Mechanical Activation of the Phosphorites (Karatau Pool) by using Organic-Mineral Co-Activators for Multicomponent Mineral Fertilizers

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Abstract

Deficiency of mineral fertilizers in the agricultural sector for last 15–20 years has decreased. Therefore with the purpose of partial reduction of this deficiency it was developed a new polycomponent NPK fertilizer, which contains humate and vermiculite. The given fertilizer has been produced from the natural South Kazakhstan raw materials in accordance with an acid-free way. The given article contains the data and physicochemical properties of initial materials prepared on the basis of phosphorite fines of Zhanatas and Chulaktau deposits and sinter return. Characteristics of vermiculite and the internal overburden rocks formed at the mining brown coal on the Lenger deposit are represented. During the experimental research except the above-stated natural raw materials the following substances were used at manufacture of the polycomponent fertilizer: ammonia saltpeter, ammonium sulphate produced by the OJSC "Grodno-Azot", halurgical potassium chloride produced by "Belaruskaliy" and potassium hydroxide, a chemical reagent of a grade "pure". The given article contains the data about the chemical composition of initial raw materials and conditions of mechanical-chemical activation of the initial materials at various values of components concentration, temperature and time at the polycomponent fertilizer manufacture. The plan and research results of phosphorite's activation with the analysis of a disperse structure of nonactivated and activated Zhanatas phosphorite are represented. The determination of nonactivated and activated phosphorites specific surface was performed with use of a device PSH-8A according to the method based on the measurement of hydraulic resistance of a powder material's layer at filtration of an air low-pressure stream.

1. Introduction

Production of mineral fertilizers is one of the most profitable and financial stable branches not only in a chemical complex, but also in the industry as a whole.

Now in the world the largest producers of mineral fertilizers are: China controlling 21% of the market, the USA (13%), India (10%), Russia (8%) and Canada (8%). Since 2006 the highest rates of growth show the markets of the countries of South East Asia and Latin America.

Besides, the centers of production of phosphoric and nitric fertilizers are distributed on areas of consumption, and potash – to areas of production of raw materials. According to it today the largest producers of nitric and phosphorus-containing fertilizers are – in Asia – China and India, in North America – the USA, and producers of potash fertilizers – the states having a source of raw materials, such as Canada, Russia and Belarus [4].

That fact testifies to high degree of concentration of world production of mineral fertilizers and raw materials for their receiving that nearly 80% of production of ammonia which is used when receiving nitric and difficult fertilizers are the share of 15 countries. It should be noted that about 85% of volume of world production of phosphorus-containing ore are concentrated in 7 countries, in 6 countries more than 85% of universal volume of chloride potassium are issued.

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The chief producer of phosphorus-containing compounds in the Republic of Kazakhstan is Kazfosfat Limited Liability Partnership. The company is the main producer of 20 different types of production, such as yellow phosphorus, sodium tripolyphosphate, mineral fertilizers, etc.

It should be noted that in black soil of the Republic of Kazakhstan, during development virgin and laylands, losses of a humus made 25–30%, and on irrigated – 40–50%. By calculations of agrochemists-soil scientists, annual losses of a humus in agriculture of our country make from 0.8 to 1.2 t/ha [1].

Now 60% of arable lands are poor and contain less than 4% of a humus that has an adverse effect on quantity and quality of a crop of plants [2, 4].

Significative factors for the market of mineral fertilizers are a state and prospects of development of world economy, a situation in the world agrarian market and the market of energy resources.

By International Fertility Association data world phosphatic capacities in 2013 had to make 248 million *t* that is equivalent to growth by 30% in relation to 2008 [5].

In 2013 world capacities for processing of phosphates, according to IFA forecasts, will reach 42.5 million *t* of P_2O_5 that on 9.1 million *t* it is more, than in 2008.

To 40 new installations on production of monoammonium phosphate, diammonium phosphate and threefold superphosphate will be built in 10 countries, from them 18 – in China. New capacities are planned also in Africa, the Western and East Asia, Latin America.

Than more general content of active ingredients in fertilizer, especially is more valuable than it quality indicators. It is well-known that difficult fertilizers are necessary for various cultures, soils, climatic and other conditions with a different ratio and the content of nitrogen, phosphorus and the potassium, $N:P_2O_5:K_2O$ characterized by the mass relation.

2. Experimental

2.1. Main objectives of research

For development of the production technology new multicomponent the nitrogen-phosphorus-potassium-humate and vermiculite – containing mineral fertilizer of the prolonged action is investigated a chemical composition and physical and chemical properties at mechanochemical activation of the main raw materials – phosphorite.

3. Materials and Methods

3.1. Physical and chemical characteristics and properties of initial materials

3.1.1. Phosphatic raw materials

The phosphoritec raw materials, applied production of NPP (nitrogen, phosphorous, potassium) fertilizers and fertilizers in general, receive by crushing of lumpy and trivial natural phosphorite [6].

Functions of each type of mineral fertilizers are strictly specific in this compound, mineral components of these fertilizers (nitrogen, phosphorous, potassium) can't fully be interchanged. Therefore, phosphorus is necessary for plants for root system, potassium improves resilience to diseases, and nitrogen – the major element which is responsible for growth and productivity.

