INFLUENCE OF MECHANOCHEMICAL PROCESSING OF PHOSPHORITES TO FUSIBLE PROPERTIES

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Annotation. This article analyzes numerous studies on the mechanochemical activation of phosphorites and suggests the possibility of converting phosphorus anhydride into an almost completely digestible form through the use of mechanochemical methods for processing natural phosphates to produce mineral fertilizers. It has been shown that an increase in the amount of absorbable forms of phosphorus and an increase in the reactivity of phosphates are associated with structural changes caused by mechanical impact.
Key words. mechanochemical activation, phosphorites, Aznek ores, assimilability, soluble form, calcium phosphate, ultrafine grinding, sintering.

Annotatsiya. Ushbu maqolada fosforitlarning mexanokimyoviy faollashuvi bo'yicha olib borilgan ko'plab tadqiqotlar tahlil qilinib, mineral o'g'itlar olish uchun tabiiy fosfatlarni qayta ishlashning mexanik kimyoviy usullarini qo'llash hisobiga fosfor angidridini deyarli to'liq o'zlashtiriladigan shaklga aylantirish imkoniyati ifodalangan. O’zlashuvchan fosfor shakllari miqdorining ko'payishi va fosfatlarning reaktivligining o'sishi mexanik ta'sir tufayli yuzaga keladigan tarkibiy o'zgarishlar bilan bog'liqligi ko’rsatilgan.
Kalit so‘zlar: mexanokimyoviy faollashtirish, fosforitlar, Aznek koni, o’zlashuvchanlik, eruvchan shakl, kalsiy fosfat, o'ta nozik maydalash, sinterlash.

Аннотация. В данной статье проанализированы многочисленные исследования по механохимической активации фосфоритов и высказана возможность перевода фосфорного ангидрида в практически полностью усваиваемую форму за счет использования механохимических методов переработки природных фосфатов для получения минеральных удобрений. Показано, что увеличение количества усваиваемых форм фосфора и повышение реакционной способности фосфатов связаны со структурными изменениями, вызванными механическим воздействием.
Ключевые слова: механохимическая активация, фосфориты, Азнекские руды, усвояемость, растворимая форма, фосфат кальция, ультратонкое измельчение, спекание.

Introduction

The global introduction of agricultural chemicals has led to the formation of a powerful international industry for their production, as well as a wide network of logistics and distribution. According to the International Association of Fertilizer Manufacturers, in comparison with the 60s of the last century, the world consumption of mineral fertilizers by 2015 increased by almost 6 times. Currently, the market is one of the most monopolized. Five countries are the largest producers on it: China, the USA, India, Russia and Canada. These states account for about 60% of the total volume of agrochemical products produced [1]. Since the second half of the 20th century, the world chemical industry, including the production of chemicals for agriculture, has gone from the extensive development of large-capacity industries through technical and technological renewal and structural restructuring to a resource-saving and science-intensive stage of development characteristic of the entire modern post-industrial economy. Developing countries have housed the production of products with a low degree of industrial processing, which include the large-scale production of basic mineral fertilizers. Throughout the world, the production of mineral fertilizers is steadily increasing, as this is one of the most important factors in providing food for the ever-increasing population of the planet. The supply of phosphorus-containing fertilizers in Uzbekistan is 25-30%. This is explained by the shortage of high-quality phosphate raw materials [2].

A study of phosphorites from the Aznek deposits during heating carried out using thermoderivatography and IR-spectroscopy methods up to 1000°C, as well as physicochemical analysis of solid heat treatment products made it possible to describe some of the processes occurring during these processes. A significant difference was noted in the behavior of these phosphorites, associated with different genesis and chemical and mineralogical composition of these deposits. The fundamental possibility of using thermogravimetry for a qualitative description of the processes occurring during heat treatment of phosphorites and accompanied by mass loss is observed [3].

Above 550–650°C, changes continue in crystal structure of francolite with the emission of CO_2 which is more intensive in neutral gaseous atmosphere than in oxidizing. In neutral gaseous atmosphere the emission of SO_2 is also fixed in Aznek phosphorites indicating the substitution of sulphur into francolite structure at lower temperatures, or some sulphur could be deposited into the francolite structure already during different geological processes. So far, it is the first clear evidence about the introduction of sulphur into the francolite structure at thermal treatment of phosphorite.

