THE EFFECT OF IMPURITY COMPOSITION OF PHOSPHATE ROCK ON THE TECHNOLOGY OF ITS PROCESSING AND PROPERTIES OF FINAL PRODUCTS

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ABSTRACT. The composition of phosphate rock and the impurities contained in it have a determining effect on the choice of processing technology, production capacity, consumption factors, properties of the final product and other important parameters. When developing methods for processing phosphate raw materials in target products, it is very important to study and take into account the impurities contained in it and their effect on technology. In this article, based on the summary of scientific and production experience and the latest researches by JSC "NIUIF", the oldest and the only scientific & research institute in Russia on phosphorus-containing fertilizers, the influence of impurities containing carbonates, calcium, iron, aluminum, magnesium, fluorine, chlorine, sodium, potassium, rare earths, silicon dioxide on process parameters of processing phosphate raw materials and properties of the final product is considered in detail. The methods of finding the optimal options for organizing of technological process of processing phosphate raw materials and stabilization of the quality of products are shown.

Keywords: phosphate rock, impurities, wet phosphoric acid, phosphorus-containing fertilizers, granule structure, caking, granule strength

ВЛИЯНИЕ НА СЪДЪРЖАНИЕТО НА ПРИМЕСИ ВЪВ ФОСФАТНИТЕ СКАЛИ ВЪРХУ ТЕХНОЛОГИЯТА ЗА ПРЕРАБОТКАТА ИМ И СВОЙСТВАТА НА КРАЙНИТЕ ПРОДУКТИ
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РЕЗЮМЕ. Съставът на фосфатната скала и съдържащите се в нея примеси имат определящ ефект върху избора на технология за обработка, производствен капацитет, фактори на потребление, свойства на крайния продукт и други важни параметри. При разработването на методи за преработка на фосфатни суровини в крайни продукти е много важно да се проучат и да се вземат предвид съдържащите се в тях примеси и техният ефект върху технологията. В тази статия, въз основа на научния и производствения опит и най-новите изследвания на "НИУИФ", най-старият и единствен научно-изследователски институт в Русия за торове, съдържащи фосфор, се разглежда въздействието на примеси, съдържащи карбонати, калций, желязо , алуминий, магнезий, флуор, хлор, натрий, калий, редки земни елементи, силициев диоксид върху параметрите на процеса на преработка на фосфатни суровини и свойствата на крайния продукт. Описани са методите за намиране на оптимални възможности за организиране на технологичния процес на преработка на фосфатни суровини и стабилизиране на качеството на продуктите.

Ключови думи: фосфатни скали, примеси, мокра фосфорна киселина, торове съдържащи фосфор, структура на гранулата, спичане, здравина на гранулата

Introduction

Phosphorus is quite a common element, its content in the earth's crust according to various estimates is 0.08-0.12% of its mass. In total, more than 120 phosphate minerals are known in nature, mostly chemically stable, insoluble in water and in soil solutions (Kopylev, 1981). The minerals of the apatite group are of the largest industrial value among them, as well as phosphorites that form large deposits.

Like any natural mineral substance, phosphate rock (of apatite and phosphorite nature), besides the main target component (phosphorus, usually expressed through percentage of P_2O_5 content), contains also various impurities: calcium and magnesium carbonates, compounds of iron, aluminum, silicon, fluorine, sodium, potassium, chlorine, strontium, rare earth elements, organic substances, etc. Many of these impurities, even after beneficiation of phosphate rock, have a significant influence on choosing the processing technology, the output of the target component, process mode parameters, capacity, consumption ratios of raw materials and energy resources and other indices.

Main exposition

The increased content of carbonates leads to intense foaming while processing phosphate rock via acidic methods, due to the release of carbon dioxide CO_2, especially in combination with organic impurities. This leads to reduction of operation volumes of the reactors, malfunction of the pumps, and as a result, disruption of the entire technological process. In practice, it was confirmed that phosphate rock with CO_2

content of more than 8% cannot be practically used to produce wet phosphoric acid (WPA) without special methods and means of defoaming applied (Evenchik and Brodskiy, 1987).

The specific consumption of sulfuric acid in the production of WPA (and, consequently, the production economy to some extent), and also the specific rate of production waste – phosphogypsum, depend on the calcium content in the phosphate rock.

