The book addresses the issues of chemical and physico-chemical interaction occurring in multicomponent water-salt systems, which are formed at separate stages of the production of complex NP and NPK fertilizers, including gray and magnesium-containing fertilizers. Particular attention is paid to chemical interactions between the individual components, occurring at the stages of granulation and drying, depending on the method and types of input nitrogen, potassium and magnesium-containing components. The book is intended for specialists of industrial enterprises of mineral fertilizers and design organizations, researchers, graduate students and students engaged in the field of chemical technology of inorganic substances.

Oleg Dormeshkin

Interactions between components of complex fertilizers

Chemical and physico-chemical interactions at the stages of mixing, granulating and drying during their production

Dormeshkin Oleg, Dr. Sc. (Engineering), professor, vice-rector, Belarusian State Technological University, Prize winner of the National Academy of Science of Belarus, scientific interests – development of new technologies of the fertilizers on the base of conversion, mechanochemical and acid processes; problems of recycling industrial wastes.

978-613-9-45198-2

LAP LAMBERT Academic Publishing

Oleg Dormeshkin

Interactions between components of complex fertilizers

Oleg Dormeshkin

Interactions between components of complex fertilizers

Chemical and physico-chemical interactions at the stages of mixing, granulating and drying during their production

LAP LAMBERT Academic Publishing

Cover image: www.ingimage.com

Publisher:
LAP LAMBERT Academic Publishing
is a trademark of
International Book Market Service Ltd., member of OmniScriptum Publishing Group
17 Meldrum Street, Beau Bassin 71504, Mauritius

Printed at: see last page
ISBN: 978-613-9-45198-2

Interactions between components of complex fertilizers. Chemical and physico-chemical interactions at the stages of mixing, granulating and drying during their production.

Oleg Dormeshkin, Belarusian State Technological University, Minsk, Republic of Belarus,   E-mail: Dormeshkin@yandex.ru

Abstract

The main direction of fertilizers assortment optimization is increasing of the complex fertilizers production, which makes it possible to reduce the cost of their soil application up to 70% and to optimize mineral nutrition of plants. In order to optimiz the process, as well as to predict the properties of final products, possible interactions occurring at separate stages should be taken into account.

Processes taking place at the stages of sulfuric and phosphoric acid decomposition of phosphate raw materials as well as at the stage of ammonization have been properly studied and described in literature. However, the information on chemical transformations occurring during complex fertilizers production with the introduction of different kinds of nitrogen and potassium-based components at the stages of mixing, granulating and drying is insufficient to justify an optimal technological regime, qualitative descriptions and mineralogical composition of products. So when urea is introduced as nitrogenous component, it may be present in the product, either alone or in the form of the double salt $CO(NH_2)_2 \cdot NH_4Cl$, as well as the adduct $CaSO_4 \cdot 4CO(NH_2)_2$ depending on the conditions of the process. Introduction of magnesium in the quantity of 2 to 10% to the composition of complex fertilizers is accompanied by additional chemical interactions and essential changes in product composition.

This chapter presents data on chemical and physico-chemical transformations occurring at the stages of mixing, drying and granulation of complex NPK, NP (S, Ca, Mg) fertilizers on the basis of ammonium phosphate and superphosphates, with the introduction of different types of nitrogen-potassium-and magnesium-containing components, based on the studies conducted by the author, as well as under his supervision. Due to the complexity of chemical and mineralogical composition of industrial complex fertilizers, for better understanding of the ongoing transformations, the chemical processes initially have been studied on the model mixtures based on individual salts. For further research the following basic brands of fertilizers have been selected: 7:15:19; 10:15:15; 20:15:10; 16:12:20; 12:12:12; 13:13:13; 15:15:15.

It has been established that the chemical processes and phase composition of complex fertilizers obtained on the basis of acid processing of phosphate raw material with the subsequent introduction of nitrogen-potassium-and magnesium-containing components are significantly different from the composition of mixed fertilizers and mixed complex fertilizers obtained by the method of compacting as well as by bulk-blending technology.

Depending on the brands of the received fertilizers, potassium in the products is presented in the forms of syngenite $K_2Ca(SO_4)_2 \cdot H_2O$, double dihydrophosphates or potassium ammonium sulfate, as well as potassium chloride when introducing it in excess.

It has been established that exchange interaction leading to the formation of double sulfates of magnesium ammonium-, hydro-and dihydrophosphates of magnesium as well as dual hydrogen magnesium-ammonium. The polyhalite formation is confirmed by the magnesium compounds participation in the processes of potassium chloride conversion. These processes have a considerable impact not only on the chemical and mineralogical composition but also on the technological and physical-mechanical properties of the fertilizers.

Keywords: complex fertilizers, phase composition, chemical transformations, X-ray diffraction pattern, mixing, granulating, drying, production.

1. Introduction

The main direction of optimization of the range of mineral fertilizers is increase in production and use of complex fertilizers, which helps to reduce the cost of their application by 65 70% and optimize the mineral nutrition of plants.

Thus, more than 200 brands of complex fertilizers are offered in the European market today, while the share of simple phosphate fertilizers produced in Russia as one of the largest exporting countries of mineral fertilizers is only 1.6% of the total production. Since the mid-1980s, virtually all complex fertilizers are produced only in granular form, taking into account the requirements of agriculture and the world market of mineral fertilizers as the main consumers.

The main methods of granulation of complex fertilizers are: 1) chemical granulation; 2) steam granulation; 3) compaction; 4) bulk-blending.

As a rule, chemical granulation includes the stage of ammonization of intermediate phosphoric-nitric suspensions before feeding into the granulator or their direct neutralization in the ammonium-granulator. Chemical and steam granulation refers to the methods of granulation by rolling, while the necessary plasticity of the material is achieved due to the liquid phase contained in the suspension or additional introduction of the liquid phase with circulating flows or in the form of steam (steam granulation).

In the USA the bulk-blending system is the most common, which involves blending of ready granulated fertilizers with subsequent introduction of mixed fertilizers on fields without long-distance transportation. The pressing and crushing stages are introduced additionally after the mixing stage to eliminate the effect of segregation and obtaining granules “three in one”. This principle is the basis of the compaction method, which involves compacting pre-shredded single-component fertilizers in presses of special design, followed by crushing, sieving, and additional processing. Köppern (Germany) is one of the most well-known European manufacturers of compaction equipment.

The quality of complex fertilizers produced at all enterprises of CIS countries, Europe, Asia, America, and other regions of the world is strictly regulated by the relevant regulatory documentation. The main indicators that are regulated by these documents are: 1) the content of the main components (for fertilizers – the main nutrients, trace elements, moisture, and a number of impurities; for technical products – the content of the main components); 2) the physical properties of the product (granulometric composition, static strength, and crumbling). But according to the requirements that came into force in the territory of the European Economic Community (EU), products/substances are subject to the procedure of "pre-registration" in accordance with the regulations REACH for products entering the markets of these countries. The principal difference of the requirements of REACH regulations is the need to specify all the identification indicators of substances, including the full chemical composition (including impurities and additives), the molecular and structural formula of single and multi - compound substances, the EU-name, and other identifiers of substances (for substances with variable composition). Experience shows that the necessary information is not available in the technical documentation available at the enterprises. Thus, in the description of qualitative and mineralogical composition of complex potash-containing fertilizers, the majority of the technical documentation indicates the presence of potassium in the potassium chloride [1]. At the same time, the presence of liquid phase in the granulated mixture (from 1.5 to 18% depending on the granulation method), as well as ammonium and calcium phosphates, calcium and ammonium sulfates, and a number of other salts determine the probability of interaction between potassium chloride, nitrogen, and phosphorus-containing components at the stages of mixing, granulating, and drying. The course of topochemical reactions is not excluded. Additional complication of chemical and phase composition of complex fertilizers is observed when microelements are introduced into their composition in the form of appropriate salts, which also enter into chemical interaction with the main components of fertilizers.

2. Chemical transformations, occurring on the stages of drying and granulation of urea-containing NP, NPK fertilizers on the basis of superphosphates

Manufacturers and researchers pay considerable attention to the processes of obtaining complex fertilizers with the introduction of urea. The use of urea is advisable from an agrochemical point of view and is safer than ammonium nitrate. In addition, urea is the most concentrated among nitrogen fertilizers. The interest in obtaining fertilizers on the basis of urea – superphosphate (ammonium phosphate) systems is also due to the fact that the additive formation reactions occur between the components of the mixture. Fertilizers containing urea adducts slowly release nitrogen into the soil, which allows obtaining complex fertilizers of prolonged action on their basis [2, 3].

However, it is difficult task to obtain complex fertilizers with the introduction of urea. Direct mixing of urea and superphosphate (ammonium phosphate) is undesirable, since the differences in the physical properties of these fertilizers lead to segregation. The introduction of urea in conjunction with retour is associated with the formation of a large number of additional liquid phase, increasing the retour and caking of the product. It is obvious that the inclusion of the possible interactions occurring in the individual stages is essential for decision of tasks of optimization of technological process and prediction of the properties of the target products. However, while the processes occurring at the stages of sulfuric and phosphoric acid decomposition of phosphate raw materials and ammonization in the presence of urea are studied in sufficient detail [3,4], the data on chemical transformations occurring in the production of urea-containing complex fertilizers at elevated temperatures at the stages of granulation and drying are fragmentary and insufficient to justify the optimal technological mode and description of the qualitative and mineralogical composition of the final products.

Depending on the process conditions, the amount and ratio of reagents, urea introduced into the process as a nitrogen-containing component may be present in the product individually or in the form of a double salt

$CO(NH_2)_2 \cdot NH_4Cl$. Additionally, the formation of adduct of tetra urea calcium sulfate $CaSO_4 \cdot 4CO(NH_2)_2$ is possible. In addition, almost all technologies for the production of complex NK, PK and NPK fertilizers provide for the introduction of a potassium-containing component (potassium chloride) at the granulation stage together with retour [2]. Potassium chloride can also be added to the ammonium suspension before it is fed into the granulator [3], which is also accompanied by the flow of additional chemical interactions and changes in the mineralogical and qualitative-quantitative composition of the products.

In this regard, this section contains data on chemical transformations occurring during heating at the stages of drying and granulation in the production of urea-containing NP and NPK (S, Ca) fertilizers. The data is obtained on the basis of a series of studies conducted by the author and under his leadership.

2.1 Chemical transformations occurring at heating of the model systems $Ca(H_2PO_4)_2 \cdot H_2O$-$CO(NH_2)_2$, $Ca(H_2PO_4)_2 \cdot H_2O$ - $NH_4H_2PO_4$, $Ca(H_2PO_4)_2 \cdot H_2O$ - $NH_4H_2PO_4$, $Ca(H_2PO_4)_2 \cdot H_2O$ - $NH_4H_2PO_4$ - $CO(NH_2)_2$, $H_3PO_4 \cdot CO(NH_2)_2$ – $Ca(H_2PO_4)_2 \cdot H_2O$, $H_3PO_4 \cdot CO(NH_2)_2$ – $CaSO_4 \cdot 2H_2O$, $H_3PO_4 \cdot CO(NH_2)_2$ – $H_2SO_4 \cdot 2CO(NH_2)_2$

The Experimental Part

The complexity of the chemical and mineralogical composition of industrial complex fertilizers is associated with a complex composition of phosphate feedstock. Initially, for a better understanding of the ongoing transformations, chemical processes were studied on model mixtures obtained on the basis of individual salts of reactive qualification (Table 1).

The following substances were used as the starting materials: urea phosphate $H_3PO_4 \cdot CO(NH_2)_2$ synthesized by the method [5]; urea sulfate $H_2SO_4 \cdot 2CO(NH_2)_2$, synthesized using data on its solubility in water [6] and identified by chemical analysis and IR spectroscopy; calcium dihydrogen-phosphate monohydrate $Ca(H_2PO_4)_2 \cdot H_2O$; ammonium dihydrogen-phosphate $NH_4H_2PO_4$, urea $CO(NH_2)_2$; and gypsum $CaSO_4 \cdot 2H_2O$ of “analytical grade” qualification. To establish chemical transformations occurring during heating in the above-mentioned systems, the model mixtures were subjected to heat treatment under polythermal conditions and under isothermal conditions at temperatures corresponding to the extremum positions on the DTA (Differential Thermal Analysis) curves established by the thermal analysis method.

