

Study of Conversion Processes in Multicomponent Systems in Manufacture of Integrated Magnesium-containing Fertilizers

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Abstract—Conversion processes occurring upon introduction of various kinds of magnesium-containing raw materials in separate technological stages of fabrication of integrated NP fertilizers based on ammonium phosphates and NPK fertilizers produced by acid decomposition of phosphate raw materials were studied. It was found that there occur exchange interaction processes yielding double magnesium-ammonium sulfates, magnesium hydro- and dihydrophosphates, and double magnesium-ammonium hydrophosphate. The involvement of magnesium chlorides in the conversion processes is confirmed by the formation of polyhalite.

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The quality of mineral fertilizers manufactured by all plants in Belarus, Russia, and other CIS countries is subject to the corresponding regulatory documents: GOST (State Standards), TU (Technical Specifications), etc. In this case, the main parameters controlled by these documents are the content of nutrient elements (and in the first place, nitrogen, phosphorus, and potassium) and physical properties of a product. At the same time, to enter foreign markets in conformity with the requirements on the territory of EU countries, these products (substances) are to be registered in conformity with REACH regulation whose fundamental distinctive feature is the need to specify all the identification parameters of the substances, including the chemical composition (together with impurities and additives) and the molecular and structural formula of single- and multicomponent substances, the EU designation, etc. According to the experience, the technical documentation available at plants, including technological regulations and inspection reports, have no required evidence. The data reported by separate authors markedly differ. At the same time it has been found that manufacture of integrated fertilizers involve various chemical interactions in separate stages, including those of granulation and drying stages; exchange reactions of potassium chloride with ammonium salts, formation of

double salts (phosphates and sulfates), joint hydrolysis of carbamide, and dehydration of acid phosphates and phosphoric acid to give polyphosphates [1-3]. When calcium chloride is introduced into partly or fully neutralized phosphoric acid suspension containing calcium sulfates, sulfur compounds of varied composition and structure are additionally formed: syngenite $K^2Ca(SO_4)_2 \cdot 2H_2O$, gorceyite $K^2Ca^5(SO_3)_6 \cdot 6H_2O$, double potassium-ammonium dihydrophosphates and sulfates, and potassium dihydrophosphate. Depending on the process conditions and on the relative amounts of reagents, carbamide introduced into the process as a nitrogen-containing component is present in the product both individually and as the compound $CO(NH_2)_2 \cdot H_2O \cdot NH_4Cl$. In addition, the formation of an adduct of calcium sulfate with tetracarbamide, $CaSO_4 \cdot H_2O \cdot 4CO(NH_2)_2$ is identified.

One of stable tendencies in the market of integrated NP and NPK fertilizers is that the manufactured amounts of magnesium-containing fertilizers grow. 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. For example, it has been found at the Research Institute for Fertilizers and Insectofungicides (Russia) for a number of cultures (fall rye, buckwheat, panic, corn, etc.) that 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 a larger crop, but also in a higher starch content of potatoes and sugar content of beet [4]. Therefore, most of foreign manufacturers have in their assortment integrated magnesium fertilizers, with the content of magnesium being as high as 8-10%. Apparently, introduction of magnesium compounds will be accompanied by additional chemical processes and make the phase composition of the fertilizers more complex.

The goal of the study was to examine conversion processes occurring upon addition of various kinds of magnesium-containing raw materials in separate technological stages of production of integrated NP and NPK fertilizers.

EXPERIMENTAL

The role of the base brand of an NP fertilizer was played by a fertilizer based on ammonium phosphates, produced by ammonization of extraction phosphoric acid to prescribed pH values by the conventional technology of ammophos fabrication [5]. The amount of the magnesium-containing additive being introduced was calculated on the basis of magnesium content in the target product of 2 and 5 wt % in terms of MgO. In the case of introduction of magnesium compounds in amounts of 2 and 5 wt % in terms of MgO, the ammonization of the phosphoric acid suspension was performed to pH 4.5 and 4.1, respectively. As the magnesium-containing additive served basic magnesium carbonate with 41.5 wt % MgO and magnesium sulfate, both of pure grade.