The compounds of iron and aluminum (sesquioxides) are perhaps the most harmful impurities (especially iron), which largely determine the suitability of phosphate rock for acid processing. In sulfuric acid decomposition of phosphates with higher iron content, an excessive amount of sulfuric acid is consumed, and the recovery of P_2O_5 is greatly reduced due to precipitation of insoluble iron phosphates (P_2O_5 retrogradation). In addition, filtration of the extraction slurry gets worse. Aluminum phosphates are more soluble than iron phosphates, and therefore, are less likely to contribute to retrogradation. The content of sesquioxides in phosphate rock is limited not by their absolute content, but by their ratio to the content of P_2O_5. In practice it was confirmed that in phosphate rock suitable for sulfuric acid processing, the ratio of Fe_2O_3 content to P_2O_5 content should be not more than 8, that is:

$$\frac{C_{Fe_2O_3}}{C_{P_2O_5}} \times 100 \leq 8 \qquad (1)$$

The content ratio of the sum of sesquioxides ($Fe_2O_3 + Al_2O_3$) to P_2O_5 should be not more than 12 (Kopylev, 1981; Evenchik and Brodskiy, 1987), that is:

$$\frac{C_{(Fe_2O_3+Al_2O_3)}}{C_{P_2O_5}} \times 100 \leq 12 \qquad (2)$$

While processing phosphates by nitric acid and hydrochloric acid methods, the content of sesquioxides is less important due to its lower solubility in these acids (Evenchik and Brodskiy, 1987; Kononov et al., 1988), but it also leads to losses of P_2O_5. That's why, phosphate rock with ratio Fe_2O_3 to P_2O_5 of more than 12 is also unsuitable for nitric acid decomposition (Kopylev, 1981). For production of thermal phosphates by sintering, the content of sesquioxides is not significant (Evenchik and Brodskiy, 1987). And the electrothermal method allows to process practically any phosphate rocks, including low-quality ones (Pozin, 1983). The presence of sesquioxides ($Fe_2O_3 + Al_2O_3$) in the slurry (when sulfuric acid method of decomposition of phosphates is applied) affects both the size and shape of generated $CaSO_4$ crystals, which in turn affects the washing of phosphogypsum (Kopylev, 1981; Kononov et al., 1988).

The magnesium compounds in the sulfuric acid process of WPA production decrease the acid activity and increase its viscosity, so for this process it is recommended to use phosphate rock with the ratio (Kopylev, 1981; Evenchik and Brodskiy, 1987):

$$\frac{C_{MgO}}{C_{P_2O_5}} \times 100 \leq 7 \div 8 \qquad (3)$$

While decomposing of phosphates with nitric and hydrochloric acid, magnesium impurities are not really significant. In the production of thermal phosphates, magnesium impurities do not cause negative effect, and they are even useful in the production of magnesium fused phosphates (Evenchik and Brodskiy, 1987).

The behavior of fluorine contained in phosphate rock is of great importance (especially in fluorapatite-based rock). When the phosphate rock is decomposed by acids, fluorine transfers into hydrogen fluoride, which then reacts with silicon-containing minerals:

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \qquad (4)$$
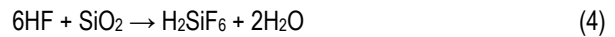
Part of the produced fluorosilicic acid is released in a gas phase as equimolecular mixture of $2HF + SiF_4$. The remaining amount of H_2SiF_6 transfers into the solution, where it reacts with excess SiO_2:

$$2H_2SiF_6 + SiO_2 \rightarrow 3SiF_4 + 2H_2O \qquad (5)$$
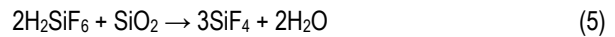
The silicon tetrafluoride is volatile and also passes into gas phase. Fluorine distribution between gas, liquid and solid phases depends on the phosphate rock processed, processing mode, and other factors (Kononov et al., 1988). During concentration (evaporation) of WPA, up to 80% of fluoride contained in it, is released during the gas phase. Fluorine compounds during processing of phosphate rock primarily have a negative impact in terms of increasing corrosion. In addition, as it will be proved later, fluorine can worsen the quality characteristics of the final products.

Chlorine also significantly increases the corrosion of the equipment, therefore, for sulfuric acid processing, its content in phosphate rock should not exceed $0,03 \div 0,04\%$. Impurities of alkali metals (sodium, potassium) form poorly soluble compounds of silicon fluorides Na_2SiF_6 and K_2SiF_6. This leads to increased clogging and deposits accumulation in the piping of filtering equipment, so it is preferable that the total content of Na_2O and K_2O in the phosphate rock should not exceed $0,4 \div 0,6\%$ (Kononov et al., 1988).