Therefore, the changes in SSA and pore volume of studied samples at thermal treatment and in solubility of constituent elements in 2% citric acid indicate clearly the relationship between the solubility, SSA and porosity data of studied phosphorite samples. The results of thermal and MS analysis indicated certain differences in the thermal behaviour of phosphorite samples studied depending on their origin and gaseous atmosphere used [4].

At thermal treatment of phosphorite samples, the emission of the physically bound water, water from dehydration of gypsum, thermooxidation of organic matter, dehydroxylation of goethite and muscovite, thermooxidative decomposition of pyrite and the emission of constitutional water from phosphorite structure continue up to 500–550 °C in oxidizing and up to 600–650°C in neutral gaseous atmosphere. At temperatures higher than 1050–1100°C, the emission starts of SO_2 resulting from decomposition of anhydride. The content of oxygen in gaseous atmosphere suppresses the liberation of carbonate and sulphate groups from the structure of francolite [3].

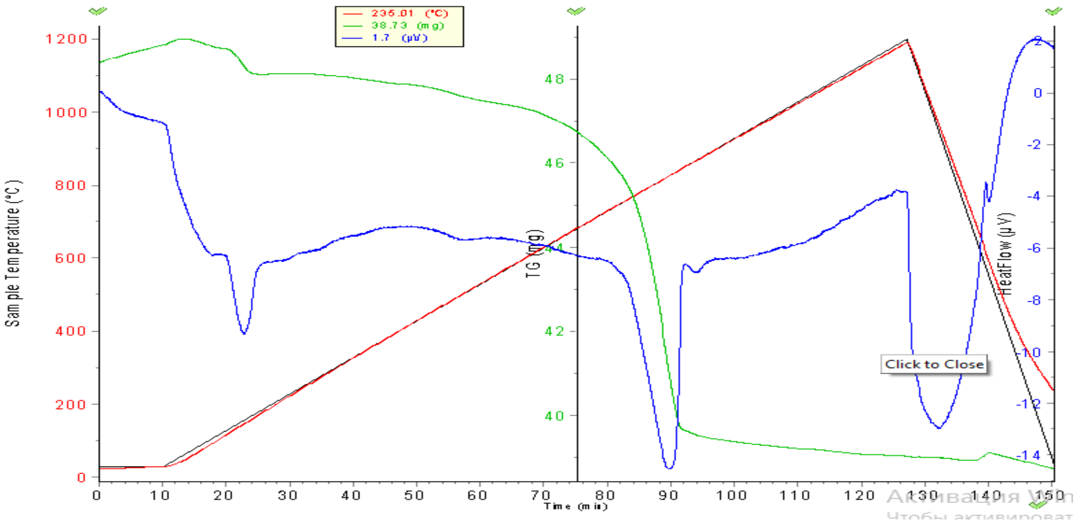

Fig.1. Thermographical changes in phosphorite raw materials from Aznek ores.

The results of analysis made possible to analyse and understand differences of changes in francolite structure at thermal treatment in different gaseous atmosphere. The content of SO_4^{2-} group in the structure of Aznek phosphorite was fixed in IR-spectra both in ore and concentrated samples treated at 500°C and 950°C. Systematic study of solubility of constituent elements (P_2O_5, CaO, Fe_2O_3 and SO_4^{-2}) in 2% citric acid and the changes of physical characteristics (SSA, porosity) at thermal treatment of samples at different temperatures enable to understand the relationship between these characteristics, having high level importance in the case of exploitation of phosphorite.

Mechanochemical activation is, in fact also ultrafine grinding but carried out in the presence of any chemical reagent. Mechanochemical activation of phosphate ores is a promising way to create environmentally friendly technology production of phosphate fertilizers. Active systematic research carried out over a long period has shown that the mechanical activation of phosphate rock can be considered a promising way to increase the efficiency of the production and use of phosphate and complex fertilizers. The chemical exposure method is especially important for the processing of phosphate rocks due to the complex and variable chemical composition and poor workability in its majority substandard. Mechanical activation of phosphate ores in planetary mills allows to convert ~80-90% of phosphorus into easily soluble forms and receive ready-made fertilizers. The data presented in mechanical activation of phosphorus ores of various types and compositions showed that even from such sparingly soluble ores as phosphorites of Aznek, 75-85% of phosphate becomes soluble in 2% citric acid form.