Sample number	Composition of model mixtures	Components molar ratio
1	$Ca(H_2PO_4)_2 \cdot H_2O$- $CO(NH_2)_2$	1:1
2	$Ca(H_2PO_4)_2 \cdot H_2O$- $CO(NH_2)_2$	1:2
3	$Ca(H_2PO_4)_2 \cdot H_2O$ -$NH_4H_2PO_4$	1:1
4	$Ca(H_2PO_4)_2 \cdot H_2O$ -$NH_4H_2PO_4$	1:2
5	$Ca(H_2PO_4)_2 \cdot H_2O$- $NH_4H_2PO_4$- $CO(NH_2)_2$	1:1:1
6	$H_3PO_4 \cdot CO(NH_2)_2 – Ca(H_2PO_4)_2 \cdot H_2O$	1:1
7	$H_3PO_4 \cdot CO(NH_2)_2 – CaSO_4 \cdot 2H_2O$	1:1
8	$H_3PO_4 \cdot CO(NH_2)_2 – H_2SO_4 \cdot 2CO(NH_2)_2$	1:1

Table 1. Composition of model mixtures

Heat treatment products were studied by chemical, X-ray phase analysis, and IR spectroscopy. Colorimetric determination was carried out using spectrophotometer SP 8001 company “Metertech ”. The thermal analysis was carried out using a derivatograph of OD-103 type. The X-ray diffraction study was performed using Bruker diffractometer “D8 Advance” (USA). The IR spectra were recorded on IR Fourier spectrometer NEXUS in the range of 300 to 4000 cm^{-1}. The database [7] was used in decoding the data of x-ray phase analysis, the assignment of IR spectra bands was carried out using reference literature [8, 9].

Discussion of results

Heating of the model mixtures are accompanied by formation of liquid phase and its subsequent crystallization, solid phase sintering, ammonia emission, and change in acidity of the products of heat treatment. Differential-thermal analysis of mixtures shows that when they are heated, there are processes accompanied by a two-stage mass loss and a number of thermal effects. The endothermic effect is observed on the DTA curves of all mixtures at a temperature of 90, 125°C. In addition, the exothermic effect is observed on the DTA curves of urea-containing mixtures at 125, 150°C.

Analysis of published data [9-12] helps to conclude that the flow of the following processes is possible during heating of the systems studied at 90-125ºC: decomposition of calcium dihydrogen phosphate to calcium hydrogen phosphate and ortho-phosphoric acid; removal of crystallized water from $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaSO_4 \cdot 2H_2O$, constitutional water from H_3PO_4 and $NH_4H_2PO_4$ to form polyphosphate acids and ammonium polyphosphates; hydrolysis of urea with formation of ammonium carbonate; melting of the eutectic mixture containing urea and removal of ammonia; decomposition of urea with the removal of NH_3 and CO_2; decomposition of urea phosphate with removal of CO_2, NH_3, H_2O and formation of ortho - and polyphosphates of ammonium.

With further heating to 150°C, there are processes accompanied by loss of mass, so the maximum is observed on the curves of DTA at 125-150°C, which is due to the imposition of endo - and exothermic effects accompanying the decomposition processes and interaction of the components of mixtures. In particular, acid neutralization reactions, exchange reactions, the formation of double salts of calcium-ammonium (orthophosphates, polyphosphates, sulfates) can be attributed to the processes occurring with the release of heat.

The results of chemical analysis of the products of thermal treatment of mixtures are presented in Tables 2, 3.

According to chemical analysis (Table 2) only the products of thermal treatment of mixtures of phosphate and urea sulfate urea is completely soluble at 95°C. Products of heat treatment of a mixture of phosphate of urea and gypsum, calcium-dihydrogen phosphate and ammonium are almost soluble in water.

Unlike the original mixtures, lemon-soluble forms and polyphosphates are present along with water-soluble orthophosphates in the heat treatment products of other model mixtures. Phosphates (insoluble in water, but soluble in citric acid) are formed at 90-95°C. The proportion of water-soluble phosphates is 50-80% in these products. In the products of thermal treatment of all the model compounds (with the exception of sample 3 at 95°C) the presence of polyphosphates is fixed. Moreover, with the increase in temperature, their content increases. The highest polyphosphates content (up to 90% of the total phosphorus content) is found in heat treatment products of model mixtures containing phosphate and urea sulfate (sample 8). At lower temperatures (90-95°C), at which dehydration of phosphoric acid proceeds to a small extent, the content of phosphorus polyforms is higher in the heat treatment of urea-containing model compounds. This is probably due to the increase in the speed of polycondensation of phosphoric acid due to the hydrolysis of urea, leading to the withdrawal of one of the polycondensation products (water) from the reaction zone.

An increase of phosphorus polyforms content in the products of heat treatment of model mixtures containing urea and ammonium dihydrogen phosphate is also possible due to the direct interaction of these components with the formation of ammonium polyphosphates, which is confirmed by the literature data [12].

It should be noted that when the model mixtures are heated, both water-soluble and water-insoluble polyphosphates are formed. Of the water-soluble compounds in heat treatment products, the presence of ammonium polyphosphates, from insoluble-calcium polyphosphates and double ammonium calcium polyphosphates is possible.

Thus, the obtained data prove the possibility of formation of water-soluble ortho- and polyphosphates of ammonium and citric-soluble hydrogen phosphate and calcium polyphosphates, as well as double ortho- and polyphosphates of calcium-ammonium, and in the process of heating calcium hydrogen phosphate, calcium phosphate-ammonium double phosphates, polyphosphate acids and their salts. The presence of the urea, which is the base, creates the conditions for increasing the pH, reducing the proportion of water-soluble forms of phosphorus, while increasing the content of polyphosphates in the product. Moreover, the formation of polyphosphates in the presence of urea occurs at lower temperatures compared with the literature data.

To confirm the conclusions about the nature of the processes occurring during the heating of model mixtures, the products of heat treatment of the mixtures were investigated by X-ray phase analysis and IR spectroscopy, which confirmed the formation of the following compounds in the process of heating: calcium hydrogen phosphate, ammonium dihydrogenphosphate, ammonium polyphosphates, double ortho- and pyrophosphates ammonium calcium, ammonium pyrophosphate, calcium sulfate and ammonium calcium phosphate. The initial $Ca(H_2PO_4)_2 \cdot H_2O$ is present only in the composition of the product obtained by heat treatment of the model mixture $Ca(H_2PO_4)_2$-H_2O $NH_4H_2PO_4$ (sample 3) at 95°C. The presence in the products of heat treatment of urea-containing mixtures of calcium hydrogen phosphate already at temperatures of 90-95°C allows to conclude that acceleration of the dehydration of calcium dihydrogen phosphate in the presence of urea and a decrease in the temperature of its course.

Model composition, sample	Temperature, °C	Various forms of phosphorus content					
		$P_2O_{5вод.}$			$P_2O_{5усв.}$		
		ortho, %	poly		ortho, %	poly	
			%	% от $P_2O_{5вод.}$		%	% от $P_2O_{5усв}$
$Ca(H_2PO_4)_2 \cdot H_2O$- $CO(NH_2)_2$, sample 1	95	30,7	6,5	17,5	40,3	6,8	14,4
	105	13,6	16,7	55,1	32,3	22,7	41,3
	140	12,9	20,8	61,7	31,1	25,5	45,1
$Ca(H_2PO_4)_2 \cdot H_2O$- $CO(NH_2)_2$, sample 2	90	13,8	9,1	39,7	24,3	21,8	47,3
	125	18,1	11,3	38,4	31,6	21,6	40,6
$Ca(H_2PO_4)_2 \cdot H_2O$ -$NH_4H_2PO_4$, sample 3	95	57,1	0,7	1,2	57,0	0,2	0,3
	125	26,4	29,3	52,6	27,1	28,6	51,3
	150	19,9	39,4	66,4	21,1	37,0	63,7
$Ca(H_2PO_4)_2 \cdot H_2O$ -$NH_4H_2PO_4$, sample 4	115	43,7	16,5	27,4	43,7	15,8	26,6
	150	18,8	42,0	69,1	16,1	48,0	74,9
$Ca(H_2PO_4)_2 \cdot H_2O$- $NH_4H_2PO_4$ - $CO(NH_2)_2$, sample 5	105	25,8	16,4	38,9	39,0	17,5	31,0
	140	11,7	35,8	75,4	19,9	38,9	66,2
$H_3PO_4 \cdot CO(NH_2)_2$-$Ca(H_2PO_4)_2 \cdot \cdot H_2O$, sample 6	105	22,5	18,7	45,4	32,5	25,7	44,2
	150	18,6	27,4	59,6	20,1	39,8	66,4
$H_3PO_4 \cdot CO(NH_2)_2$-$CaSO_4$ $2H_2O$, sample 7	105	7,5	18,5	71,2	8,0	19,6	71,0
	150	8,6	19,8	69,7	9,0	19,8	68,8
$H_3PO_4 \cdot CO(NH_2)_2$ + $H_2SO_4 \cdot 2CO(NH_2)_2$, sample 8	95	2,8	23,8	89,5	products completely soluble in water		

Table 2. Distribution of different forms of phosphorus (P_2O_5) heat treatment products model mixtures

The formation of calcium hydrogen phosphate during heat treatment in the investigated temperature range is noted for all model mixtures, and the reflex corresponding to the characteristic interplanar distance of calcium hydrogen phosphate (d = 2.96 Å) is characterized by maximum intensity. When decomposition of calcium dihydrogen phosphate, in addition to calcium hydrogen phosphate, phosphoric acid is formed, which is confirmed by the visual appearance of the liquid phase, which transforms upon cooling into a glassy state due to the formation of phosphate salts.

Model composition, sample	Temperature, °C	Nitrogen content (in terms of N), %			Content of different forms of nitrogen in aqueous solution,% of total nitrogen	
		amide nitrogen, N вод	ammonia nitrogen		amide nitrogen	ammonia nitrogen
			N вод	N лим		
$Ca(H_2PO_4)_2 \cdot H_2O$–$CO(NH_2)_2$, sample 1	95	7,6	2,0	1,9	79,5	20,5
	105	1,5	4,1	5,2	26,8	73,2
	140	0,4	4,0	4,7	9,2	90,8
$Ca(H_2PO_4)_2 \cdot H_2O$–$CO(NH_2)_2$, sample 2	90	7,1	3,9	4,7	64,5	35,5
	125	1,9	4,6	5,0	29,2	70,8
$Ca(H_2PO_4)_2 \cdot H_2O$–$NH_4H_2PO_4$-$CO(NH_2)_2$, sample 5	105	0,18	7,08	7,27	2,5	97,5
	140	0	5,50	6,24	0	100
$H_3PO_4 \cdot CO(NH_2)_2$-$Ca(H_2PO_4)_2 \cdot H_2O$, sample 6	105	1,0	5,3	7,3	12,0	88,0
	150	0,1	5,1	6,8	1,4	98,6
$H_3PO_4 \cdot CO(NH_2)_2$-$CaSO_4 \cdot 2H_2O$, sample 7	105	0,040	5,79	5,86	0,7	99,3
	150	0,036	4,78	4,80	0,7	99,3
$H_3PO_4 \cdot CO(NH_2)_2$-$H_2SO_4 \cdot 2CO(NH_2)_2$, sample 8	95	0,67	15,95	-	4,0	96,0

Table 3. Results of the chemical analysis of urea-contain products heat treatment of model mixtures on nitrogen content

As can be seen from Figure 1, when the mixture of $H_3PO_4 \bullet CO(NH_2)_2$ + $Ca(H_2PO_4)_2 \cdot H_2O$ is heated at 105°C, ortho- and polyphosphates of ammonium and calcium hydrogen phosphate are formed; on the X-ray diffraction pattern of the heat treatment product at 150°C there are no reflexes characteristic of

$NH_4H_2PO_4$. In addition, the reflexes characteristic of anhydrous calcium dihydrogen phosphate, including those that are sufficiently intense, do not belong to the X-ray diffraction patterns. It can be assumed that the presence of concentrated phosphoric acid in the mixture with $Ca(H_2PO_4)_2•H_2O$ creates the conditions for the formation of anhydrous $Ca(H_2PO_4)_2$, which is confirmed by the literature data [9, 10]. The calcium-ammonium phosphates are identified in heating products of the mixture $H_3PO_4·CO(NH_2)_2+Ca(H_2PO_4)_2·H_2O$, which corresponds to the data obtained by the authors earlier [13]. The presence of $NH_4)_4Ca_3H_6(P_2O_7)_4·3H_2O$ и $(NH_4)_2CaH_4(P_2O_7)$ is most likely in the resulting products. According to the data of [14], these diphosphates incongruently dissolve in water with formation of precipitates $NH_4CaHP_2O_7$ and $NH_4Ca_2H_3(P_2O_7)_2·3H_2O$, respectively. In addition, the presence of water-insoluble diphosphate $(NH_4)_2Ca_3(P_2O_7)_2·6H_2O$, which is slowly converted to $Ca_2P_2O_7·4H_2O$, is also likely [1]. Taking into account all these compounds, unidentified reflexes do not remain on the X-ray diffraction patterns of the heat treatment products of this mixture, although the presence of ammonium and calcium dihydrodiphosphates is not excluded, and in the presence of a high background is amorphous phase.

