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RESEARCHES OF PHYSICAL AND CHEMICAL FEATURES OF PROCESSES OF COMPLEX FERTILIZERS PRODUCING IN THE PRESENCE OF MAGNESIUM CONTAINING COMPONENTS

The physicochemical laws of the producing of magnesium-containing compound fertilizers based on superphosphate production and ammonium phosphate with the involvement of the Kovdorsky apatite concentrate and various types of magnesium-containing raw materials are described. The influence of the main technological parameters and the optimal conditions for combined decomposition of phosphate raw materials and technical product – dolomite, providing the producing of magnesium-containing fertilizers with specified chemical and physical properties with a content of magnesium (not more than 5 wt %) are determined.

New scientific facts about the rheological properties of phosphate suspensions, intermediate and end products, produced at different stages in the suspension of complex magnesium fertilizers based on various types of magnesium containing raw materials are received. It allows the researches to define the optimal conditions and the ways of introduction of magnesium, nitrogen and potassium containing components in the technological process. The physical and chemical mechanisms are examined. The chemical transformations activity at various stages producing of complex magnesium-containing fertilizers based on magnesium digestion of phosphate raw material and/or dolomite followed by carbamide introduction, gaseous ammonia neutralization, and the addition of magnesium sulfate and potassium chloride is defined.

The presented data formed the basis for developing a flexible resource-saving technology of the complex magnesium-containing fertilizers obtainment that provides the diversification possibilities, the obtainment of concentrated long-acting fertilizers with improved physical properties.

Key words: magnesium-containing fertilizers, complex fertilizers, phase mixture, phosphate raw material, magnesium, sulfuric acid, decomposition, neutralization.

Introduction. Increase of manufacture and consumption of complex magnesium-containing fertilizers is one of the stable global tendencies in manufacturing of miniral fertilizers. Increase in consumption of high analysis fertilizers, increase in productivity of agronomic crop and as a result decrease of nutrient elements, including magnesium make the problem of magnesium lose compensation more urgent.

Magnesium-containing fertilizers make positive effect on the back of NPK on the size of the crop and on its quality. According to a number of numerous agrochemical research introduction of magnesium, as a part of multicomponent fertilizers is the most efficient for open ground.

Inspite of the industrial base manufacturing the wide range of miniral fertilizers at OJSC “Gomel chemicals plant”, OJSC “Hrodno Azote”, OJSC “Belaruskalium”, there is no a manufacture of magnesium-containing fertilizers in the Republic of Belarus. Because of this OJSC “Gomel chemicals plant” sets up the construction of a new production department on manufacturing of magnesium sulfate with a capacity of 7000 tonnes per year and enlargement assortment of multicomponent magnesium-containing NP, NPK and NPKS fertilizers.

Within the frameworks of the establishment of one of the most important trends of fundamental and applied research, a comples work has been carried out aimed at studying of physicochemical base and development of technological principals of manufacturing of multicomponent magnesium-containing fertilizers with the help of raw-material base of the Republic of Belarus.

According to the literature data and technological process used by OJSC “Gomel chemicals plant” in manufacturing of miniral fertilizers and facilities, the most practical is a complex magnesium-containing fertilizer by means of sulfuric decomposition of phosphate and magnesium-containing raw-material with the following neutralizing of the forming phosphoric suspension, granulation and drying of end product.

In accordance with this, within the frame works of the research the following tasks are to be carried out:

– investigate physicochemical peculiarities of introduction of magnesium-containing components at different stages of manufacturing of compound magnesium-containing fertilizers on the basis of multicomponent systems forming during the manufacture of superphospates and ammonium phosphates;

Table 1

Influence of magnesium and phosphor-containing raw material on sulfuric acid decomposition ($C(H_2SO_4)$ = 45 wt %; T = 65ºC; t = 90 min; mass proportion of phosphate raw material : dolomite 1.5)