Average chemical compositions of components the furnace charges used in the course of receiving fertilizers of prolonged action, are given in Tables 1–3.

The advantage of a phosphoritic flour is duration (for a number of years) its actions. Introduction of phosphorites to the soil one of the most important methods of increase of fertility depends from grind tannins. For increase in efficiency of a phosphoritec flour its processing by small doses of acids (4–8% of flour weight) by sour salts of nitric or phosphoric acids, and also organo-mineral additives (humuses), potassium containing salts (waste of beet sugar plants) is offered. In this case production cheap nitrogen – phosphorus – potassium – gray calcium-magnesium of containing fertilizer with organic (humuses) additives is possible.

3.2. Vermiculite raw materials

In the territory of the Southern Kazakhstan area three fields of vermiculite are revealed and in details reconnoitered: Kulandinsky, Zhilandinsky and Iris.

Ore represents the friable weight consisting of field spars, amphiboles and micas which is covered with a cover of modern deposits, with power up to 3–5 m.

Average power of an ore deposit of vermiculite of the Kulandinsky field makes about 20 m in which the content of vermiculite fluctuates from several percent to 35%.

When using substratum for cultivation of plants vermiculite can serve a good stimulator in biological fixing of nitrogen from the atmosphere. The

Table 1
Chemical composition of phosphoritec raw materials [7–9]

	Contents of components, %							
	P_2O_5	insoluble rest	K_2O	CaO	MgO	R_2O_3	C_{free}	CO_2
Phosphoritic fines	20.1	26.4	0.6	34.7	2.1	4.7	traces	5.8
Fines of return process agglomerations	21.9[H]	26.9	0.7	37.8	2.4	4.9	0.1	0.1

Table 2
Chemical composition of Kulandinsky vermiculite

Contents, %								
Na_2O	K_2O	Fe_2O_3	FeO	Al_2O_3	SiO_2	CaO	MgO	H_2O
6.5	6.5	6.0	2.0	13.5	38	3.0	19.5	5.0

Table 3
Chemical contents of Lenger minefield internal overburdens

Contents, %									
Na_2O	K_2O	Cr_2O_3	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	C_{free}	MnO
0.5	0.5	0.1	9.3	8.3	49.9	1.8	1.8	2.8	01.–0.6

dehydrated vermiculite possessing ion-exchange properties, can be used for increase of comprehensibility of phosphorus by a cotton and other agricultures.

The average chemical composition of Kulandinsky vermiculite is given in Table 2.

Value pH vermiculite makes about 7.0, and heat conductivity of 0.05 W/(m^2·K). Temperature of melting about 1315 °C, the beginning of agglomeration 1260 °C.

3.3. Brown coal

Brown coals belong to humic coals of technological group of the ZB brand according to GOST 25543-88. The characteristic of coal fields of the Republic of Kazakhstan it is shown in Table 3.

3.3.1. Indicators of the technical analysis

Methods of the technical analysis [10] determined an ash-content, moisture content, sulfur and phosphorus, an exit of the volatiles, the highest and lowest warmth of combustion. Average ash-content of coal Expert = 21%; warmth of combustion of a dry ash less condition of 27.6–28.4 Mj/kg, warmth of combustion of working fuel at humidity of 10–14% – 14.7 Mj/kg; exit of volatiles – 40 of %.

The ash-content of coal is defined by the content of nonflammable mineral impurity which part carbonates of calcium $CaSO_3$, $MgCO_3$ magnesium, $CaSO_4$ plaster are $2H_2O$, FeS_2 sulfide, rare elements.

The milling ability coefficient characterizes fuel resilience to grind and is defined in accordance with GOST 15489-70. Tests showed that the coefficient, milling ability of brown coal is in limits 1.22–1.29 (the coefficient of a milling ability of reference fuel is equal 1.0).

3.3.2. Internal overburden breeds

In the course of coal mining by waste it is considered to be containing and overburden breeds, low-grade coals, coal and coal and pedigree slimes.

Granulometric structure of dump breeds the most various. In dry dumps the sizes of 100–150 mm, and in hydrodumps – particles of 0.5–1.0 mm prevail.

When performing research the following materials were used:

1. Phosphorites of the pool of Karatau (Zhanatas and Chulaktau minefields);
2. Vermiculite (Kazakhstan);
3. Brown coal (Kazakhstan);
4. Overburden breed of Lenger minefield;
5. Ammonium saltpeter;
6. Ammonium sulfate, producer of JSC Grodno Azot;
7. Potassium chloride halurgic producer of JSC Belaruskali;
8. Potassium hydroxide, reactant of "pure" classification.

Samples were analyzed in the form of free powders in the air atmosphere that didn't allow to define the contents in fluorine materials. The maintenance of other elements are relative. Existence in a phosphoritec fines Zhanatas and Chulaktau of microelements of Ti, Cr, Mn, Fe, Ni, Zr, Ba pays attention. As a part of vermiculite the maintenance of Fe and Ti, existence of Cr, Ni, Ba, Co, in brown coal Co, Ni, Cu is very great.