Compounds of rare-earth elements (REE) contained in some types of phosphate rock (for example, in the Khibiny apatite concentrate there is about 1% of REE) can adversely affect the crystallization of calcium sulfate dihydrate, worsen the filtration of phosphogypsum and increase its moist content (Kononov et al., 1988). The compounds of cerium and strontium significantly slow the hydration of calcium sulfate hemihydrate to dihydrate (Kopylev, 1981), as a result of which the two-stage hemihydrate-dihydrate process for certain kinds of phosphate rocks becomes problematic and poorly feasible.

Silicium dioxide, which is present in the form of silica and hardly soluble silicates and is part of the so-called insoluble precipitate, in most cases has no harmful effect on acid processing of natural phosphates. However, its high content in phosphate rock can lead to increased erosion of equipment and create difficulties in the filtration stage (Kononov et al., 1988). During the decomposition of phosphate rock with nitric acid, the presence of silicium dioxide, which is soluble in nitric

acid, increases the rate of nitric acid consumption and worsens the slurry filtering conditions, which in turn leads to increase of P_2O_5 and calcium nitrate losses during washing (Evenchik and Brodskiy, 1987).

Impurities can exert influence not only each one separately, but also in combination with each other. For example, the favorable effect on the shape and size of calcium sulfate crystals in the sulfuric acid production of WPA is provided by SiF_6^{2-} ions in combination with Al^{3+} ions (Kopylev, 1981). Based on the research conducted by NIUIF, our specialists proposed a method (Grinevich et al., 2016) that allowed to greatly intensify the dihydrate process of WPA production to produce the easily filtered $CaSO_4 \cdot 2H_2O$ by introducing an acid-soluble aluminum-containing additive into the decomposition zone, providing high P_2O_5 yield and shifting the crystallization zone of calcium sulfate dihydrate to higher temperatures and P_2O_5 content (high-temperature dihydrate).

In international practice there is no strict regulation for the quality of phosphate rock, however, certain requirements for exported rock have been established. Thus, phosphate rock intended for production of WPA should contain at least 31% of P_2O_5, not more than 3.5% of R_2O_3 ($Fe_2O_3 + Al_2O_3$), not more than 0.4% of MgO, 10,5% of insoluble precipitate and the ratio of CaO/P_2O_5 should be 1.45÷1.55 (Angelov et al., 2000).

Impurity elements can also complicate the process mode even in production of final products: mineral fertilizers and feed phosphates. When WPA is concentrated with an increased content of sesquioxides and especially magnesium, a viscous, non-transportable liquid is formed, so it is assumed that in phosphate rock used for production of concentrated acid the ratio should be (Evenchik and Brodskiy, 1987):

$$\frac{C_{MgO}}{C_{P_2O_5}} \times 100 \leq 5÷6 \qquad (6)$$

When the content of magnesium is high, either the technologies for production of mineral fertilizer from non-concentrated WPA are applied (Evenchik and Brodskiy, 1987; Kononov et al., 1988), or the technologies with evaporation/concentration of completely or partially neutralized slurries (Kononov et al., 1988; Grishaev et al., 2014).

The deposits on the heating surfaces of the equipment for concentration of WPA contain an increased content of impurity elements, same as various deposits and sludges in pipelines and equipment, while neutralizing WPA with ammonia during the production of mineral fertilizers (Bushuyev, 2009; Bushuyev, 2011). All of that can complicate the processing and lead to additional shutdowns for cleaning the equipment.

The increased content of impurities in the initial phosphate rock and in WPA produced from it can limit the production of some of the final products. For example, liquid complex fertilizers (LCF) of grade 11:37 cannot be produced from WPA with high content of sesquioxides and magnesium without its preliminary purification. The same impurities, as well as fluorine, can be an obstacle for the production of feed monocalcium phosphate. The impurities, passing from phosphate rock through WPA into fertilizers, can influence the

quality of the latter ones. Some impurities are useful from agrochemical point of view. So, calcium, magnesium and sulfur are the macro-elements necessary for proper development of plants (Pozin, 1983). Other impurities, such as iron, copper, zinc, manganese, cobalt, molybdenum, etc., are the micro-elements, which are also very important for the realization of vital functions of plants, if not contained in excessive quantities. There is also an amount of harmful impurities - lead, mercury, arsenic, cadmium, whose content in fertilizers and feed phosphates is strictly regulated in a number of countries, including the Russian Federation. From this point of view, the Khibiny apatite concentrate used at PhosAgro plants is a unique, most environmentally friendly type of phosphate rock that does not contain harmful impurities and allows for any kinds of products to be produced from it.