The main crystalline phase formed by heating a mixture of $H_3PO_4·CO(NH_2)_2 + CaSO_4·2H_2O$ (sample 7) is hydrated calcium sulfate. In addition, as a result of the exchange decomposition, ammonium sulfate is formed. There are also low-intensity reflections on the X-ray diffraction patterns of these products, which can be attributed to double calcium-ammonium - koktaite $(NH_4)_2Ca(SO_4)_2·H_2O$ and, possibly, to double calcium-ammonium sulfates of a different composition.

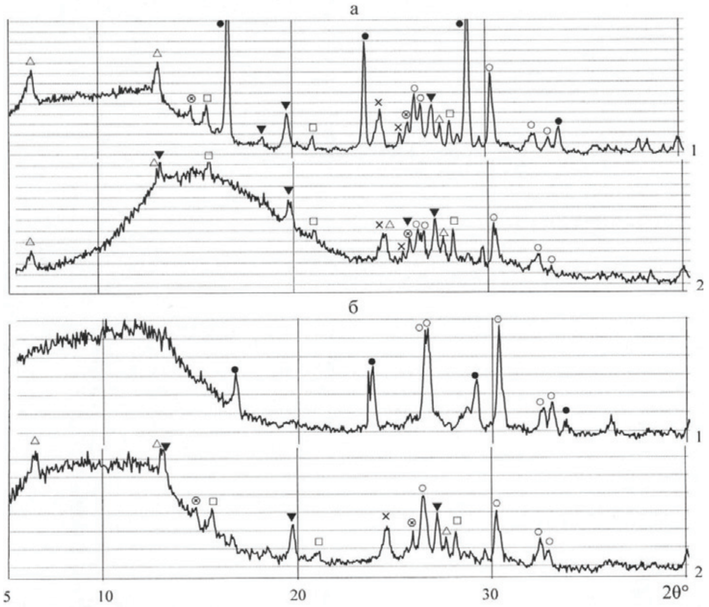


Figure 1.X-ray diagrams of heat treatment product mixtures:

а) $H_3PO_4\cdot CO(NH_2)_2 + Ca(H_2PO_4)_2\cdot H_2O$: 1 – 105°C, 2 – 150°C;

б) $Ca(H_2PO_4)_2\cdot H_2O + NH_4H_2PO_4 + CO(NH_2)_2$: 1 – 105°C, 2 – 140°C

Phase: ○ $CaHPO_4$;× $Ca(H_2PO_4)_2$; ● $NH_4H_2PO_4$;⊗ $(NH_4)_{n+2}P_nO_{3n+1}$;
△ $(NH_4)_4Ca_3H_6(P_2O_7)_4\cdot 3H_2O$; ▼ $(NH_4)_2CaH_4(P_2O_7)_2$; □
$(NH_4)_2Ca_3(P_2O_7)_2\cdot 6H_2O$;

Urea is present in significant amounts only in the products of heat treatment of the mixtures of $Ca(H_2PO_4)_2\cdot H_2O$ -$CO(NH_2)_2$, which confirms the data [12] on the intensification of urea decomposition in the presence of ammonium dihydrogen phosphate. Moreover, the relative intensity of the reflex, corresponding to the characteristic interplanar distance of the urea (d = 4.01 Å), decreases significantly with the temperature increasing. So for sample 1 at a temperature of 90°C it is 100%, and at 125°C it drops to 5%. A feature of the product obtained by heat treatment of a mixture of $Ca(H_2PO_4)_2\cdot H_2O$ -$CO(NH_2)_2$

with a molar ratio of 1:1 at 95°C is the presence of urea phosphoric acid, while directly heating mixtures containing urea phosphoric acid, and its decomposition takes place. This is probably due to the fact that the crystallization of urea phosphoric acid occurs, obviously, when the model mixture containing urea and the phosphoric acid formed during its decomposition is cooled.

The composition of the products obtained by heating all model mixtures in the temperature range of 90-125°C, corresponding to the first endothermic effect, includes ammonium dihydrogen phosphate. In products of heat treatment of mixtures of calcium dihydrogen phosphate with urea, polyphosphates of ammonium are identified, which confirms the conclusions reached earlier on the course of the reactions of formation and polycondensation of orthophosphoric acid and urea transformations with the formation of various ammonium salts during the heating of model mixtures. The formation of ortho- and polyphosphates of ammonium is possible as a result of the interaction of ortho- and polyphosphate acids with both the products of urea transformation - ammonia and ammonium carbonate, and directly with urea, as evidenced by the data of [12]. In this case, both individual crystalline ammonium salts and mixtures of polyphosphates with different degree of polymerization can be formed. It can be assumed that the cause of significant fluctuations in the pH of aqueous solutions of heat treatment products is the formation of polyphosphates with varying degrees of substitution of hydrogen for the ammonium ion.

In the products of heat treatment of model mixtures containing ammonium dihydrogen phosphate, at temperatures 125-150°C, double calcium-ammonium pyrophosphates were detected. The presence in some samples of ammonium nitrogen in water-insoluble form, as well as differences in the ratios of ortho- and polyphosphates in aqueous and in citric acid solutions, suggests that unidentified phase present in some heat treatment products are also double calcium-ammonium phosphates.

On the basis of the data obtained, it was concluded that the following chemical transformations take place during heat treatment at the stages of drying and granulation in the preparation of complex urea-containing fertilizers:

– monocalcium phosphate decomposition:

$Ca(H_2PO_4)_2 \cdot H_2O \rightarrow CaHPO_4 + H_3PO_4 + H_2O$; (1)

– hydrolysis of urea:

$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3$; (2)

– urea decomposition:

$2CO(NH_2)_2 \rightarrow NH_3 + NH_2CONHCONH_2$; (3)

– polycondensation :

$nH_3PO_4 \rightarrow H_{n+2}P_nO_{3n+1} + (n-1)H_2O$; (4)

– interaction of ammonium carbonate and ammonia with ortho- и polyphosphoric acids :

$$\left.\begin{matrix} (NH_4)_2CO_3 \\ NH_3 \end{matrix}\right\} + \left\{\begin{matrix} H_3PO_4 \\ H_{n+2}P_nO_{3n+1} \end{matrix}\right. \rightarrow \begin{matrix} NH_4H_2PO_4 \\ (NH_4)_{(n-x)}H_{(2+x)}P_nO_{3n+1} \end{matrix} + CO_2; \quad (5)$$

– reactions of exchange interaction:

$Ca(H_2PO_4)_2 + 2(NH_4)_2H_2P_2O_7 \rightarrow (NH_4)_2CaH_4(P_2O_7)_2 + 2NH_4H_2PO_4$; (6)

$Ca(H_2PO_4)_2 + 2(NH_4)_2H_2P_2O_7 + 2NH_3 \rightarrow (NH_4)_4CaH_2(P_2O_7)_2 + 2NH_4H_2PO_4$ (7)

$2Ca(H_2PO_4)_2 + 2(NH_4)_2H_2P_2O_7 + H_2O \rightarrow NH_4Ca_2H_3(P_2O_7)_2 \cdot H_2O + 3NH_4H_2PO_4 + H_3PO_4$; (8)

$3Ca(H_2PO_4)_2 + 4(NH_4)_2H_2P_2O_7 + 3H_2O \rightarrow (NH_4)_4Ca_3H_6(P_2O_7)_4 \cdot 3H_2O + 4NH_4H_2PO_4 + 2H_3PO_4$; (9)

$2Ca(H_2PO_4)_2 + (NH_4)_3H_2P_3O_{10} + 2{,}5H_2O \rightarrow NH_4Ca_2P_3O_{10} \cdot 2{,}5H_2O + 2NH_4H_2PO_4 + 2H_3PO_4$. (10)

The formation of the above products is not excluded without preliminary decomposition of the starting materials, in particular:

- interaction of urea with ortho- and polyphosphoric acids:

$CO(NH_2)_2 + 2H_3PO_4 + H_2O \rightarrow 2NH_4H_2PO_4 + CO_2$; (11)

$nCO(NH_2)_2 + 2nH_3PO_4 \rightarrow 2(NH_4)_nH_2P_nO_{3n+1} + nCO_2 + (n-2)H_2O$; (12)

–interaction of urea and ammonium dehydrogen phosphate:

$nCO(NH_2)_2 + nNH_4H_2PO_4 + H_2O \rightarrow (NH_4)_nH_2P_nO_{3n+1} + 2nNH_3 + nCO_2$; (13)

– interaction of calcium dihydrogen phosphate with the products formed by urea transformations:

$Ca(H_2PO_4)_2 \cdot H_2O + NH_3 \rightarrow CaHPO_4 + NH_4H_2PO_4 + H_2O$; (14)

$2Ca(H_2PO_4)_2 \cdot H_2O + (NH_4)_2CO_3 \rightarrow 2CaHPO_4 + 2NH_4H_2PO_4 + CO_2 + 3H_2O$.(15)

In phosphate systems:

$H_3PO_4 \cdot CO(NH_2)_2 + H_2O \rightarrow NH_4H_2PO_4 + NH_3 + CO_2$; (16)

$H_3PO_4 \cdot CO(NH_2)_2 + Ca(H_2PO_4)_2 \cdot H_2O \rightarrow 2NH_4H_2PO_4 + CaHPO_4 + CO_2$; (17)

$2H_3PO_4 \cdot CO(NH_2)_2 + H_2O \rightarrow (NH_4)_2H_2P_2O_7 + 2NH_3 + 2CO_2$; (18)

$nH_3PO_4 \cdot CO(NH_2)_2 + H_2O \rightarrow (NH_4)_nH_2P_nO_{3n+1} + nNH_3 + nCO_2$; (19)

$2H_3PO_4 \cdot CO(NH_2)_2 + 3Ca(H_2PO_4)_2 \cdot H_2O \rightarrow (NH_4)_4Ca_3H_6(P_2O_7)_4 \cdot 3H_2O + 2CO_2 + 2H_2O$ (20)

$H_3PO_4 \cdot CO(NH_2)_2 + 2Ca(H_2PO_4)_2 \cdot H_2O \rightarrow (NH_4)_2CaH_4(P_2O_7)_2 + CaHPO_4 + CO_2 + 3H_2O$. (21)

In sulfate systems:

$H_2SO_4 \cdot 2CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2SO_4 + 2NH_3 + 2CO_2$; (22)

$2H_3PO_4 \cdot CO(NH_2)_2 + CaSO_4 \cdot 2H_2O \rightarrow (NH_4)_2SO_4 + Ca(H_2PO_4)_2 + 2NH_3 + 2CO_2$; (23)

$2H_3PO_4 \cdot CO(NH_2)_2 + 2CaSO_4 \cdot 2H_2O \rightarrow (NH_4)_2Ca(SO_4)_2 \cdot H_2O + Ca(H_2PO_4)_2 + 2NH_3 + 2CO_2 +$

$+ H_2O$ (24)

$nH_3PO_4 \cdot CO(NH_2)_2 + CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot xH_2O + (NH_4)_nH_2P_nO_{3n+1} + nNH_3 + nCO_2 +$

$+ (1-x)H_2O$. (25)

Summarizing the results of the above complex of studies of chemical transformations that occur when heating model systems including components of complex urea-containing fertilizers, it can be concluded that in the presence of phosphoric acid and calcium dihydrogen phosphate in the system, polyphosphates are formed at temperatures lower than the initial poly-condensation temperature of individual compounds. The presence of urea in the system promotes the flow of these processes, which, due to water released during the dehydration of phosphoric acid, undergoes hydrolytic decomposition with the formation of ammonium salts. In addition, when heated in the systems under study, the formation of double salts of calcium-ammonium-phosphates and sulfates occurs.

