_2O_5+K_2O)$ ratio in the target product at $KCl = 0.04 \text{ t}$

Figure 5. Influence of the ammonia salt peter and ground phosphate rock rates on the $N/(P_2O_5+K_2O)$ ratio in the target product at $KCl = 0.063 \text{ t}$

Figure 6. Influence of the ammonia salt peter and ground phosphate rock rates on the $N/(P_2O_5+K_2O)$ ratio in the target product at $KCl = 0.097 \text{ t}$

Figure 7. Influence of the ammonia saltpeter and ground phosphate rock rates on the $N/(P_2O_5+K_2O)$ ratio in the target product at $KCl = 0.131\ t$

Figure 8. Influence of the ammonia saltpeter and ground phosphate rock rates on the $N/(P_2O_5+K_2O)$ ratio in the target product at $KCl = 0.154\ t$