Some impurities, especially such as fluorine, magnesium, iron, aluminum, can affect the physical & chemical and structural & mechanical properties of granular phosphorus-containing fertilizers. As per the research conducted by NIUIF, fluorine increases caking of granular ammonium-phosphate-based fertilizers, and also reduces their static strength (Norov et al., 2012). Figure 1 shows the dependence of caking and static strength of diammonium phosphate (DAP) granules of fertilizer grade 10:46 on the content of fluorine in it.
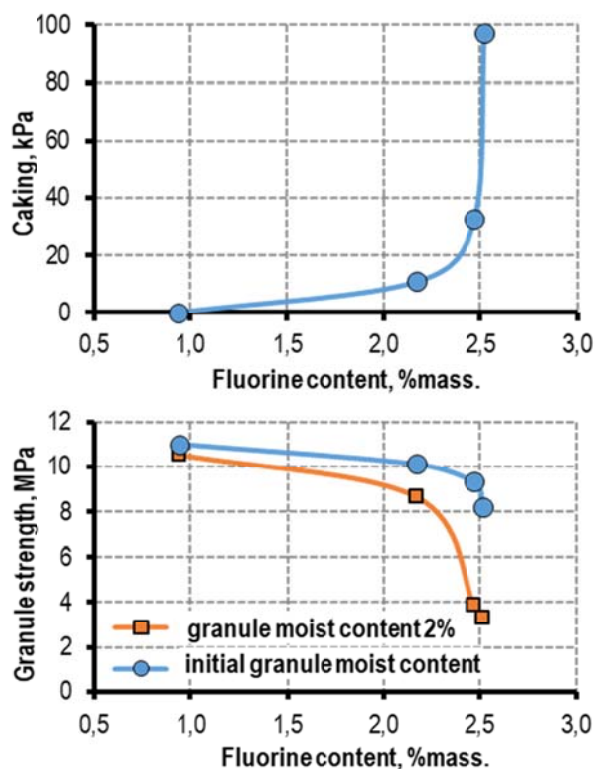

Fig. 1. Dependence of caking and static strength of industrially produced DAP granules on the content of fluorine

You can see from the graphs that with increase of fluorine content, DAP caking increases, and the strength of the granules decreases, and this becomes especially evident with a mass fraction of fluorine of more than 2%. It was also noted that the effect of fluorine increases with increase of the extent of WPA neutralization, i.e. in fertilizers based on DAP, this effect appears to a higher extent than in fertilizers based on

monoammonium phosphate (MAP). Our x-ray phase analysis proved that the fluoride compounds in MAP are represented mainly by aluminum, sodium and potassium silicofluorides, and in DAP – by fluorophosphates $NH_4AlHPO_4F_2$ and $NH_4FeHPO_4F_2$.

In the production of DAP in aqueous weak-alkaline medium, ammonium silicofluoride is hydrolyzed as per the reaction:

$$(NH_4)_2SiF_6 + 4NH_3 + (n+2)H_2O \rightarrow 6NH_4F + SiO_2 \cdot nH_2O(gel) \quad (7)$$
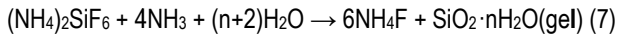
The obtained ammonium fluoride NH_4F is a much more hygroscopic compound than $(NH_4)_2SiF_6$. In addition, during neutralization, ammonium fluoride reacts with ammoniated iron and aluminum phosphates with formation of an amorphous, poorly filtered colloidal precipitate of fluorophosphate of ammonium, iron and aluminum (Kononov et al., 1988).

$$NH_4(Fe,Al)(HPO_4)_2 + 2NH_4F \rightarrow NH_4(Fe,Al)HPO_4F_2 + (NH_4)_2HPO_4 \quad (8)$$
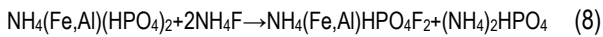
Due to the formation of these compounds, the ammoniated phosphate slurries become more viscous, and to maintain their mobility, higher water content is required. This, in turn, reduces the extent of supersaturation of solutions, leads to decrease in the number of nucleating seeds, decrease of crystallization rate, and increase of crystal size during granulation.