2.2 Features of chemical transformations occurring at the stage of granulation and drying of complex fertilizers in the presence of KCl

The Experimental Part

For the research, the following basic fertilizer grades are defined: 7:15:19; 10:15:15; 20:15:10; 16:12:20; 12:12:12; 13:13:13; 15:15:15. The choice of base marks is conditioned by the results of analysis of the world market of producers of phosphorus-containing and complex fertilizers. The chemical processes with the introduction of potassium chloride in the granulation stage together with the retour have been studied on model mixtures obtained on the basis of individual salts of reactive qualification. Calcium dihydrogen phosphate monohydrate $Ca(H_2PO_4)_2 \cdot H_2O$, ammonium dihydrogen phosphate $NH_4H_2PO_4$, ammonium sulfate $(NH4)_2SO_4$, potassium chloride KCl, urea $CO\ (NH_2)_2$ and gypsum $CaSO_4 \bullet 2H_2O$ of “analytical grade” qualification.

For the production of these grades, the use of ammonium sulfate as a result of ammonization of sulfuric acid is envisaged as nitrogen containing components, in addition to ammonia and urea. As a phosphorus-containing component, when potassium chloride was introduced into the slurry prior to the granulation step, the use of a non-filtered phosphoric acid suspension formed during the decomposition of phosphate raw material in an extractor using the technology implemented at the Gomel Chemical Plant (Belarus) was envisaged [15]. Correction of the composition of individual grades is carried out by the introduction of phosphogypsum.

Discussion of results

The results of the studies presented in Figures 2 and Tables 4, 5 confirm the flow in the stage of mixing, granulation and drying of conversion processes involving potassium chloride, as well as the significant influence of the method of KCl introducing on the chemistry and the phase composition of the products formed.

The analysis of the phase composition of the products obtained by introducing potassium chloride together with the retour directly at the granulation stage allows us to conclude that in this case the decomposition of KCl proceeds only partially (Table 4).

Fertilizer brands	Identified phase
12:12:12	KCl;$NH_4H_2PO_4$; $(NH_4)_2SO_4$;$CaSO_4 \cdot 0{,}5H_2O$; $(NH_4,K)H_2PO_4$; $CaHPO_4 \cdot 2H_2O$; $Ca_{10}(PO_4)_6(OH)_2$;NH_4Cl; $CO(NH_2)_2$; $CaSO_4$; $(K,NH_4)_2SO_4 \cdot H_2O$
13:13:13	KCl;$NH_4H_2PO_4$; $(NH_4)_2SO_4$; $CaHPO_4 \cdot 2H_2O$; $CO(NH_2)_2$; $CaSO_4 \cdot 0{,}5H_2O$; $CO(NH_2)_2 \cdot NH_4Cl$; $Ca_{10}(PO_4)_6(OH)_2$; NH_4Cl; $CO(NH_2)_2$
15:15:15	KCl; $NH_4H_2PO_4$; $CaHPO_4 \cdot 2H_2O$; $CO(NH_2)_2$; $(NH_4)_2SO_4$; $(K,NH_4)H_2PO_4$; $Ca_{10}(PO_4)_6(OH)_2$; $NH_4Cl \cdot CO(NH_2)_2$; $CaSO_4$; $(K,NH_4)_2SO_4 \cdot H_2O$

Table 4. Phase composition of complex fertilizers produced by the introduction of KCl at the stage of granulation

This is indicated by the presence on X-ray diffraction patterns of high intensity peaks corresponding to KCl, as well as ammonium sulfate and dihydrogen phosphate. Obviously, the phase composition of complex fertilizers obtained by the compaction method, as well as the bulk-blending technology, will be similar. At the same time, the presence of potassium-ammonium sulfate and potassium-ammonium dihydrogen phosphate in the products of double salts indicates a partial conversion of potassium chloride directly into the granulator. The appearance of peaks characteristic of calcium hydrogen phosphate confirms the assumption of a reaction between ammonium dihydrogen phosphate and calcium sulfate. The latter can partially turn into hydroxyl apatite.

Potassium salts in products are presented as the syngenite $K_2Ca(SO_4)_2 \cdot H_2O$, KH_2PO_4, double dihydrogen phosphates or potassium-ammonium sulfates. Moreover, the presence of urea in the fertilizer brands 10:15:15, 15:15:15, 20:15:10 and 20:15:10 promotes the acceleration of the process of exchange decomposition by binding the resulting ammonium chloride as a urea adduct with ammonium chloride and a shift in the equilibrium in the direction of the reaction products. This is confirmed by the presence on X-ray diffraction patterns of fertilizer reflexes, characteristic for ammonium chloride or its connection with urea $CO(NH_2)_2 \cdot NH_4Cl$.

Additional formation of the calcium hydrophosphate and ammonium chloride will occur as a result of the transformation of gypsum in singenit, as well as conversion of potassium chloride. Formation of calcium hydrophosphate and hydroxylapatite are confirmed as shown in [16]. Thus, the introduction of potassium chloride directly at the stage of granulation in conjunction with retur leads to a change in the chemistry of the process and phase composition of the product.

Research and analysis of phase composition of the products produced by the introduction of potassium chloride in partially or completely neutralized suspension before the stage of granulation and drying prove intensive interaction between individual components of the system. Draws attention in particular absence of KCl reflexes (except mark 16:12:20 containing excessive amounts of potassium chloride in relation to urea) that allows you to draw a conclusion about the almost complete conversion

Fertilizer brands	Identified phase
7:15:19	$K_2Ca(SO_4)_2 \cdot H_2O$; NH_4Cl; $(NH_4, K)H_2PO_4$
10:15:15	$K_2Ca(SO_4)_2 \cdot H_2O$; $NH_4H_2PO_4$; NH_4Cl; $CO(NH_2)_2 \cdot NH_4Cl$; $(K, NH_4)_2SO_4$
15:15:15	$CO(NH_2)_2 \cdot NH_4Cl$; $CO(NH_2)_2$; $K_2Ca(SO_4)_2 \cdot H_2O$; $CaSO_4$; $(NH_4,K)H_2PO_4$;$K_2Ca_5(SO_4)_6 \cdot H_2O$
20:15:10	$CO(NH_2)_2 \cdot NH_4Cl$; $CO(NH_2)_2$; $CaSO_4$; $(NH_4,K)H_2PO_4$; $(K,NH_4)_2SO_4$; NH_4Cl
16:12:20	$CO(NH_2)_2 \cdot NH_4Cl$; $CO(NH_2)_2$; KH_2PO_4; $CaSO_4$; $(NH_4,K)H_2PO_4$; $(K,NH_4)_2SO_4$; KCl

Table 5. Phase composition of complex fertilizers with the introduction of KCl before stage granulation in ammoniate suspension

Figure 2 indicates that the X-ray diffraction patterns of fertilizer samples of the brands 10:15:15, 7:15:19, 20:15:10 and 16:12:20 differ slightly, whereas the X-ray diffraction pattern sample of grade 15:15:15 is significantly different. The correlation between the phase composition and the fertilizer brand or, in other words, the dependence of the chemistry of the conversion process on the reagents proportion is the following. In the fertilizers of brands 7:15:19 and 10:15:15, which contain sulfuric acid enters, there are syngenite, ammonium chloride, ammonium and potassium ammonium dihydrogen phosphates, and with a high content of sulfuric acid, potassium-ammonium sulfates, with sulfates ammonium and calcium are not detected. In fertilizers of brands 20:15:10 and 16:12:20 that contain urea and does not include sulfuric acid, there are adduct urea with ammonium chloride, ammonium dihydrogen phosphate or potassium-ammonium, calcium and potassium-ammonium sulfates, and, when a large amount of potassium chloride is added, potassium dihydrogen phosphate. At the same time, there is no evidence of syngenite in these samples. Entered into the process urea and formed during the conversion of potassium chloride ammonium chloride can be present in the final product either individually or as $CO(NH_2)_2 \cdot NH_4Cl$ depending on the conditions of the process, the amount and ratio of the initial reagents. Fertilizer brand 15:15:15 is an intermediate between these brands: for its production sulfuric acid and urea are used. The phase composition of this fertilizer is the most complex one. It is represented practically by all the compounds mentioned: dihydrogen phosphate and potassium-ammonium sulfate, urea and its adduct with ammonium chloride, syngenite and calcium sulfate, it is also possible the presence of georgeite $Ca_5K_2(SO_4)_6 \cdot H_2O$ - potassium-calcium sulfate with a higher content of calcium sulfate than in the case of syngenite. It should be noted that the compounds $NH_4H_2PO_4$, KH_2PO_4, K_2SO_4, $(NH_4)_2SO_4$,as well as double salts of different compositions $K_x(NH_4)_{1-x}H_2PO_4$ and $K_x(NH_4)_{2-x}SO_4$ are characterized by close interplanar distances, and the differences on their X-ray diffraction patterns appear either in the position of low-intensity reflections, or in different intensities of the main reflexes.

In particular, this refers to ammonium and potassium ammonium dihydrogen phosphates. Therefore, the presence of small amounts of all these compounds is not excluded. There are other double salts, the formation of which is possible in these systems, having close radiographs or coinciding major interplanar distances, and therefore difficult to identify.

Thus, the fertilizers of brands 7:15:19; 10:15:15; 20:15:10; 16:12:20, 15:15:15, obtained by introducing potassium chloride before the granulation stage into a partially or completely neutralized phosphoric acid suspension, can be divided by phase composition into two types: fertilizers where nitrogen is mainly present in ammonium form and fertilizers containing potassium mainly in the form of potassium-calcium sulfate - syngenite. In fertilizers containing more nitrogen in the amide form, potassium is presented in the form of dihydrogen phosphates and sulfates; in addition, calcium sulfate is part of these fertilizers. Phosphorus in all fertilizer brands is represented by ammonium, potassium dihydrogen phosphates and their double salts. Fertilizers of the brands 12:12:12, 13:13:13, 15:15:15, obtained with the introduction of potassium chloride directly at the stage of granulation together with the retour, contain potassium mainly in the form of potassium chloride. The partial flow of the conversion process in the granulation and drying step leads to the formation of a certain amount of double salts of potassium-ammonium sulfates and potassium-ammonium dihydrogen phosphates.