As the base brand of an NPK fertilizer was chosen the 15 : 15 : 15 brand, which is one of mineral fertilizers most demanded in the world market and is a balanced full integrated 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 the first quarter of 2015 [6]. The amount of the magnesium-containing additive being introduced was 5 wt % in terms of MgO in the product. As magnesium-containing additive serves lime (dolomite) dust produced by Dolomit OAO (Belarus) with a total mass fraction of calcium and magnesium carbonates of no less than 80 wt %. Dolomite was introduced in the stage of the acid decomposition of

phosphate raw materials by the double-stage scheme developed with the participation of the author. This scheme provide under the optimal conditions reaching the maximum degree of decomposition of raw materials in the optimal technological mode. As phosphate raw materials served Kovdor apatite concentrate containing (wt %): P₂O₅ 38.2, CaO 52.92, MgO 1.93, Fe₂O₃ 0.39, Al₂O₃ 1.26, F 1.1, and moisture 0.42.

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 photocolometric method with a phosphorus-vanadium-molybdenum complex. The 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 precipitates and solutions being formed was determined by complexometry, and that of potassium, by flame photometry.

As the result of an analysis was taken the arithmetic mean of parallel determinations, 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 ± 0.01 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).

The X-ray phase analysis (XPA) was made with a Bruker D8 Advance X-ray diffractometer (United States). The interplanar spacings were calculated by the Wolf-Bragg law. The database [7] was used in identification of the X-ray diffraction patterns.

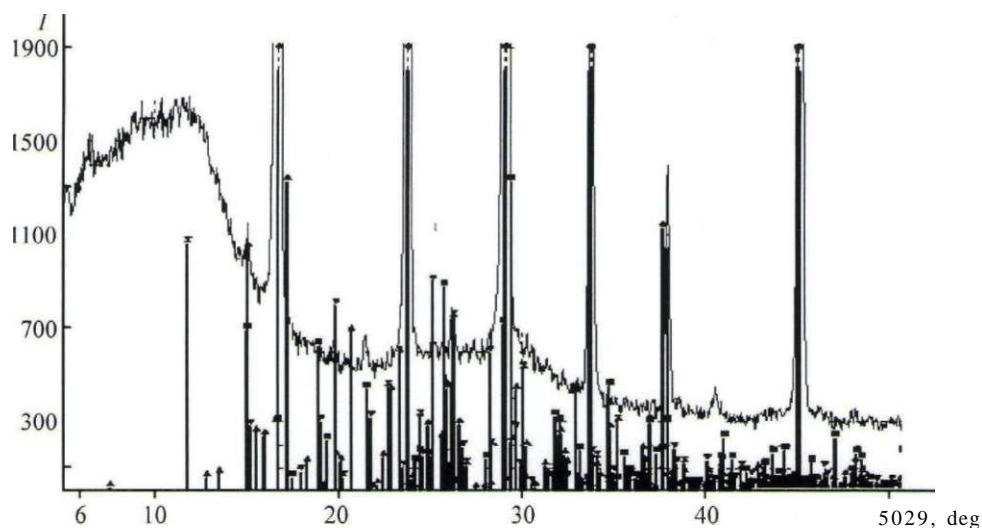


Fig. 1. X-ray diffraction pattern of a fertilizer with addition of basic magnesium carbonate. (*I*) Intensity and (2θ) Bragg angle; the same for Fig. 2. Phase: (*I*) $\text{NH}_4\text{H}_2\text{P}_2\text{O}_7$; magnesium-containing phases: (2) $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, (J) $\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$, (4) $\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2$, and (5) $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$.

RESULTS AND DISCUSSION

The results of a chemical analysis of the resulting NP fertilizers for the content of various forms of phosphorus and magnesium on using various kinds of magnesium-containing additives are listed in Table 1.