In addition, it is known from literature that the presence of ammonium fluoride in solutions of ammonium phosphates interferes with the crystallization of diammonium phosphate and shifts it toward higher pH values (Pozin, Zinyuk et al., 1976; Dokholova et al., 1986). Increase of fluorine content in the initial WPA increases solubility of its ammonium products (Pozin, Kopylev et al., 1976; Kuvshinnikov, 1987). All of that has allowed us to conclude that the increase of the content of fluorine compounds hinders the process of mass crystallization during granulation, increases crystallization time and the size of formed crystals. As a result, the number of phase contacts between the crystals decreases, the structure of the granules becomes more porous and less stable and themobility of water-salt complexes in granules is ensured. That is why caking increases and the strength of granules decreases. This is confirmed by our microscopic studies. Figure 2a, b shows enlarged photographs of the surface and a slice of DAP granule with low and high fluorine content. You can see that DAP granules with fluorine content of less than 1% have a better, denser structure, the surface of the granules is homogeneous, even, and smoother. The slice of the granule is also homogeneous in volume, the granule is dense, monolithic, without visible agglomerates.
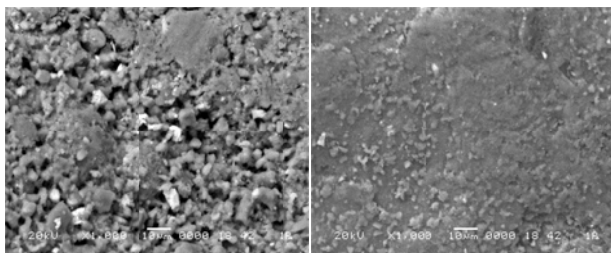
DAP with total fluorine content of more than 2 %mass.   **DAP with total fluorine content less than 1 %mass.**

Fig. 2a. DAP granule surfaces with different fluorine content (magnification×1000)
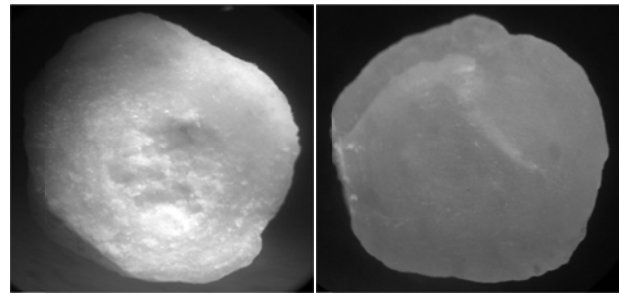
DAP with total fluorine content of more than 2 %mass   **DAP with total fluorine content less than 1 %mass**

Fig. 2b. DAP granule slices with different fluorine content (magnification×25)

DAP granules with fluorine content of more than 2% are heterogeneous both in surface and volume. The surface is inhomogeneous, uneven, locally formed by agglomerates of particles that creates a porous, friable structure. The slice of the granule is not homogeneous, the nucleus of the granule and the surface layer can be distinguished visibly in the photograph. The volume of the granule is represented by intergrowths of agglomerates of crystals, the packing of which is not sufficiently dense.

The silica gel $SiO_2 \cdot nH_2O$ released in the reaction (7) also negatively affects the processes of granule formation. To separately assess the extent of fluorine and silica gel effect on the properties of fertilizers, DAP granules with different fluorine content were obtained at NIUIF's Testing Center, where HF was used for changing of fluorine content in one series of testing, and H_2SiF_6 was used for this purpose in another series of testing. Then these samples were tested for strength and caking (Fig. 3).
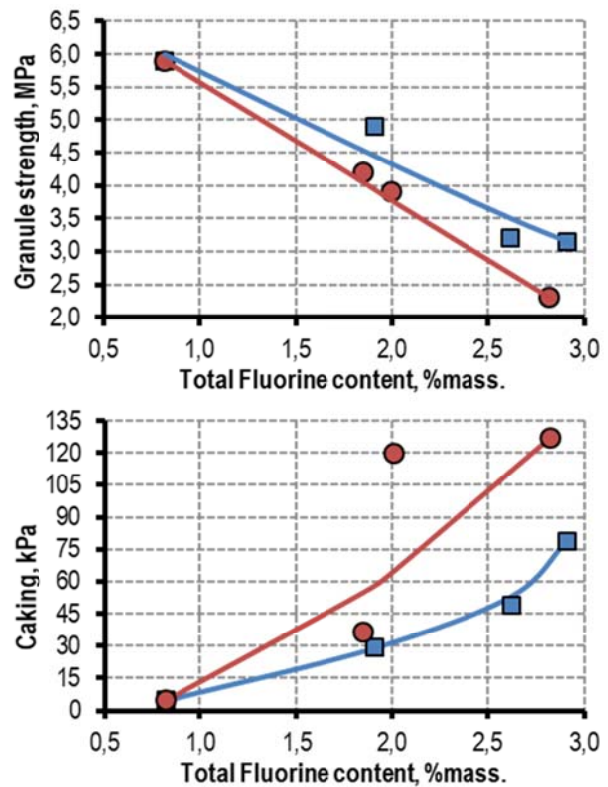