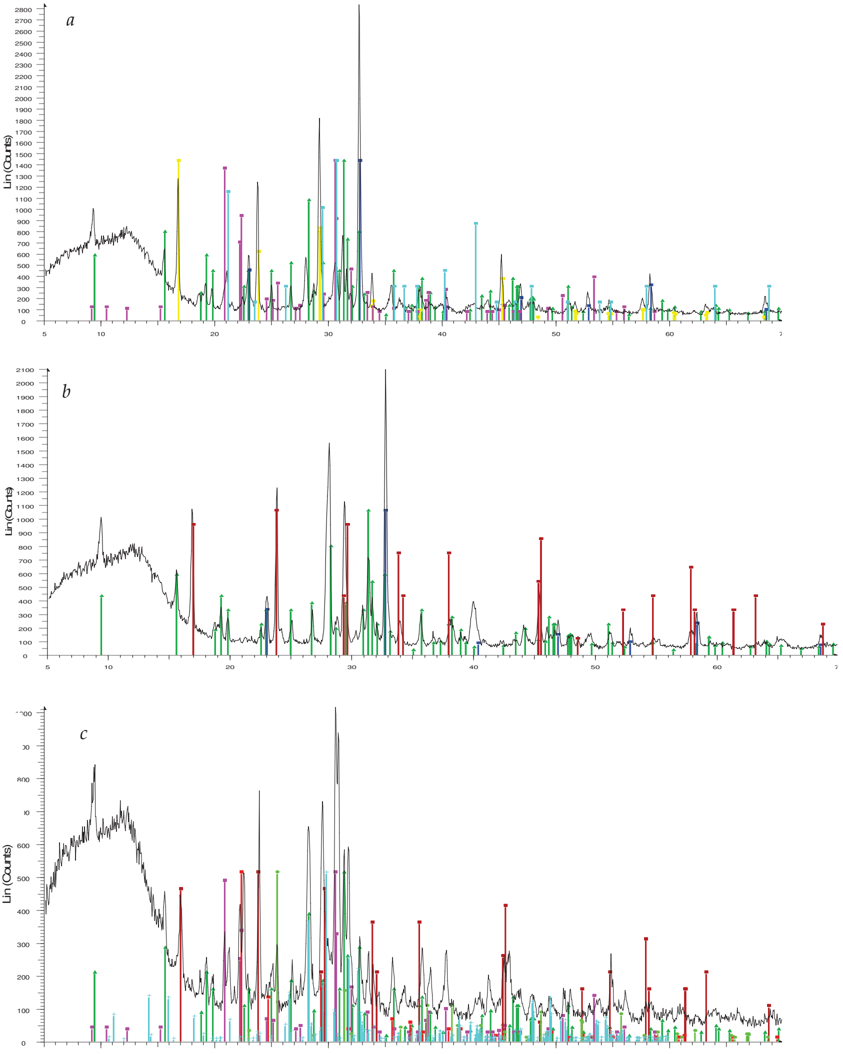


Figure 2 X-ray diagrams of complex NPK fertilizers brands:
a– 10:15:15; *b* – 7:15:19; *c* – 15:15:15

According to the results of the study, it can be concluded that in the preparation of complex NPK fertilizers based on a urea-containing ammoniated phosphoric acid suspension and the introduction of potassium chloride before the granulation stage, followed by drying the suspensions formed, the following chemical reactions occur:

$KCl + NH_4H_2PO_4 \rightarrow KH_2PO_4 + NH_4Cl;$ (26)

$xKCl + NH_4H_2PO_4 \rightarrow K_x(NH_4)_{1-x}H_2PO_4 + xNH_4Cl;$ (27)

$2KCl + (NH_4)_2SO_4 \rightarrow K_2SO_4 + 2NH_4Cl;$ (28)

$xKCl + (NH_4)_2SO_4 \rightarrow K_x(NH_4)_{2-x}SO_4 + xNH_4Cl;$ (29)

$CO(NH_2)_2 + NH_4Cl \rightarrow CO(NH_2)_2 \cdot NH_4Cl;$ (30)

$K_2SO_4 + CaSO_4 \cdot 2H_2O \rightarrow K_2Ca(SO_4)_2 \cdot H_2O + H_2O;$ (31)

$2KCl + CaSO_4 \cdot 2H_2O + (NH_4)_2SO_4 \rightarrow K_2Ca(SO_4)_2 \cdot H_2O + 2NH_4Cl + H_2O;$ (32)

$2KCl\ (NH_4)_2 + Ca(SO_4)_2 \cdot H_2O \rightarrow K_2Ca(SO_4)_2 \cdot H_2O + 2NH_4Cl.$ (33)

Thus, the chemism of the process of obtaining complex fertilizers with the introduction of potassium chloride before the granulation stage into partially or completely ammoniated phosphoric-acid suspensions and the phase composition of the products formed is significantly different from the composition of fertilizer mixtures, mixed complex fertilizers obtained by the compaction method, and also by bulk-blending technology. As a result, complex fertilizers obtained with the introduction of potassium chloride before to the granulation stage and the application of rolling granulation methods in the drum type apparatus are superior in their physical and agrochemical properties to similar fertilizer brands, produced by other methods. Therefore, the granule strength is 2.5-2.8 MPa, the moisture absorption rate of not more than 0.37 mmol $H_2O/(g \cdot hour)$, i.e. the fertilizer will not practically cake when stored. Since the solubility of syngenite in water is not high (0.25 g/100 g H_2O), fertilizers containing it will have the properties of slow acting potassium. The resulting granules are characterized by a homogeneous composition, without visible inclusions of potassium chloride. The improvement in physical properties is probably caused by the presence of calcium sulfate in the studied system, as well as by the formation of double salts containing calcium sulfate and promoting the formation of a dense film of fine calcium sulfate crystals on the surface of a solid phase (granules), which prevents the release of urea and ammonium chloride on to the surface, to the greatest extent contributing to the increase in hygroscopicity and caking of compound fertilizers.

The proceeding conversion processes and the resulting products will determine the physico-chemical, physico-mechanical, agrochemical properties of the fertilizers obtained, which should be taken into account in the development of new technologies for complex NP and NPK (Ca, S) fertilizers, including urea-containing systems.

3. Chemism, phase composition, and physico-mechanical properties of NP and NPK fertilizers on the basis of ammonium phosphates. Influence of nitrogenous components

At present, significant volumes of complex and complex-mixed fertilizers in the world are produced on the basis of ammonium phosphates obtained by ammonization of extraction phosphoric acid, followed by granulation and drying of ammoniated phosphate suspension. One of the largest and most popular fertilizers in the world market on the basis of ammonium phosphates is ammophos, which is one of the most concentrated types of NP fertilizers (the total nutrient content exceeds 60%), which reduces transport costs considerably, but is not balanced by the ratio of the main nutrients. To obtain fertilizers of the balanced brands, nitrogen-containing (ammonium nitrate, urea) and potassium-containing components are additionally introduced into the reaction mixture derived after ammonization of extraction phosphoric acid. NP(K) fertilizers (nitroammophos (nitroammophoska), karboammofos (karboammofoska)) obtained in this process are highly concentrated ballastless fertilizers containing all the nutrients in water-soluble form, and can be received with any desired ratio nutrient demand of customers. A review of the literature on the methods for obtaining complex fertilizers on the basis of ammophos, as well as conversion processes taking place in multicomponent systems when they are obtained is, in particular, presented in the work [1]. However, in the literature there are no systematic data on the chemical processes taking place at the stages of granulation and drying in multicomponent systems in the production of NP and NPK fertilizers by mixing ammophos with various types of nitrogen- and potassium-containing components, as well as their effect on the physico-mechanical properties of the target products of complex NP and NPK fertilizers. The author’s results of studies on the effect of the type of nitrogen-containing components on the phase composition and properties of NP and NPK fertilizers obtained by mixing ammophos, ammonium nitrate, urea, potassium chloride, and establishing the chemism of the processes occurring at the granulation stage and drying between individual components are represented in this section.

The Experimental Part

The objects of this study are fertilizers with a mass ratio of nutrients N : P_2O_5 : K_2O, equal to 1 : 1 : 0 and 1 : 1 : 1, and the ratio of nitrogen of ammonium nitrate to nitrogen of urea $N(NH_4NO_3) : N[CO(NH_2)_2]$, equal to 1 : 0; 3 : 1; 1 : 1; 1 : 3; 0 : 1. The receipt of all fertilizer brands was carried out according to the expenditure rates given in Table 6.

It should be noted that the drying of fertilizers that contain a mixture of ammonium nitrate and urea takes a longer period of time compared to fertilizers that include one of the nitrogen-containing components. This is probably connected to the formation of a eutectic mixture of NH_4NO_3 и $CO(NH_2)_2$, containing 53,5% NH_4NO_3 and melting at 44.6°C [11]. In addition, there is evidence of increasing mutual solubility of the two substances in the system $NH_4NO_3 – CO(NH_2)_2 – H_2O$ [17].

This leads to an increase in the mass and concentration of the liquid phase in the wet product, which makes it difficult to remove water during its drying. Obviously, for the same reasons, it is not possible to obtain fertilizers with the ratio $N(NH_4NO_3):N[CO(NH_2)_2]$, equal to 1 : 1 and 1 : 3, in granulated form.

Discussion of results

The X-ray phase analysis of the obtained fertilizers is represented in Table 7. According to the X-ray phase analysis of initial fertilizer in admixture ammophos contains ammonium sulfate in significant quantity – relative intensity maximum reflex $(NH_{4)2}SO_4$ radiograph

$N(NH_4NO_3)$: $N[CO(NH_2)_2]$	Type of fertilizer	Source substances consumption per 100 g of the fertilizer, g				Fertilizer brands
		Ammophos	Ammonium nitrate	Urea	Potassium chloride	
1 : 0	NP	46,08	53,92	–	–	24,0 : 24,0
3 : 1		47,74	41,88	10,38	–	24,8 : 24,8
1 : 1		49,53	28,93	21,54	–	25,8 : 25,8
1 : 3		51,42	15,04	33,54	–	26,7 : 26,7
0 : 1		53,49	–	46,51	–	27,8 : 27,8
1 : 0	NPK	32,90	38,50	–	28,60	17,1 : 17,1 : 17,1
3 : 1		33,77	29,62	7,34	29,27	17,6 : 17,6 : 17,6
1 : 1		34,63	20,23	15,06	30,08	18,0 : 18,0 : 18,0
1 : 3		35,57	10,41	23,20	30,82	18,5 : 18,5 : 18,5
0 : 1		36,54	–	31,77	31,69	19,0 : 19,0 : 19,0

Table 6. Monoammonium phosphate-based fertilizer recipe

$N(NH_4NO_3)$: $N[CO(NH_2)_2]$	The main phase	Impurities
NP fertilizers		
1 : 0	$NH_4H_2PO_4$; NH_4NO_3	$(NH_4)_5(NO_3)_3SO_4$
3 : 1	$NH_4H_2PO_4$; NH_4NO_3; $CO(NH_2)_2$	
1 : 1	$NH_4H_2PO_4$; $CO(NH_2)_2$; $(NH_4)_5(NO_3)_3SO_4$	$(NH_4)_2HPO_4$
1 : 3	$NH_4H_2PO_4$; $CO(NH_2)_2$; $(NH_4)_5(NO_3)_3SO_4$	$(NH_4)_2SO_4$; $(NH_4)_2HPO_4$
0 : 1	$NH_4H_2PO_4$; $CO(NH_2)_2$	$(NH_4)_2SO_4$
NPK fertilizers		
1 : 0	$NH_4H_2PO_4$; KNO_3; NH_4Cl	$(K, NH_4)NO_3$; $K(NH_4)_3(NO_3)_2SO_4$; $K_2(NH_4)_2(NO_3)_2SO_4$; KCl
3 : 1	$NH_4H_2PO_4$; KNO_3; NH_4Cl; $CO(NH_2)_2 \cdot NH_4Cl$	
1 : 1	$NH_4H_2PO_4$; KNO_3; NH_4Cl; $CO(NH_2)_2$; $CO(NH_2)_2 \cdot NH_4Cl$	$(K, NH_4)NO_3$; $K(NH_4)_3(NO_3)_2SO_4$; $K_2(NH_4)_2(NO_3)_2SO_4$; KH_2PO_4; K_2SO_4; KCl
1 : 3	$NH_4H_2PO_4$; $CO(NH_2)_2$; $CO(NH_2)_2 \cdot NH_4Cl$; KCl; $(K, NH_4)NO_3$	$K(NH_4)_3(NO_3)_2SO_4$; $K_2(NH_4)_2(NO_3)_2SO_4$; KH_2PO_4; NH_4Cl; $(K, NH_4)_2SO_4$
0 : 1	$CO(NH_2)_2$; $(K, NH_4)H_2PO_4$; KCl; $CO(NH_2)_2 \cdot NH_4Cl$	KH_2PO_4; K_2SO_4

Table 7. Phase composition of fertilizers on basis of monoammonium phosphate

MAP is 10%. The content of other impurities in ammophos, as well as all impurities in ammonium nitrate, urea and potassium chloride is insignificant. On their X-ray diffraction patterns, the relative intensity of reflexes that are not related to the main substance does not exceed 4%. Nevertheless, it should be noted that impurities $(NH_4)_2SO_4$ and a mixed salt $(NH_4)_5(NO_3)_3SO_4$ can be identified in ammonium nitrate. It has been established that $NH_4H_2PO_4$ and $CO(NH_2)_2$ are included in NP fertilizers without any changes. At the same time, the relative intensity of $CO(NH_2)_2$ reflections increases with the increase in its content in the mixture. Ammonium nitrate is present as an individual compound only in fertilizers with the ratio $N(NH_4NO_3)$: $N[CO(NH_2)_2] \geq 3$. In the ratio $N(NH_4NO_3)$: $N[CO(NH_2)_2] \leq 1$ ammonium nitrate enters into the composition of fertilizers in the form of mixed salt with ammonium sulfate $(NH_4)_5(NO_3)_3SO_4$. In turn, the impurity of $(NH_4)_2SO_4$ in the form of an individual compound appears only in fertilizers with a small content of ammonium nitrate or if it is absent. With an introduction of potassium chloride to the mixture of nitrogen-containing fertilizers its interaction with ammonium salts takes place, as a result of which NH_4Cl or its compound with urea $CO(NH_{2)2}\cdot NH_4Cl$ is included in all the products. As well as in the case of obtaining fertilizers based on a phosphate-acid suspension using ammonium nitrate and urea as nitrogen compounds, it is NH_4NO_3 that is converted first from the present ammonium salts. The main potassium- and nitrate-containing phase in fertilizers with the ratio N (NH_4NO_3): $N[CO(NH_2)_2] \geq 1$ is KNO_3, also there are impurities of other nitrates and potassium salts. With a small content of ammonium nitrate, individual KNO_3 is not detected; it has been established that it is a part of fertilizers in the form of nitrates and potassium-ammonium nitrates-sulfates. There is also a small amount of other potassium salts in the impurity products of KCl, KH_2PO_4, K_2S_4O, (K, $NH_{4)2}SO_4$. The interaction of KCl with $NH_4H_2PO_4$ occurs to a large degree only when the fertilizer is obtained without the addition of ammonium nitrate. The main phosphate phase in this product is $(K, NH_4)H_2PO_4$.