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 fraction 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 ammonium dihydrophosphate $\text{NH}_4\text{H}_2\text{P}_2\text{O}_7$ is the main phase of the resulting fertilizers, which seems to be quite reasonable

(Figs. 1 and 2). 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 Figs. 1 and 2 are given for fertilizers containing 5% MgO. The reflections of impurities present in the product obtained with addition of basic magnesium carbonate (Fig. 1) are also identified in the X-ray diffraction pattern of the product obtained upon addition of magnesium sulfate (Fig. 2). At the same time, the X-ray diffraction pattern of the latter also shows higher intensity impurity-related reflections at $2\theta = 11-12$, $20-22$, and $28-30^\circ$.

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

Table 1. Content of selected components in magnesium-containing integrated NP fertilizers

Magnesium-containing additive	Magnesium-containing additive			
	P_2O_5		Mj ₂ O	
	water-soluble	accessible	water-soluble	total
Basic magnesium carbonate	46.0	56.3	3.7	5.7
Magnesium sulfate	42.3	46.2	3.8	5.5
	48.6	51.0	0.2	2.0

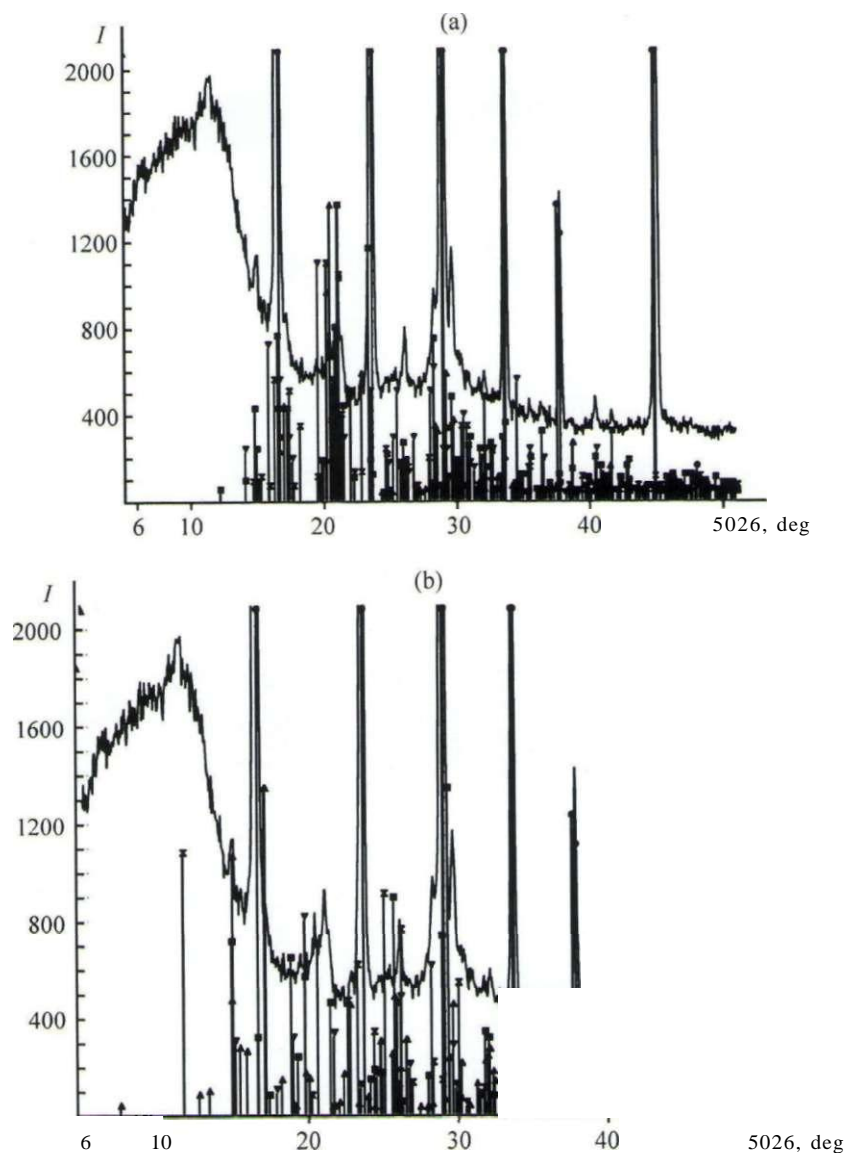


Fig. 2. X-ray diffraction pattern of a fertilizer with addition of magnesium sulfate. Phase: (1) $\text{NH}_4\text{H}_2\text{PO}_4$; (a) sulfate phases: (2) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, (3) $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, (4) $(\text{NH}_4)_2\text{SO}_4$, (5) $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and (6) $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$; (b) phosphate phases: (7) $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, (8) $\text{Mg}(\text{H}_2\text{P}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$, (9) $\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2$, and (10) $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$.

dihydrophosphates $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{P}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2$, and double magnesium-ammonium hydrophosphate $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Figs. 1 and 2).