Fig. 3. Dependence of DAP granule caking and strength on the content of fluorine (red line: with addition of H_2SiF_6 (resulting in silica gel formation); blue line: with addition of HF (without formation of silica gel)

The results of these studies show that the presence of silica gel also contributes to deterioration of the structural and mechanical properties of fertilizers: the strength of the granule is reduced, and caking increases to a higher extent than with the same content of fluorine when there is no silica gel.

Some impurities, on the contrary, improve the properties of fertilizers, such as iron, aluminum and especially magnesium (Kuvshinnikov, 1987; Norov et al., 2012). The studies conducted by JSC "NIUIF" proved that even with a slight change of magnesium content (for several deciles of a percent), the properties of phosphorus-containing fertilizers significantly change (Fig. 4).
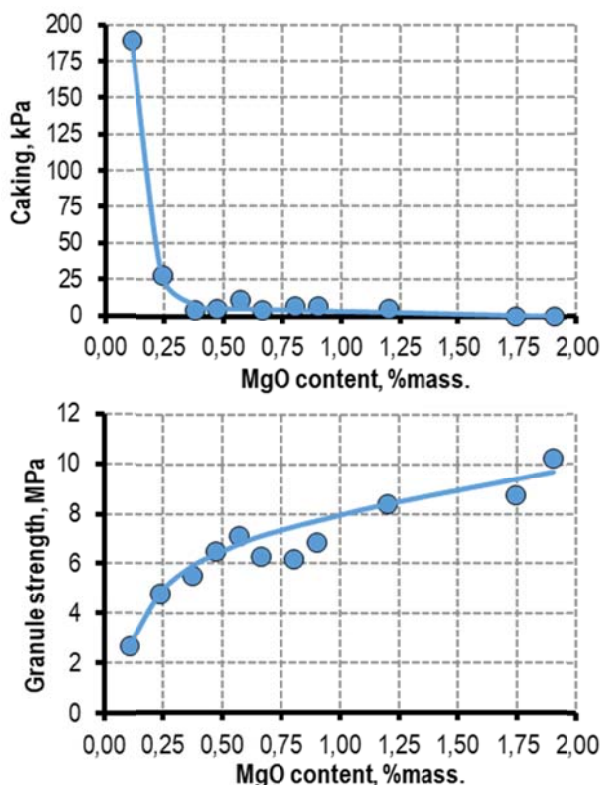

Fig. 4. Dependence of DAP caking and static strength of DAP granules on MgO content in fertilizer (fluorine content in DAP at about 2,5 %mass.)

Hereof it means that even when the magnesium content in DAP is about 0.4-0.5 percent in conversion to MgO, the caking rate decreases sharply and the static strength of the granules increases. With such insignificant change in impurity, this effect can be explained only due to change in the structure of the granules. This is also confirmed by the results of comparative studies of DAP granules under the microscope (Fig. 5a, b), which showed that granules with magnesium additives have a better, denser structure, the granules are composed of smaller crystals, have less porosity, the surface of the granules is more homogeneous, even and smooth, the slice is also homogeneous, without visible flaws.