Order of introduction of reagents	Distribution of different forms P_2O_5, %, from $P_2O_{5\ initial}$			K_1	K_2	K_d
	wat.	dig. sed.	tot. sed.			
Mutual decomposition of dolomite and Covdor apatite	49.09	1.39	54.95	50.48	46.44	48.46
Decomposition of dolomite with following introduction of apatite in 15 min	65.14	1.23	39.31	66.37	61.92	64.15
Decomposition of apatite with following introduction of dolomite in 75 min	63.29	0.88	32.25	64.17	68.63	66.40

Note. $m(P_2O_{5init})$ – mass of P_2O_5 in a portion of apatite; $m(P_2O_{5\ wat})$ – mass of water-soluble P_2O_5; $m(P_2O_{5\ dig.sed})$ and $m(P_2O_{5\ tot.sed})$ – mass of digestible and total P_2O_5 in dried out sediment; $K_1 = (m(P_2O_{5\ wat}) + m(P_2O_{5\ dig.sed})) / m(P_2O_{5\ init})$; $K_2 = 1 – (m(P_2O_{5\ tot.\ sed}) – m(P_2O_{5\ dig.sed})) / m(P_2O_{5\ init})$; $K_d = (K_1 + K_2) / 2$.

– investigate phase and mineralogical composition, reologic and physicomechanical properties of the products forming at different stages of manufacture of complex magneum-containing fertilizers depending on the kind and way of introduction of magnesium-containing raw-material;

– investigate influence of certain technological parameters and kind of magnesium-containing raw-material during the manufacture of complex fertilizers.

Main part. According to the analysis of the known methods of manufacture of complex magnesium-containing fertilizers, the most interesting method is based on mutual decomposition of polyhalite and phosphate by nitric acid with the following mixture of nitric acid extract with carbamide and potassium chloride [1]. However, as there is no production of nitrophosphate in the Republic of Belarus, authors studied the possibility of introduction of magnesium-containing raw material at different stages of decomposition of phosphatic raw material with sulfuric and phosphoric acids.

As a basic brand of fertilizers, brand 15:15:15:5 was chosen as one of the most popular brand of mineral fertilizers in the world market, which is a balanced full complex magnesium-containing fertilizer.

During the research influence of conditions of introduction of magnesium-containing raw material, duration and temperature of the decomposition process and concentration of sulfuric acid on the process of acid decomposition and basic technological parameters have been studied.

According to the data, represented by Table 1, mutual introduction of dolomite with phosphatic raw material has a negative impact on the content of different forms P_2O_5, which decreases from 65.14% to 49.09% and on general level of decomposition of phosphatic raw material, which decreases from 66.4% to 48.46%, that is stipulated by magnesium in dolomite. Other researchers also have noted its negative impact on the process of acid decomposition of phosphatic ores [2, 3].

Analysis of the obtained data makes it possible to make a conclusion that it is necessary to introduce dolomite into suspension which is formed after decomposition of the main part of apatite into one of the following sections of the reactor. During the mutual introduction of the initial phosphor and magnesium-containing raw material, norm of consumption of sulfuric acid has been calculated in accordance with a condition of mutual decomposition of apatite and dolomite. That is why in case of introduction of apatite at the beginning of the process, real amount of sulfuric acid turned out to be in abundance which contributed maximal level of decomposition of raw material (K_d = 66.40%).

Results of the research of the influence of the temperature on total level of decomposition of apatite with dolomite are in Table 2. Maximal level of decomposition of 96.37% is achieved at the temperature of 90°C, however the process of decomposition at the above mentioned temperature was accompanied by considerable solidification of the suspension up to the complete lose of fluidity. This happens due to the negative influence of the forming magnesium phosphates, which is also proved by the literature data. Introduction of extra amount of liquid necessary for normal fluidity providing possibility of the following processing of suspension is not desirable as it can be the result of wataer balance abnormality and considerable increase of expenditure of energy on its following removal at the stage of drying out [4]. Taking into account the above mentioned, optimal temperature is 80°C, at which the level of decomposition is 91.26%, under the condition of high level of fluidity of the forming suspension.

It has been established that during the first 90 min decomposition of the fundamental amount of the raw material takes place and under further increase of decomposition duration to 180 min and over solidification of suspension to its complete lose of fluidity is observed. This is explained by the increase and forming of calcium sulphate particles forming during decomposition of phosphate raw material and dolomite, that makes the following processing of the forming suspension impossible in accordance with the existing technology. Thus, optimal duration of the process should be 90–120 min.