The influence of mechanical activation on the physicochemical properties of phosphate and apatite were studied in detail in connection with the problem of developing acid-free method for producing phosphate fertilizers. It has been shown that the speed dissolution of apatite and phosphorite in weak acids as a result of mechanical activation increases significantly [5].

According to the investigations [1], in the process of mechanical activation apatite decomposes into amorphous tri-calcium phosphate - α-$Ca_3(PO_4)_2$ (a high temperature form of tricalcium phosphate) and fluorite. Temperature melting point of apatite is 1900K, and α-tricalcium phosphate is 2050K. This indicates that during indentation after the mechanical process activation, the substance was in an excited state.

Table 1.

Dependence of assimilability of P_2O_5 in different solutions relating to their particles size.

Assimilability of P_2O_5 in citric acid, %							
Sizes of articles, mm	t, minute	5	10	20	30	60	120
4-2		2,7	2,7	3,0	5,2	7,3	7,8
1-0,5		3,4	3,8	4,7	6,0	8,2	8,9
0,25-0,125		3,9	5,0	6,6	7,8	8,9	9,2
0,064 >		5,4	6,7	8,9	11,7	12,7	13,0
Assimilability of P_2O_5 in Trilone-B, %							
Sizes of articles, mm	t, minute	5	10	20	30	60	120
4-2		1,6	1,7	1,9	2,6	2,8	3,1
1-0,5		2,4	2,6	2,8	3,3	3,7	4,2
0,25-0,125		3,0	3,2	4,5	5,0	5,1	5,7
0,064 >		3,2	3,4	4,6	5,1	5,6	5,9
Assimilability of P_2O_5 in water, %							
Sizes of articles, mm	t, minute	5	10	20	30	60	120
4-2		0,9	1,0	1,3	1,8	2,1	2,4
1-0,5		0,9	1,1	1,5	1,9	2,2	2,6

0,25-0,125	1,0	1,3	1,9	2,0	2,4	2,6
0,064 >	1,4	1,7	2,0	2,2	2,5	2,8

The essence of mechanical activation of phosphate rock is fine grinding carried out in special grinders -activators characterized by high energy intensity. This process provides a very intense effect on phosphorite particles which its crystal structure is deformed, the degree of its amorphousness, the specific surface area increases, and as a result of all this, the solubility of phosphate in 2% increases significantly (almost 2 times) citric acid.
Mechanical activation, or ultrafine grinding, is carried out in energy-intensive grinding units:

- impact action - impact-centrifugal mills, jet mills, disintegrators;
- abrasive action - roller mills;
- combined impact and abrasion action – vibration mills, planetary mills, etc. [6].

Experiment shows that 80% of the increase in yield from the use of standard phosphate rock is provided by its fine fraction (-0.1 mm), Constituting approximately half by weight in phosphate rock [7].
The effectiveness of the other half of the standard phosphate rock flour, consisting of larger particles (fraction +0.1 mm), is very low and when applied to the soil, it provides only a 20% share in the total yield increase.
Technological process for the production of thermo-alkaline phosphates and fused phosphates is simple and consists mainly of sintering phosphorites with soda at 1100-1200°C, followed by grinding the resulting spec. It is noted that the digestibility of thermal phosphates in a large degree depends on the fineness of grinding [8].
The degree of assimilability of thermophosphates depends on the fineness of grinding them. The most effective are associations with dispersion of particles in less 0,064 mm [9].
Thus, as a result of generalization of researching works on mechanical activation of phosphate raw materials, we can state that mechanical activation of natural phosphate raw materials:

- increases the reactivity of phosphorite;
- increases the content of soluble forms of P_2O_5;
- allows to reduce fluorine content;
- makes it possible to use activated natural phosphates in as fertilizers.

Conclusion

In conclusion, the use of chemical reagents in the process mechanochemical activation is due to their influence, leading to improving the solubility of phosphates.

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