The equations of chemical reactions involving initial substances and products formed in these systems at the stages of KCl introduction and drying of products is the exchange reaction between KCl and ammonium salts with the formation of KH_2PO_4, K_2SO_4, KNO_3, NH_4Cl, salts of potassium-ammonium, potassium-calcium and other compounds of complex composition, have the following appearance:

$NH_4H_2PO_4 + KCl = KH_2PO_4 + NH_4Cl$; (34)

$(NH_4)_2SO_4 + 2KCl = K_2SO_4 + 2NH_4Cl$; (35)

$NH_4NO_3 + KCl = KNO_3 + NH_4Cl$; (37)

$NH_4H_2PO_4 + xKCl = K_x(NH_4)_{1-x}H_2PO_4 + xNH_4Cl$; (37)

$(NH_4)_2SO_4 + xKCl = K_x(NH_4)_{2-x}SO_4 + xNH_4Cl$; (38)

$CaSO_4 \cdot 2H_2O + K_2SO_4 = K_2Ca(SO_4)_2 \cdot H_2O + H_2O$; (39)

$5CaSO_4 \cdot 2H_2O + K_2SO_4 = K_2Ca_5(SO_4)_6 \cdot H_2O + 9H_2O$; (40)

$(NH_4)_2Ca(SO_4)_2 \cdot H_2O + 2KCl = K_2Ca(SO_4)_2 \cdot H_2O + 2NH_4Cl$; (41)

$2CaSO_4 \cdot 2H_2O + (NH_4)_2SO_4 + K_2SO_4 = = 2K(NH_4)Ca(SO_4)_2 \cdot H_2O + 2H_2O$; (42)

$3NH_4NO_3 + K_2SO_4 = K(NH_4)_3(NO_3)_2SO_4 + KNO_3$; (43)

$(NH_4)_4(NO_3)_2SO_4 + KCl = K(NH_4)_3(NO_3)_2SO_4 + + 2NH_4Cl$, (44)

as well as the formation of urea adduct with ammonium chloride $NH_4Cl \cdot CO(NH_2)_2$ and the dehydration of $CaHPO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$ present in the suspension.The formation of these products is in accordance with the data on conversion processes [16], the flow of which is possible in multicomponent systems in the production of complex fertilizers.

The results of chemical analysis and hygroscopicity studies of the obtained fertilizers are presented in Table 8. The absolute deviation of the experimental values from the calculated values for practically all samples and components is ± (0.2-3.0)%. The content of polymeric phosphates in the obtained fertilizers is insignificant. With a longer drying of fertilizers that contain approximately equal amount of ammonium nitrate and urea, it is possible to convert amide nitrogen to ammonium to a minor extent. This may be due to the presence of impurities $(NH_4)_2HPO_4$ in the corresponding products.

The data given in Table 3 indicate that ground fertilizers obtained with the introduction of a single nitrogen-containing component are characterized by a lower hygroscopicity compared to fertilizers containing mixtures of ammonium nitrate and urea. At the same time the hygroscopicity depends on the composition of this mixture: fertilizers with the ratio $N(NH_4NO_3)$: $N[CO(NH_2)_2]$

= 1 : 1 are the most hygroscopic. The hygroscopic point of granular fertilizers is also low and makes 35-40%.

$N(NH_4NO_3)$: $N[CO(NH_2)_2]$	Content, %				Hygroscopic point, %
	$N(NH_4^+)$	$CO(NH_2)_2$	$P_2O_{5\text{ водн}}$	$P_2O_{5\text{ усв}}$	
NP- fertilizers					
1 : 0	15,0	–	19,6	21,0	51
3 : 1	13,3	9,5	22,6	24,6	20
1 : 1	11,7	18,9	25,4	26,8	18
1 : 3	9,5	33,0	25,7	26,9	33
0 : 1	6,5	48,4	23,9	25,7	48
NPK- fertilizers					
1 : 0	11,2	–	13,8	14,1	47
3 : 1	10,5	6,7	16,1	16,5	35
1 : 1	9,9	15,5	22,2	23,3	25
1 : 3	6,9	21,4	17,8	19,0	38
0 : 1	5,2	30,3	17,9	18,3	48

Table 8. Composition and properties of complex fertilizers on basis of monoammonium phosphate

The reason for the high hygroscopicity of the obtained fertilizers can be the presence of mixed and double salts in their composition. The literature contains information concerning the fact that in fertilizers obtained by mixing ammonium nitrate with ammonium sulfate or with chloride and potassium nitrate, there are $3NH_4NO_3 \cdot (NH_4)_2SO_4$, $2NH_4NO_3 \cdot (NH_4)_2SO_4$ or $NH_4NO_3 \cdot 2KNO_3$ compounds. It is noted that these compounds are hygroscopic [16].

Thus, complex NP and NPK fertilizers on the basis of ammophos are multicomponent systems that contain acid phosphates of ammonium, potassium, and potassium-ammonium; potassium sulfate, potassium-ammonium; urea and its compounds with the salts present; ammonium and potassium chlorides. These substances have a significant effect on the physical and mechanical properties of the final product and can be found in fertilizers in the form of individual compounds and solid solutions. When obtaining complex fertilizers of a balanced composition with low hygroscopicity on the basis of ammophos, it is preferable to introduce one nitrogen-containing component – ammonium nitrate or urea, and not their mixtures

4. Conversion processes in multicomponent systems in manufacture of complex magnesium-containing NP и NPK fertilizers

One of the persistent trends of the complex NP and NPK fertilizers market is increasing volumes of magnesium-containing fertilizers manufacture. Magnesium is part of chlorophyll, pectins and fitina, which determines its importance in the life of plants: it is involved in the movement of phosphorus in plants, activates some enzymes (e.g., phosphates), accelerates the formation of carbohydrates affects redox processes in the tissues of plants and formation of fruits [18]. Chlorophyll contains about 10% of the total amount of magnesium in the green parts of plants. Good plants magnesium enhances regenerative processes in them and leads to greater accumulation of organic compounds recovered – essential oils, fats, etc. [19]. Formation in the leaves of such pigments as carotene and xanthophyll is also associated with magnesium. High harvests crops consume magnesium from 1 up to 7 g of MgO per 1 m^2. The greatest amount of magnesium is absorbed by potatoes, fodder and sugar beet, tobacco, legumes and beans herbs. Introduction of nitrogen, phosphate and potash fertilizers usually increases the need for plants in magnesium because it is important for them to maintain a certain share of these elements. Different magnesium-containing fertilizers are used to remove this shortcoming.

In the open ground, magnesium-containing fertilizers exert a positive influence on the background of NPK, both on the gross crop and on its quality. Based on numerous agrochemical studies of the effectiveness of different types of magnesium-containing fertilizer it has been proved that the multilateral magnesium-containing fertilizers:-two-, three- or four-part (magnesium phosphate, magnesium-ammonium phosphates, potassium-magnesium salts without chlorine, etc.) most appropriate for application [20]. For example, it has been found by the Russian researchers that for a number of crops (fallrye, buckwheat, panic, corn, etc.) the yield of grain increased by a factor of 1.5-2 upon application of magnesium on the background of NPK. In other experiments, introduction of magnesium fertilizers resulted not only in larger harvest, but also in a higher starch content of potatoes and sugar content of beet [4]. Magnesium and its salts have a positive effect on the physical properties of fertilizers. In particular, an increase in the content of magnesium in phosphoric acid source and ammoniated suspensions increases the strength of granules, reduces caking of fertilizers, increases the efficiency of granules surface treatment of conditioning additives [21].Therefore, most of foreign manufacturers of mineral fertilizers in Europe, Asia, Belarus, CIS countries have in their assortment integrated magnesium fertilizers, with the content of magnesium being as high as 8-10%, that corresponds to the quantitative indicators for microelements.

As a source of magnesium both for direct application on soils and for fertilizer processing the following types of raw materials can be used: magnesium silicates - dunite, serpentinite, olivenite; carbonate rocks - dolomite, magnesite, etc.; raw natural salt - carnallite, kainite, langbejnit, polygalit, kieserite, etc. Traditionally, the fertilizer producers use as the major sources of magnesium three types of material: dolomite limestone ($CaCO_3 \cdot MgCO_3$); potassium-magnesium sulfate ($K_2SO_4 \cdot MgSO_4$); magnesium oxide (MgO).

Known methods of producing magnesium-containing fertilizers differ not only by the types of used magnesium-containing raw materials, but also by the ways of its introduction into the technological process. In particular, other magnesium-containing components are added at the stage of granulation and drying [22]. It is proposed to undertake the decomposition of magnesium-containing raw material source separately by nitric acid with magnesium nitrate formation and then adding it into nitric acid suspension [23].

Apparently, introduction of magnesium compounds will be accompanied by additional chemical processes and make the phase composition of the fertilizers more complex. However, so far this has not received the necessary attention by both producers and researchers, as evidenced by the analysis of the literature.

This section is focused on the results of the studies of conversion processes, taking place upon introduction of different kinds of magnesium-containing raw material at separate technological stages of complex NP and NPK fertilizers production. The results obtained made it possible to reveal chemical transformations occurring during the introduction of magnesium-containing components at different technological stages, set the phase composition of products and justify the choice of an optimal technological regime and scheme of magnesium-containing complex fertilizers production taking into account the type of raw material and the basic technology.

The Experimental Part

The role of the basic brand of an NP fertilizer was played by a fertilizer based on ammonium phosphates, produced by ammonization of wet-process phosphoric acid to prescribed pH values by the traditional technology of ammophos production [1].The amount of the magnesium-containing additive being introduced was calculated on the basis of magnesium content in the target product (fertilizer) of 2 and 5 % in terms of MgO. In the case of introduction of magnesium compounds in amounts of 2 and 5 % in terms of MgO, the ammonization of the phosphoric acid suspension was performed to pH 4.5 and 4.1, respectively. Basic magnesium carbonate with 41.5 % MgO and magnesium sulfate, both of pure grade, were used as magnesium-containing additives.