However, even under these conditions, maximal level of decomposition with using of sulfuric acid only, is not over 90–92%. To acieve the composition of phosphor of the specified brand of fertilizers in accordance with technological balance it is necessary to introduce extra amount of phosphor acid and it is necessary to study the process of decomposition of magnesium and phosphor-containing raw material with the mixture of sulfuric and phosphor acid together. The results of the research are in Tables 3–4. Covdor apatite and dolomite of the field "Ruba" have been used as the initial raw material, concentration of sulfuric acid in liquid phase varied from 25 to 63.62 wt %, phosphor – from 10 to 25 wt %, duration of the decomposition process – from 60 to 240 min.

Analysis of the obtained data makes it possible to make a conclusion that under the mutual decomposition by the mixture of acids the coefficient of decomposition increases in comparising with decomposition only by sulfuric acid from 90–92% to 97.55% (Table 3). Thus, the regime of acid decomposition, under which there is the maximal coefficient of decomposition of phosphate raw material, is organizing of the stage process: initial decomposition by the mixture of sulfuric and phosphor acids of phosphate raw material under the concentration of sulfuric acid in a liquid phase of 55 wt %, phosphor – 22 wt %, the following introduction of magnesium-containing raw material (dolomite) into one of the last section of the reactor. Temperature of decomposition is 80°C, total duration of decomposition stage is 90–120 min. Under these conditions the total level of decomposition of raw material is 96.85%.

Table 2

Influence of the temperature on the process of sulfuricacid decomposition of magnesium and phosphor-containing raw material ($C(H_2SO_4)$ = 45 wt %; *t* = 90 min; introduction of dolomite in 75 min after the beginning of the process, mass proportion of phosphate raw material: dolomite 1.5)

Temperature, ºC	Distribution of different forms of P_2O_5, % from $P_2O_{5\ init}$			K_1	K_2	K_d	Viscosity, mPa · s
	wat.	dig. sed.	tot. sed.				
65	63.29	0.88	32.25	64.17	68.63	66.4	1,298
70	87.12	0.59	11.5	87.71	89.09	88.4	1,375
80	92.01	0.24	9.97	92.25	90.27	91.26	1,543
90	95.19	0.6	3.66	95.79	96.94	96.37	3,157

Table 3

Influence of concentrated sulfuric acid and phosphor acid in liquid phase on decomposition of the initial raw material by the mixture of acids (*T* = 80ºC; *t* = 90 min)

Concentration of the acid in the liquid phase, wt %		Different forms of P_2O_5 in sediment, % from $P_2O_{5\ init}$		K_2, %
sulfuric	phosphor	$P_2O_{5\ tot}$	$P_2O_{5\ dig}$	
25	10	8.05	1.08	93.03
35	14	3.01	0.56	97.55
45	18	27.52	1.11	73.59
55	22	4.8	1.13	96.33
63.62	25	8.04	0.47	92.43

Table 4

Influence of the process duration on decomposition of the initial raw material by the mixture of sulfuric and phosphor acids ($C(H_2SO_4)$ = 55 wt %; $C(H_3PO_4)$ = 22 wt %; *T* = 80ºC)

Duration, min	Different forms of P_2O_5 in sediment, % from $P_2O_{5\ init}$		K_2, %
	$P_2O_{5\ tot}$	$P_2O_{5\ dig}$	
60	25.56	0.74	75.18
90	4.8	1.13	96.33
120	3.74	0.59	96.85
240	3.95	0.98	97.03

Reologic properties of inter and finished products are one of the most important factor at the development of the technology of obtaining multicomponental fertilizers determining conditions of introduction of separate components and its equipment. That is studying of reological properties of suspensions depending on the conditions of introduction of magnesium, nitrogen and potassium-containing components for different kind of magnesium-containing raw material.