These compounds can be formed by the following chemical reactions:

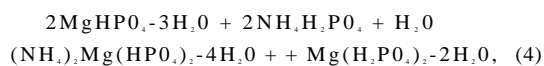
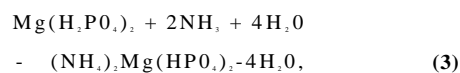
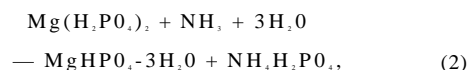
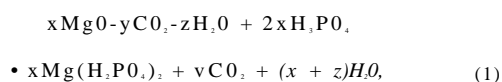
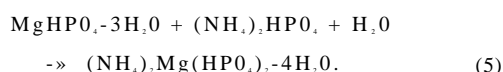


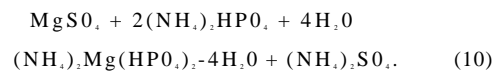
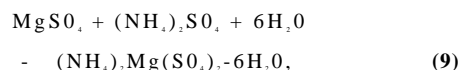
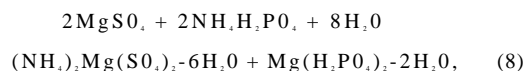
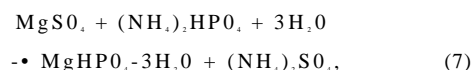
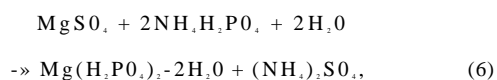
Table 2. Phase composition of NPKMg fertilizers

Phase	Structural formula
Main compounds containing phosphorus, nitrogen, potassium, and calcium	KCl, CO(NH ₂) ₂ , CO(NH ₂) ₂ -NH ₄ Cl, Ca(H ₂ PO ₄) ₂ , CaHPO ₄ , K ₂ SO ₄ , CaSO ₄ , K ₂ Ca(SO ₄) ₂ -H ₂ O, K ₂ Ca ₃ (SO ₄) ₆ -H ₂ O NH ₄ H ₂ PO ₄ , (NH ₄ , K)H ₂ PO ₄ NH ₄ Cl, (NH ₄) ₂ SO ₄ , (K, NH ₄) ₂ SO ₄
Polyphosphates	(NH ₄ PO ₃) _n , (NH ₄) ₂ H ₂ P ₂ O ₇ , Ca ₂ P ₂ O ₇ , CaH ₂ P ₂ O ₇ , NH ₄ CaHP ₂ O ₇
Magnesium-containing compounds	MgSO ₄ ·xH ₂ O, K ₂ MgCa(SO ₄) ₂ -H ₂ O, Mg(H ₂ PO ₄) ₂ -2H ₂ O MgHPO ₄ -3H ₂ O, NH ₄ MgPO ₄ -H ₂ O



When the phase composition of the product obtained with 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 found that MgSO₄·7H₂O and MgSO₄·6H₂O are the most probable phases (Fig. 2). However, the reflections at 2θ = 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 (NH₄)₂SO₄ and double magnesium-ammonium sulfates (NH₄)₂Mg(SO₄)₂·6H₂O and (NH₄)₂Mg(SO₄)₂·4H₂O. 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 Fig. 2b 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.