As the base brand of an NPK fertilizer the 15 : 15 : 15 brand was chosen, which is one of most demanded mineral fertilizers in the world market and is a good balanced complete complex fertilizer. For example, according to the information reported at the conference “Argus FSU Fertilizer 2015: Production and Logistic”, the share of this fertilizer brand in the total amount of Russia's export of integrated fertilizers was 20% in 2015. The amount of the magnesium-containing additive being introduced was 5 % in terms of MgO in the product. Lime (dolomite) dust produced by JSV “Dolomit” (Belarus) with a total mass fraction of calcium and magnesium carbonates of no less than 80 % was used as magnesium-containing additive. Dolomite was introduced at the stage of the acid decomposition of phosphate raw materials by the double-stage scheme developed with the participation of the author. Under the optimal conditions this scheme ensures the maximum degree of decomposition of raw materials in the optimal technological regime. Kovdor apatite concentrate containing: P_2O_5 – 38.2%, CaO – 52.92%, MgO – 1.93%, Fe_2O_3 – 0.39%, Al_2O_3 – 1.26%, F – 1.1%, and moisture 0.42 was used as phosphate raw materials. To make qualitative and quantitative analyses when identifying the phase composition, samples taken in separate technological stages were analyzed for the content of the corresponding elements by using the commonly accepted standard techniques. For example, the content of various forms of phosphorus was determined by the photocolorimetric method with a phosphorus-vanadium-molybdenum complex. The content of total nitrogen was determined by the hypochlorite method, and that of ammoniac nitrogen - by the chloramine method. The content of magnesium and calcium in the starting raw material and in the formed precipitates and solutions was determined by complexonometry, and that of potassium, by flame photometry. As the result of an analysis an arithmetic mean of parallel determinations was taken, the acceptable discrepancies between which did not exceed 0.2-0.5% at a confidence probability $P = 0.95$. The experimental errors in consideration of separate technological stages were evaluated by comparison of the component-wise material balance with the results of chemical analyses.

The colorimetric determinations were made with an SP 8001 spectrophotometer (Taiwan), and flame-photometric determinations, on a JENWAY PFP7 automated flame photometer (England). The pH value was monitored with a HANNA HI 221 pH-meter (Germany). The measurement accuracy at 20°C was ±-.01 pH unit. A 50K-15/0.05 liquid thermostat (Belarus) was used to simulate acid decomposition processes. The temperature was maintained to within 0.05°. The prescribed agitation intensity of the suspensions was provided by an IKA RW 20 controlled-speed agitation device (Germany). The moisture content of the samples was determined and their thermal treatment under isothermal conditions was performed with an MA 30 “Sartorius” moisture analyzer (Germany).

Results and discussion

The results of the chemical analysis of the resulting NP fertilizers for the content of various forms of phosphorus and magnesium on using different kinds of magnesium-containing additives are given in Table 9.

Magnesium-containing additive	Content of the various forms, %			
	P_2O_5		MgO	
	water-soluble	accessible	water-soluble	total
Basic magnesium carbonate	46,0	56,3	3,7	5,7
Magnesium sulfate	42,3 48,6	46,2 51,0	3,8 0,2	5,5 2,0

Table 9. Content of selected components in the composition of the magnesium-containing complex NP fertilizers +

From the data presented in Table 9, it can be seen that, irrespective of the type of a magnesium-containing additive, the target product contains both water-soluble and water-insoluble compounds of magnesium and phosphorus. The share of water-soluble compounds of magnesium decreases if the ammonization is performed to a higher pH value. Dihydrophosphate and sulfate may be present in the resulting products among the water-soluble compounds, and hydrophosphate and double magnesium-ammonium phosphates, among those insoluble in water.

The X-ray phase analysis demonstrated that the main phase of the resulting fertilizers is ammonium dihydrophosphate $NH_4H_2P0_4$, which seems to be quite reasonable (Figures 3, 4). However, reflections of other phases in X-ray diffraction patterns of fertilizers containing magnesium compounds in an amount of 2% MgO are insignificant and cannot be identified. Therefore, the XPA data in Figures 3 and 4 are given for fertilizers containing 5% MgO. The reflections of impurities present in the product obtained with addition of basic magnesium carbonate (Figure 3), are also identified in the X-ray diffraction pattern of the product obtained upon addition of magnesium sulfate (Figure 4). At the same time, the X-ray diffraction pattern of the latter also shows higher intensity impurity-related reflections at $2\Theta = 11\text{-}12, 20\text{-}22$, and 28-30°.

Apparently, addition of basic magnesium carbonate to phosphoric acid, followed by ammonization and drying of the resulting suspension, will be accompanied by the formation, together with ammonium phosphates, of other magnesium- or phosphorus-containing compounds. According to the XPA data, the following compounds are identified in this product: magnesium hydro- and dihydrophosphates $MgHPO_4 \cdot 3H_2O$, $Mg(H_2PO_4)_2 \cdot 2H_2O$, $Mg(H_2PO_4)_2$, and double magnesium-ammonium hydrophosphate $(NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O$ (Figures 3, 4).

These compounds can be formed by the following chemical reactions:

$xMgO \cdot yCO_2 \cdot zH_2O + 2xH_3PO_4 \rightarrow xMg(H_2PO_4)_2 + yCO_2 +$
$+ (x+z)H_2O$ (45)

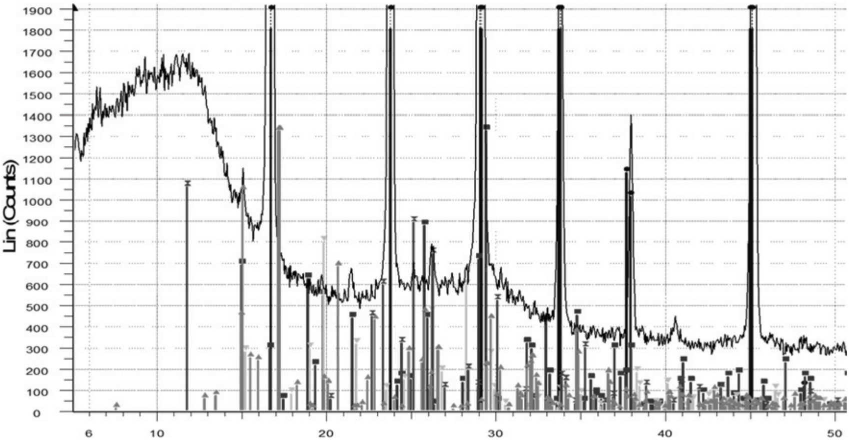
$Mg(H_2PO_4)_2 + NH_3 + 3H_2O \rightarrow MgHPO_4 \cdot 3H_2O +$
$+NH_4H_2PO_4$ (46)

$Mg(H_2PO_4)_2 + 2NH_3 + 4H_2O \rightarrow$
$(NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O$ (47)

$2MgHPO_4 \cdot 3H_2O + 2NH_4H_2PO_4 + H_2O \rightarrow$
$(NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O + Mg(H_2PO_4)_2 \cdot 2H_2O$ (48)

$MgHPO_4 \cdot 3H_2O + (NH_4)_2HPO_4 + H_2O \rightarrow$
$(NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O$ (49)

When the phase composition of the product obtained with using of magnesium sulfate as a magnesium-containing additive was identified, the possibility that hydrates of magnesium sulfates may be present in the target product was analyzed in the first place. It was established that $MgSO_4{\cdot}7H_2O$ and $MgSO_4{\cdot}6H_2O$ are the most probable phases (Figure 4). However, the reflections at $2\Theta = 28.5, 29.8°$, and some others are not characteristic of these phases. At the same time, the X-ray diffraction pattern of the product under study contains all the reflections, including those mentioned above, characteristic of ammonium sulfate $(NH_4)_2SO_4$, and double magnesium-ammonium sulfates $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ and $(NH_4)_2Mg(SO_4)_2{\cdot}4H_2O$. The presence of these compounds indicates that exchange interaction reactions occur between magnesium sulfate and ammonium phosphates, with magnesium sulfates just being the products of these reactions. It follows from Figure4-*в* that all the reflections of the magnesium- and phosphorus-containing phases contained in the fertilizer with addition of basic magnesium carbonate are also present in the X-ray diffraction pattern of the fertilizer with addition of magnesium sulfate.



2Θ°

Figure 3. X-ray diffraction pattern of the fertilizer with addition of magnesium sulphate

Phase ● – $NH_4H_2PO_4$; magnesium-containing phase:■ $MgHPO_4 \cdot 3H_2O$; ▼ $Mg(H_2PO_4)_2 \cdot 2H_2O$; $xMg(H_2PO_4)_2$; ▲$(NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O$

The data obtained suggest that, upon introduction of magnesium even in the form of a soluble sulfate, it is partly converted with formation of ammonium sulfate, water-insoluble magnesium sulfates, and double magnesium-ammonium sulfates by the following schemes:

$MgSO_4 + 2NH_4H_2PO_4 + 2H_2O \rightarrow Mg(H_2PO_4)_2{\cdot}2H_2O + (NH_4)_2SO_4;$ (50)

$MgSO_4 + (NH_4)_2HPO_4 + 3H_2O \rightarrow MgHPO_4{\cdot}3H_2O + (NH_4)_2SO_4;$ (51)

$2MgSO_4 + 2NH_4H_2PO_4 + 8H_2O \rightarrow (NH_4)_2Mg(SO_4)_2{\cdot}6H_2O + Mg(H_2PO_4)_2{\cdot}2H_2O;$ (52)

$MgSO_4+(NH_4)_2SO_4+6H_2O\rightarrow (NH_4)_2Mg(SO_4)_2{\cdot}6H_2O;$ (53)

$MgSO_4 + 2(NH_4)_2HPO_4 + 4H_2O \rightarrow (NH_4)_2Mg(HPO_4)_2{\cdot}4H_2O + (NH_4)_2SO_4;$ (54)

The results of X-ray XRD for the obtained NPKMg fertilizers listed in Table 10 suggest that the major phosphate fertilizers phases are acidic calcium orthophosphate, ammonium, ammonium-potassium. From polymeric phosphates, ammonium polyphosphates and ammonium, calcium, and ammonium-calcium diphosphates may be present. The identification of these compounds corresponds to the results of the chemical analysis, according to which the fertilizers contain water-soluble and accessible ortho-and polyphosphates and water-insoluble ammonium salts.

The main nitrogen-containing phases are the following: urea, ammonium chloride, the product of the interaction between these two – $CO(NH_2)_2{\cdot}NH_4Cl$, ammonium phosphates and sulfates, and double ammonium salts.

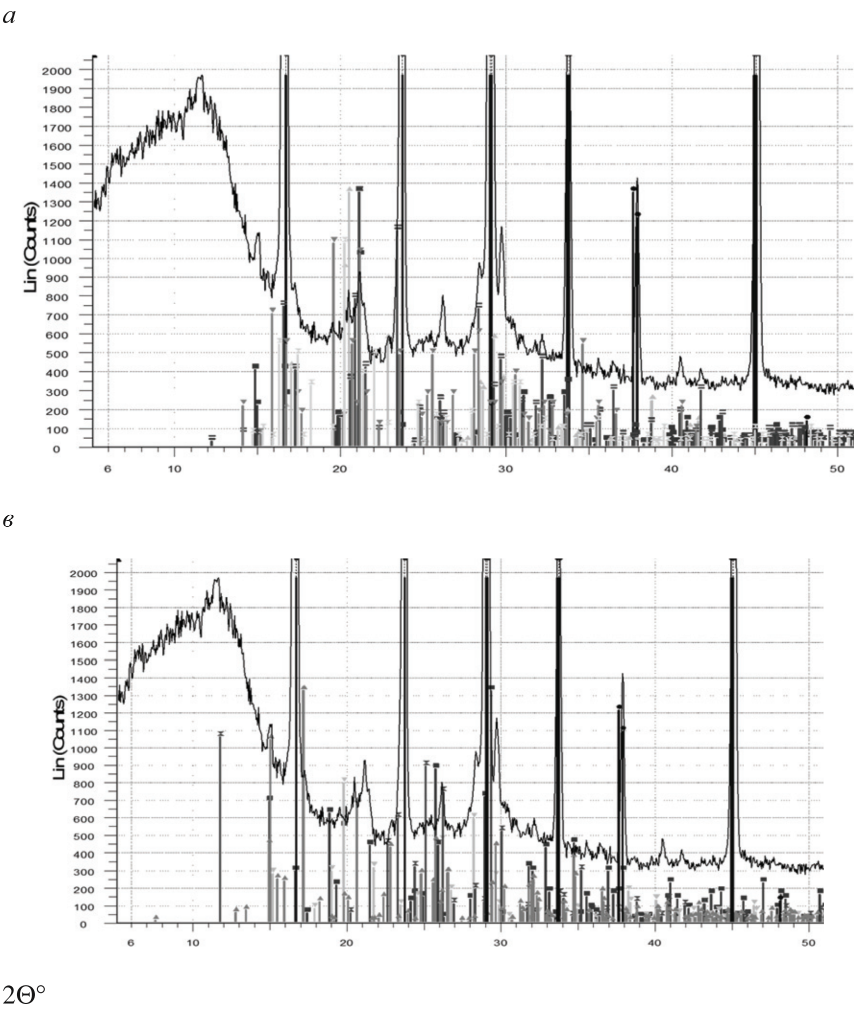


Figure 4. X-ray diffraction pattern with addition of magnesium sulphate

Phase ● – $NH_4H_2PO_4$;

а – sulfate phases: ■ $MgSO_4 \cdot 7H_2O$; ×$MgSO_4 \cdot 6H_2O$; ▲ $(NH_4)_2SO_4$;= $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$; ▼ $(NH_4)_2Mg(SO_4)_2 \cdot 4H_2O$;

в – phosphate phases: ■ $MgHPO_4 \cdot 3H_2O$; ▼ $Mg(H_2PO_4)_2 \cdot 2H_2O$; x$Mg(H_2PO_4)_2$; ▲ $(NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O$

The presence of ammonium chloride confirms the flow interaction of potassium chloride with various phosphates and sulfates with the formation of potassium sulfate, potassium-ammonium and potassium-calciumdouble salts. These compounds as well as the unreacted potassium chloride are the main potassium-containing phases in the fertilizers.