Using the system of electronic probe energy-dispersed X-ray fluorescence analysis, the distribution of impurity elements along the surface of DAP granules was determined. The results of the analysis showed that adding of magnesium several times reduces the presence of fluorine and silicon on the surface of the granules (Table 1).
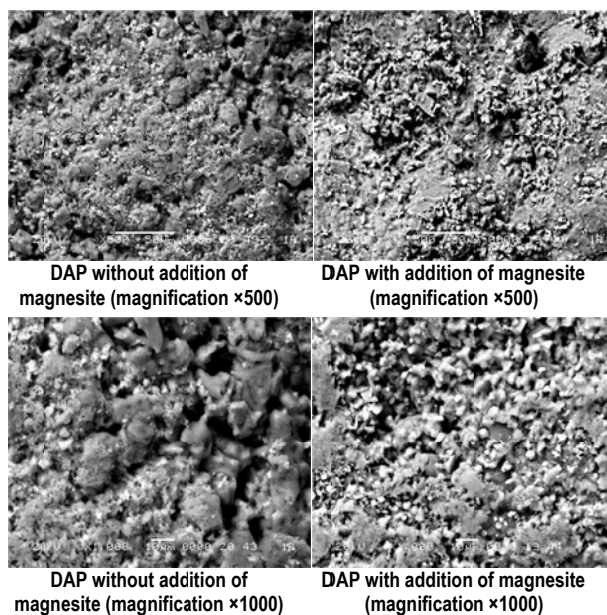

DAP without addition of magnesite (magnification ×500)

DAP with addition of magnesite (magnification ×500)

DAP without addition of magnesite (magnification ×1000)

DAP with addition of magnesite (magnification ×1000)

Fig. 5a. Electronic photographs of DAP granule surface (magnification ×500; ×1000)

Рис. 5b. Electronic photographs of a granule slice of DAP with different MgO content (magnification ×25)
1 – without adding of MgO (0,12% MgO); 2 – 0,4% MgO; 3 – 0,5% MgO

Table 1

Fluorine and silicon content on the surface of DAP granules with and without MgO additives

Content on DAP granule surface	DAP samples			
	without MgO additive	without MgO additive	with MgO additive	with MgO additive
Fluorine, %mass.	7.07	11.63	4.90	2.15
Silicon, %mass.	0.86	1.55	0.19	0.18

This can also be explained by the fact that in the presence of magnesium, the formation rate of granule crystal structure is increased, granule crystal structure unrandomization and compaction occurs, and various impurities, amorphous and slowly crystallized, will be trapped inside the granules and their release to the surface will be complicated.

By X-ray phase and chemical analysis it was confirmed that while neutralizing of WPA with ammonia in the presence of magnesium, depending on the content of impurities in the acid and the extent of neutralization, various compounds can be formed: magnesium ammonium phosphate $MgNH_4PO_4 \cdot H_2O$, complex phosphates such as $Mg_n(Al,Fe)(NH_4)_2(HPO_4)_2F_{2n+1}$, $MgNH_4HPO_4$, etc. The common thing for these compounds is that they are water-insoluble, finely dispersed, well-crystallized compounds (Kononov et al., 1988), which serve as seeds, accelerating crystallization processes and promoting the formation of granules with a strong structure and good physical & chemical and structural & mechanical properties. In addition, complex fluorophosphates bind water-soluble fluorine to insoluble compounds (Norov et al., 2012), therefore they partially neutralize its negative effect. In case crystalline hydrates are formed, for example, $MgNH_4PO_4 \cdot H_2O$, etc., additional water binding occurs, as well as local increase of the extent of supersaturation of solutions, which additionally accelerates crystallization. Such a mechanism, explaining the effect of magnesium on the properties of phosphorus-containing fertilizers, was proposed by NIUIF based on conducted studies and tests. Magnesium additives have a positive effect on the structure and properties of not only DAP, but also other types of granular phosphorus-containing fertilizers, for example, MAP, sulfoammophos (Norov et al., 2012). Ref. (Kuvshinnikov, 1987) tells about improving the properties of nitrate-containing NPK with magnesium. The studies carried out by JSC "NIUIF" showed that magnesium-containing additives also improve the properties of granular sulphur-containing, non-nitrate NPK-fertilizers based on phosphates and sulfates of ammonium and potassium chloride, for example, grade 15:15:15 (Fig. 6). The same is confirmed for other sulphur-free, non-nitrate NPK grades (13:19:19, 16:16:8, 8:20:30), NPS 16:20:0(14S), etc.
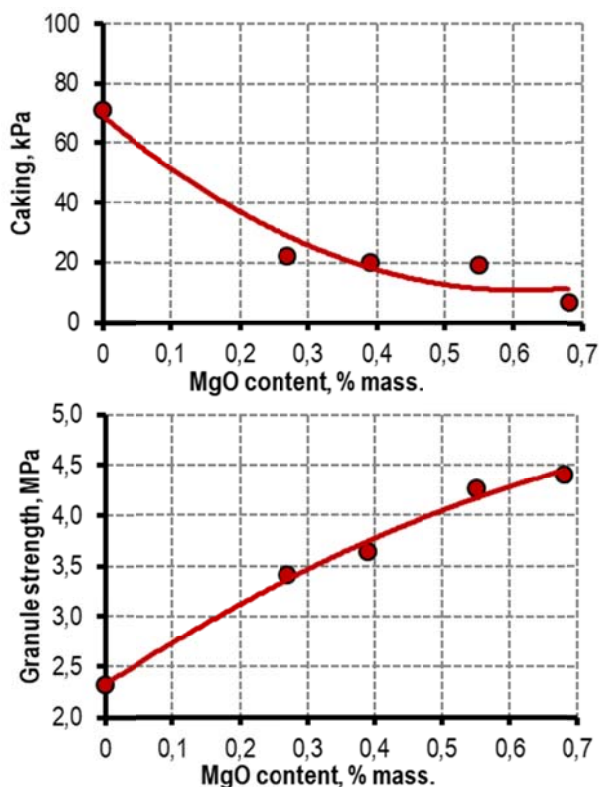