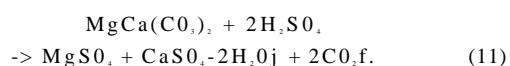
The data obtained suggest that, upon introduction of magnesium even in the form of a soluble sulfate, it is partly converted to give ammonium sulfate, water-insoluble magnesium sulfates, and double magnesium-ammonium sulfates by the following schemes



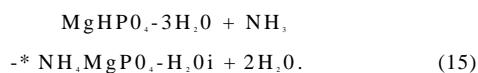
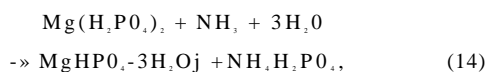
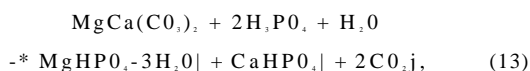
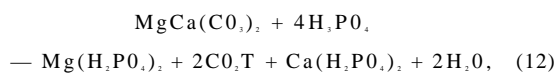
The results of an X-ray phase analysis of the resulting NPKMg fertilizers, listed in Table 2, suggest that the main phosphate phases in the fertilizers are acid calcium, ammonium, and ammonium-potassium orthophosphates. From among polymeric phosphates, ammonium polyphosphates and ammonium, calcium, and 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: carbamide; ammonium chloride; the product of interaction between these two, CO(NH₂)₂·NH₄Cl; ammonium phosphates and sulfates, and double ammonium salts. The presence of ammonium chloride confirms that potassium chloride reacts with various phosphates and sulfates to give potassium sulfate, and potassium-ammonium and potassium-calcium double salts. These compounds, as well as the unreacted potassium chloride are the main potassium-containing phases in the fertilizers.

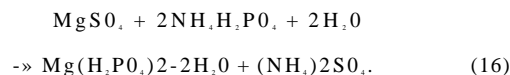
Magnesium compounds are represented by various sulfates and phosphates. According to XPA data, the products can contain magnesium sulfates $MgSO_4 \cdot nH_2O$ with $n = 1-7$. When fertilizers are dried, these crystal hydrates are partly dehydrated, and, therefore, the presence of compounds with lower content of crystallization water is more probable. Because dolomite was introduced into the reaction mixture in the initial stage, the process in which magnesium sulfate is formed can be represented by the reaction equation



The crystallization of magnesium sulfate hydrates apparently occurs 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 (in the stage of acid decomposition or ammonization)

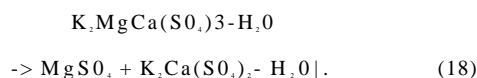
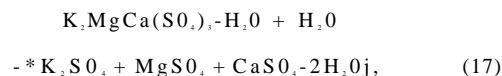


and from magnesium sulfate (in the stage of suspension evaporation and product drying):



The involvement of magnesium compounds in the processes in which potassium chloride is converted is also confirmed by the formation of polyhalite $K_2MgCa(SO_4)_3 \cdot H_2O$. According to [8], one of ways to obtain this ternary salt is by its crystallization in evaporation of an aqueous solution containing potassium and magnesium sulfates and gypsum. Polyhalite is incongruently dissolved in water to give gypsum $CaSO_4 \cdot 2H_2O$ or

syngenite $K_2Ca(SO_4)_2 \cdot H_2O$. Thus, magnesium contained in polyhalite is water-soluble:



CONCLUSIONS

(1) It was found that there occur exchange interaction processes involving magnesium-containing components, which are introduced into integrated 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 component, the hydrates $MgSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 6H_2O$ are also identified in the product.

(2) If dolomite serving as a magnesium-containing raw material in production of integrated NPK fertilizers is introduced in the stage of acid decomposition of phosphate raw materials, the products may contain magnesium sulfates $MgSO_4 \cdot nH_2O$ with $n = 1-7$. One more processes occurring in production of magnesium-containing NPK fertilizers is that in which acid magnesium phosphates or double magnesium-ammonium phosphates are formed. The involvement of magnesium compounds in the conversion of potassium chloride is confirmed by the formation of polyhalite $K_2MgCa(SO_4)_3 \cdot H_2O$.

(3) Irrespective of the nature of a magnesium-containing compound used to obtain magnesium-containing fertilizers based on ammonium phosphates, magnesium and magnesium-bound phosphorus will be present in the final product in both water-soluble and water-insoluble forms, the relative amounts of which are determined by the pH of a suspension in the stage of its ammonization.

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