Phase	Structural formulas
The main compounds containing phosphorus, nitrogen, potassium and calcium	KCl, $CO(NH_2)_2$, $CO(NH_2)_2 \cdot NH_4Cl$, $Ca(H_2PO_4)_2$, $CaHPO_4$, K_2SO_4,$CaSO_4$,$K_2Ca(SO_4)_2 \cdot H_2O$, $K_2Ca_5(SO_4)_6 \cdot H_2O$
	$NH_4H_2PO_4$, $(NH_4, K)H_2PO_4$
	NH_4Cl,$(NH_4)_2SO_4$, $(K,NH_4)_2SO_4$
Polyphosphates	$(NH_4PO_3)_n$, $(NH_4)_2H_2P_2O_7$, $Ca_2P_2O_7$, $CaH_2P_2O_7$, $NH_4CaHP_2O_7$
Magnesium-containing compounds	$MgSO_4 \cdot nH_2O$, $K_2MgCa(SO_4)_3 \cdot H_2O$, $Mg(H_2PO_4)_2 \cdot 2H_2O$
	$MgHPO_4 \cdot 3H_2O$, $NH_4MgPO_4 \cdot H_2O$

Table 10. Phase composition of NPKMg fertilizers

Magnesium compounds are represented by various sulfates and phosphates. According to the XPA data, the products may include magnesium sulfates $MgSO_4 \cdot nH_2O$ with $n = 1\text{-}7$. At the stage of fertilizers drying, these crystal hydrates are partly dehydrated, and therefore the presence of compounds with lower content of crystallization water was caused by partial dehydration. As dolomite was introduced into the reaction mixture at the initial stage, the process of formation of magnesium sulfate can be represented by the reaction equation:

$$MgCa(CO_3)_2 + 2H_2SO_4 \rightarrow MgSO_4 + CaSO_4 \cdot \cdot 2H_2O\downarrow + 2CO_2\uparrow. \qquad (55)$$

The magnesium sulfate hydrate crystallization occurs obviously in the course of evaporation of the suspension. One more process occurring when magnesium-containing fertilizers are obtained is the formation of acid magnesium phosphates or double ammonium-magnesium phosphates:

from dolomite (at the stage of acid decomposition or ammonization):

$MgCa(CO_3)_2 + 4H_3PO_4 \rightarrow Mg(H_2PO_4)_2 + 2CO_2\uparrow + Ca(H_2PO_4)_2 + 2H_2O$; (56)

$MgCa(CO_3)_2 + 2H_3PO_4 + H_2O \rightarrow MgHPO_4 \cdot 3H_2O\downarrow + CaHPO_4\downarrow + 2CO_2\uparrow$; (57)

$Mg(H_2PO_4)_2 + NH_3 + 3H_2O \rightarrow MgHPO_4 \cdot 3H_2O\downarrow + NH_4H_2PO_4$; (58)

$MgHPO_4 \cdot 3H_2O + NH_3 \rightarrow NH_4MgPO_4 \cdot H_2O\downarrow + 2H_2O$, (59)

from magnesium sulfate (at the stage of suspension evaporation and product drying):

$MgSO_4 + 2NH_4H_2PO_4 + 2H_2O \rightarrow Mg(H_2PO_4)_2 \cdot\cdot 2H_2O + (NH_4)_2SO_4$. (60)

The involvement of magnesium compounds in the processes of potassium chloride conversion is also confirmed by the formation of polyhalite $K_2MgCa(SO_4)_3 \cdot H_2O$. One of the well-known ways to obtain this triple salt is by its crystallization in evaporation of an aqueous solution containing potassium and magnesium sulfates and gypsum [14]. Polyhalite dissolved in water incongruently with formation of gypsum $CaSO_4 \cdot 2H_2O$ or syngenite $K_2Ca(SO_4)_2 \cdot H_2O$. Thus, magnesium contained in polyhalite is water-soluble:

$K_2MgCa(SO_4)_3 \cdot H_2O + H_2O \rightarrow K_2SO_4 + MgSO_4 + CaSO_4 \cdot 2H_2O\downarrow$, (61)

$K_2MgCa(SO_4)_3 \cdot H_2O \rightarrow MgSO_4 + K_2Ca(SO_4)_2 \cdot \cdot H_2O\downarrow$. (62)

It was found that there occur exchange interaction processes involving magnesium-containingcomponents, which are introduced into complex fertilizers as magnesium carbonates and sulfates and result in the formation of double magnesium-ammonium sulfates $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ and $(NH_4)_2Mg(SO_4)_2 \cdot 4H_2O$, magnesium hydro- and dihydrophosphates $MgHPO_4 \cdot 3H_2O$, $Mg(H_2PO_4)_2 \cdot 2H_2O$ and $Mg(H_2PO_4)_2$; and double magnesium-ammonium hydrophosphate $(NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O$. If magnesium sulfate is used as the starting magnesium-containing source component, the hydrates $MgSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 6H_2O$ are also identified in the products. In case of use as raw material for obtaining magnesium-containing complex NPK fertilizers dolomite, which is entered at the stage of acid decomposition of phosphate raw materials, the products may contain sulfates of magnesium$MgSO_4 \cdot nH_2O$ with $n = 1–7$. One more process occurring in production of magnesium-containing NPK fertilizers is the acid magnesium phosphate or double ammonium phosphate-magnesium formation. The involvement of magnesium compounds in the conversion of potassium chloride is confirmed by the formation of polyhalite $K_2MgCa(SO_4)_3 \cdot H_2O$. At the same time, regardless of the nature of magnesium-containing compounds, that is used to obtain magnesium-containing fertilizers based on ammonium phosphates, magnesium and phosphorus associated with it will be present in the final product in both water-soluble and water-insoluble forms, the ratio of which is determined by the value of the pH of the suspension at the stage of its ammonization.

Thanks

Thanks to my university teachers prof. Pechkovskii V.V. and prof. Vorobev N.I.

References

[1] Evenchik S. A., Brodskiy A. A., editors. *Tekhnologija fosfornykh i kompleksnykh udobreniy* (Technology of phosphoric and complex fertilizers). Moscow: Khimiya Publ.; 1987. 464 p.

[2] Pendplis Dz. *Mir sery, N, P, K.* (World of sulfa, N, P, K). 1994;3:52-59 (in Russian).

[3] Dormeshkin O.B., Vorobev N.I., Cherches G.X., Gavriluk A.N.:*Jurnal prikladnoy khimii* (Journal of applied chemistry). 2008;2:200–206 (in Russian).

[4] DormeshkinO.B., VorobevN.I., CherchesG.X., GavrilukA.N.:*Trudy BGTU* (Proceedings of BSTU). *Ser. III.* 2008;XV1:40-45 (in Russian).

[5] Sarbaev A.N., Gerbert G.P.: *Jurnal prikladnoy khimii* (Journal of applied chemistry). 1971;12:2638–2643 (in Russian).

[6] Kogan V.B., Fridman V.M., Kafarov V.V. *Spravochnik po rastvorimosti* (Solubility Reference). Moscow: ASUSSR.; 1963. Vol. 2. Book. 1. 946 p. (in Russian).

[7] JCPDS International Centre for Diffraction Data 2003.

[8] Korbrig D. *Fosfor: osnovy khimii, biokhimii, technologii* (Phosphorus: Fundamentals of chemistry, biochemistry, technology). Moscow: Mir; 1982. 432 p.

[9] GarskiI.M., VorobevN.I., MelnikovaR.J. *Svoystva I metody identifikazii veschestv v neorganicheskoy technologii* (The properties and methods of the identification of substances in inorganic technology).Minsk: Fond fundament. Issled.; 1996. 386 p.

[10] Schegrov L.N. *Fosfaty dbuchvalentnych metalov* (Phosphates of bivalent metals). Kiev: Naukovadumka; 1987. 297 p.

[11] Kucheryavyi V.I., Lebedev V.V. *Sintez I primenenie karbamida* (Synthesis and application of urea) Leningrad: Khimiya; 1970. 448 p.

[12] Kononov A.V., Sterlin V.N., Evdokimova L.I. *Osnovy technologii kompleksnych udobrenii* (The basic technology of complex fertilizers). Moscow: Khimiya Publ.; 1988. 320 p.

[13] Dormeshkin O.B., Vorobev N.I., Cherches G.X., Gavriluk A.N. *Vesti Nats. Acad. Nauk Belarusi*. .Ser. Khim. Nauk, 2010;3:98-106 (in Russian).

[14] Lehr J. R. Crystallographic Properties of Fertilizer Compounds. Chem. Eng. Bull;1967;6:37.

[15] Dormeshkin O. B., Vorobyov N. I., Pervinkin V. E. , Lyudkov A.A., Segen N.N., Kozlova A.M.(BY), Kazak V.G., Brizitskaya N.M., Grishaev I.G., Malyavin A.S.(RF) *Sposob poluchenija granulirovannogo slozhnogo udobrenija* (Way of getting of granulated complex fertilizers). Patent BY, no. 11661, 2008.

[16] Dormeshkin O. B., Vorobyov N. I., Cherches G. H., Gavrilyuk A.N. *Trudy BSTU* (Proceedings of BSTU). *Ser. III.* 2007;XV:3-8 (in Russian).

[17] Dormeshkin O. B., Vorobyov N. I. *Proizvodstvo bezchlornykh vodorastvorimykh kompleksnykh udobreniy* (Production of chlorine-free water soluble complex fertilizers). Minsk: BSTU, 2006. – 262 c.

[18] *Rol elementov v zhizni rastenii. Nauka. Novosti nauki i tekhniki* (The role of elements in plant life. Science. News of science and technology) [Internet]. 2014. Available from: http://enc.sci-lib.com/article 0000909.html. – [Accessed: 2014-08-08]

[19] Егоров В. С. Элементы питания и их роль в жизни растений. Информационный портал ландшафтно-художественной мастерской «Пейзаж» [Internet]. 2014. Available from: http://www.lan-dart.ru/03-uhod/b-sovet/03b0npk1.htm. – [Accessed: 2014-08-13]

[20] Mineev V.G., Sindyashkina R.I., Gryzlov V. P., et.al. Kompleksnye udobrenuya: Spravochnoe posobie (Integrated Fertilizers: Reference book), Moscow: Agropromizdat, 1986. 252 p.

[21] Norov A.M.: *Khimicheskaya tekhnologiya* (Chemical Technology). 2012;10:577–586 (in Russian).

[22] Begunov C.I. *Sposob poluchenija slozhnogo udobrenija* (Way of getting of complex fertilizers). Panent RF, no. 2233819, 2004.

[23] Abramov O.B. *Sposob poluchenija slozhnogo udobrenija* (Way of getting of complex fertilizers). Panent RF, no. 2294908, 2007.

Contents


More Books!
yes
I want morebooks!