Fig. 6. Influence of magnesium content on properties of NPK fertilizer grade 15:15:15

Magnesium content in phosphorus-containing fertilizers also affects the technology of their production. Acceleration of crystal structure formation of granules with the introduction of magnesium-containing additives has a positive effect on granulation process and contributes to the formation of larger granules. As a result of compaction and hardening of granule structure, diffusion transfer of water from the granule volume to its surface becomes complicated. Generally, it can complicate a bit the drying process and increase the moist content in fertilizers, but it's not critical. According to our studies, the positive effect of using the magnesium-containing additives significantly outcompetes the negative effect of moist content increase in the product. Fig. 7 shows the results of our studies by the example of NPK-fertilizer grade 15:15:15, when the use of magnesium-containing additives makes it possible to obtain fertilizers with increased moist content without deterioration and even with improvement of fertilizer properties. This is also true for other grades of phosphorus fertilizers.
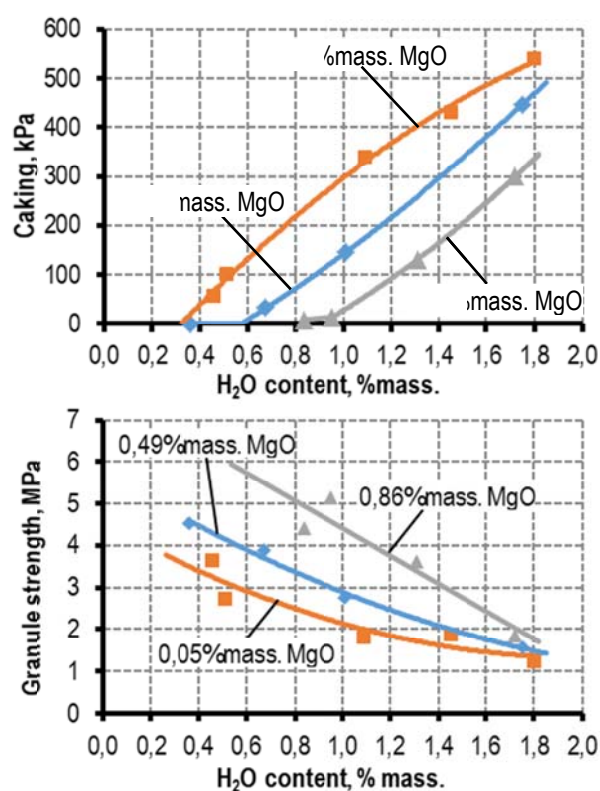

Fig. 7. Influence of content of MgO and moist on granule static strength and caking of NPK fertilizer grade 15:15:15

Since the state of granule surface also improves with the introduction of magnesium, the efficiency of its treatment with conditioning mixtures against dust and caking improves significantly as well, because air conditioners are absorbed less and longer.

Based on our research and tests, we have developed and patented a method for improving the properties of phosphorus-containing fertilizers (Chernenko et al., 2012), which has been successfully introduced at a number of Russian plants. Once the method was introduced in all these plants, the granule strength increased, while caking and dustiness of the produced fertilizers (NP, NPS, NPK and NPKS) decreased significantly.

Impurities also have a very significant effect on retrogradation of P_2O_5 and on the content of nutrients in a water-soluble, assimilable and unassimilable form, though it's a topic for another article.

Conclusion

In conclusion, it should be noted that when developing methods for processing phosphate rock into the target products, it is very important to study and take into account the impurities contained in it and their effect on the technology.

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