It is known that introduction of carbamide promotes improving of reological properties [4]. That is carbamide can be introduced at any stage. However, it is better to introduce carbamide into a sour suspension after the stage of decomposition characterizing by the smallest viscosity and maximal fluidity. Conversion processes at introduction of potassium chloride into suspension has a considerable influence on reological properties of suspensions. However, this is not always results to the loss of fluidity. At introduction of potassium chloride into a sour suspension it is possible to observe a reaction of exchange decomposition with forming of HCl, that is the most undesirable as it is connected with deterioration of the quality of the product by sharp increase of corrosive damage of equipment. To exclude possibility of the above mentioned processes it is suggested to introduce KCl into a partialy neutral suspension ($NH_3 : H_3PO_4 = 0.7–0.9$).

According to completed comples of the research the following sceme is offered: stage acid decomposition of phosphate or magnesium-containing raw material by the mixture of sulfuric and phosphor acids, introduction of nitrogen-containing component into a phosphate suspension composing ammonia and carbamide,introduction of sevenwaters magnesium sulphate and potassium chloride into partial or completely neutral suspension.

Analysis of the results of the research of reological properties of suspensions forming at all stages of technological process, at its realization under the above mentioned conditions, shows their improvement at introduction of carbamide, that can be found in literature on sdudying of reological properties of complex carbamide-containing fertilizers of the well-known brands [4], and also magnesium sulphate. At introduction of magnesium sulphate effect of viscosity decrease is more considerable due to the introduction of a large amount of water with crystalline hydrate.

It is established that conversion processes at introduction of ammonia and potassium chloride into suspension has a negative impact on reologic properties of suspensions (viscosity increases, fluidity decreases). The sharpest increase of viscosity of suspensions (from 10 to 100 timews) is observed at introduction of potassium chloride, that is why it is necessary to introduce it into a partialy neutralised suspension or at the stage of drying out and granulation together with retur.

Thus, there are three possible options of technical process realization with different ways and succession of reagents introduction, namely:

1) after acid decomposition of Covdor apatite concentrate it is necessary to introduce carbamide into phosphate suspension before ammonation, that has positive effect on mobility of suspension with the following introduction of the whole amount of magnesium sulphate and also potassium chloride;

2) during acid decomposition of dolomite, where all the following stages are carried out by analogue with the previous variant, only the last third of potassium chloride to avoid solidification of suspension should be introduced into a drum granulator-dryer together with retur;

3) after acid decomposition of dolomite all the next stages are carried out by analogue with the previous variant, at this, full amount of potassium chloride can be introduced into suspension and introduced amount of magnesium sulphate has a positive influence on mobility of suspension.

Methods of chemical and X-ray photography analysis have been used to establish phase composition of fertilizers and conversional processes carrying out under the influence of magnesium. According to the data of chemical analysis, phosphor in the obtained fertilizers is in the form of watersoluble and digestible phosphates. Besides, the former and later are in ortho- and polyforms.

The largest concentration of ammonium nitrogen in a solution prepared for establishment of digestible phosphates in comparison with water solution shows that there are double salts of ammonium with calcium or magnesium in fertilizers together with watersoluble compounds of ammonium.

During the application of magnesium-containing supplier of magnesium sulphate as the initial component, the magnesium in the obtained fertilizer is watersoluble, during the application of dolomite – there are also non-watersoluble compounds of magnesium in the products, though, decomposition of dolomite by the mixture of sulfuric and phosphor acids takes place almost completely. Possibly, it is connected with the place of introduction of a magnesium-containing compound determining the next conversion processes.

As it was established by the researcher earlier, during the obtaining of NPK of fertilizers at some stages of the process there are different chemical interaction including exchange reactions of potassium chloride with the salts of ammonium, formation of double salts (phosphates and sulphates) and also mutual hydrolysis of carbamide and dehydration of sour phosphates and phosphor acid with the formation of polyphosphates [5]. Within the course of these reactions, obtaining fertilizers are a multicomponent system and introduction of compounds of magnesium without dout will promote extra processes and phase composition of fertilizers.

The results of X-ray analysis of the obtained NPKMg of fertilizers are in Table 5. According to the obtained data, it can be concluded that sour orthophosphates of calcium, ammonium, potassium ammonium are the main phosphate phases in the obtained fertilizers. Out of polymer phosphates presence of polyphosphates of ammonium and diphosphates of ammonium, calcium, calcium-amminium is possible. Identification of these compounds corresponds to the results of the chemical analysis on the presence of watersoluble and digestible ortho and polyphosphates and also non-watersoluble salts of ammonium in fertilizers.

Carbamide, ammonium chloride, product of their interaction $CO(NH_2)_2 \cdot NH_4Cl$, phosphates and ammonium sulphates, double salts of potassium-ammonium and potassium-calcium are the main nitrogen-containing phases. The presence of ammonium chloride proves the reaction of interaction of potassium chloride with different phosphates and sulphates with the formation of potassium sulphate, double salts of potassium-ammonium and potassium-calcium. The above mentioned compounds and also unreacted potassium chloride are the main potassium-containing phases in the obtaining fertilizers.

Magnesium compounds can be presented in the obtaining fertilizers by different sulphates and phosphates. According to the X-ray analysis, magnium sulphates $MgSO_4 \cdot nH_2O$ c $n = 1–7$ can compose the products. At the stage of the drying out of the fertilizers there are partial dehydration of these crystallinehydrates, that is why the presence of the compounds with less content of crystal water is the most probable.

As dolomite was introduced into the reaction mixture at the initial stage (after decomposition of phosphate raw material) the process of formation of magnesium sulphate can be visualized by the equation of the reaction

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

Crystallyzation of hydrates of magnesium sulphate probably takes place during the process of evaporation of the suspension.

Formation of sour magnesium phosphates or double phosphates of ammonium-magnesium: from dolomite (at the stage of acid decomposition or ammonization) is one of the process taking place at the obtaining of magnesium-containing fertilizers:

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

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

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

$$MgHPO_4 \cdot 3H_2O + NH_3 \rightarrow$$
$$\rightarrow NH_4MgPO_4 \cdot H_2O\downarrow + 2H_2O.$$

From magnesium sulphate (during the evaporation of the suspension and drying out of the product):

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

Formation of polyhalite $K_2MgCa(SO_4)_3 \cdot H_2O$ proves participation of magnesium compounds in the process of the conversion of potassium chloride. According to the researchers [3] crystallization during the evaporation of water solution containing potassium sulphates, magnesium sulphates and gypsum is one of the ways of obtaining of this triple salt:

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

Table 5

Phase composition of NPKMg of fertilisers

Phases	Number of variant of obtaining NPKMg fertilizer		
	1	2	3
Main compounds containing phosphor, nitrogen, potassium, 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, $(NH_4)_2SO_4$, $(K, NH_4)_2SO_4$		NH_4Cl, $(K, NH_4)_2SO_4$
Polyphosphates	NH_4PO_3, $(NH_4)_2H_2P_2O_7$, $Ca_2P_2O_7$, $CaH_2P_2O_7$, $NH_4CaHP_2O_7$		
Magnesium-containing compounds	$MgSO_4 \cdot nH_2O$, $K_2MgCa(SO_4)_3 \cdot H_2O$, $Mg(H_2PO_4)_2 \cdot 2H_2O$		
		$MgHPO_4 \cdot 3H_2O$, $NH_4MgPO_4 \cdot H_2O$	

Polyhalite incongruently dissolves in water with gypsum forming $CaSO_4 \cdot 2H_2O$ or syngenite forming $K_2Ca(SO_4)_2 \cdot H_2O$, thus, magnesium containing in polyhalite is watersoluble:

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

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

Conclusion. As a result of the completed research complex, the following data have been obtained: chemical and reological properties of suspensions, inter and finished products forming at different stages during the obtaining of complex magnesium-containing fertilizers on the base of different kind of magnesium-containing raw material, which helped to determine a phase composition of the product and validate optimal conditions and ways of introduction of magnesium, nitrogen and potassium-containing components into technological process. Maximal positive effect of viscosity decrease is achieved at the introduction of magnesium as a component of sevenwater magnesium sulphate and nitrogen as a component of carbamide into the technological process.

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