For the purpose of the maximum modeling of real industrial conditions within carried-out scientific research work the horizontal activator of the drum type [3, 8] grinding bodies for which are steel spheres of various diameter was used.

In this work as methods of the chemical analysis the content of accessible phosphorus in the form of lemon soluble of P_2O_5, the main indicator of quality of fertilizer – degree of activity of phosphate in fertilizer. Definition of lemon soluble of P_2O_5 carried out according to GOST 20851.2-75.

3.3.3. Factorial planning of compositions of fertilizers

One of achievements of the XX century was creation of the section of the applied mathematics which has received the name "Mathematical Planning (Design) of Experiments" or "Mathematical Optimization of Experiments". In Russian extensive literature on this subject which part is provided below is published, in particular, it is necessary to mention such authors as V.V. Nalimov [9, 10], Yu.P. Adler [8], I.G. Zedginidze [12], etc. [13–19].

Application of complicated plans of multiple-factor experiments at small number of experiments, in particular, when number of experiments is less than total number of parameters of studied process, is able to afford to receive optimum result only incidentally though actually the hidden regularity is thus used.

Considering the above, we applied consecutive planning with splitting the general program of a pilot study into independent blocks.

Block 1: development of optimum conditions of carrying out mechanical, thermal and chemical activation of a phosphatic component in possible multicomponent compositions of fertilizers at separate and joint influence of the listed ways of activation.

Block 2: agrochemical tests of multicomponent compositions of fertilizers on the basis of Karataus phosphorites.

In the considered Block 1 the problem in the maximum degree is solved to translate phosphorus from non-accessible form in accessible on the basis of laboratory markers of accessible phosphorus. For the last 80 years such indicator of accessible phosphorus accepted an indicator "lemon soluble phosphorus", determined by ability of phosphates in fertilizers to pass into solution in the environment of lemon acid. The importance of this technique is confirmed by that it is included in GOST 20851.2-75. Therefore in this block as criterion function of optimization of process of activation of phosphates in fertilizers we accept an indicator of *F* relative activities phosphate ion as extent of transition of phosphates (generally calcium phosphate) in the lemon soluble form, defined by expression:

$$F = C(P_2O_5)_{l.s.}/C(P_2O_5)_{total.}$$

Planning of experiments at a stage of development of optimum technology of mechanic-thermo-chemical activation of phosphorites of the pool of Karatau.

Factors of activation of phosphorites of Karatau at preparation multicomponent the fertilized of compositions.

Aprioristic factors of mechanical, thermal and chemical activation of phosphorites of Karatau of ore sites Zhanatas and Chulaktau are listed below. Factors of mechanical activation of phosphorites:

1. Way of activation. Is defined by type of the activator (mill), is more exact – a design and design data of mills.
2. Mechanical factors of activation. In number of mechanical factors of activation in our research are carried – parameters of loading of a mill by furnace charge and grinding spheres; diameter of a drum of a mill; frequency of rotation of a drum; activation duration, diameter of spheres.
3. Physical and chemical indicators of activation. In our research their number treat – the content of ingredients of activated furnace charge; temperature.

The following temperatures were applied at implementation of thermomechanical activation: 20 °C, 100 °C, 200 °C, 250 °C.

4. Results and Discussion

Due to various nature of factors of analyzed process and expected nonlinear dependence, existence both quantitative, and qualitative factors, expectation of nonlinear model for function F, and also considering limited number of levels of a variation and a large number of ingredients, development of comprehensive plans, application in various compositions was required (binary, threefold, etc.) elements a simplex plans agrees [9].

The experiment plan (factors, variation levels) and the received results are presented in Table 4.

Table 4
Mechanochemical activation of a phosphoritec fines Zhanatas and Chulaktau without additives

Activation conditions				Contents of P_2O_5, %	
Diameter of spheres, mm	Spherical loading	Duration of activation, min	Turns of a drum, rev/min	Lemon soluble form	Relative
Phosphorite Chulaktau ($P_2O_{5\ total}$ = 21.8%)				3.5	16.05
5	15:1	30	140	4.0	18.35
6	15:1	10	60	3.1	14.22
10	5:1	30	60	2.9	13.30
Phosphorite Zhanatas ($P_2O_{5\ total}$ = 22.07%)				3.71	16.81
5	15:1	30	140	4.43	20.07
6	15:1	30	100	4.01	18.17

Apparently from the presented results, as optimum indicators of a mode of mechanical activation of phosphorites Zhanatas and Chulaktau can be accepted at a set temperature 20 °C such values of factors: diameter of spheres – 5 mm, relative spherical loading – 15 kg of spheres per kg of furnace charge, duration of activation is 30 min, the frequency of rotation of a drum of a spherical mill 140 rpm. At such parameters activity of phosphorite Zhanatas raised from 16.81% to 20.07%, and Chulaktaus phosphorite from 16.05% to 18.35%.

Research of mechanic-thermo-chemical activation of phosphorites and optimization of operation of mixture making of phosphorites with application of organic-mineral additives.

Results of researches of chemical and topochemical transformations in compositions phosphorite – an inorganic co-activated additive (F-NSA) and phosphorite – an inorganic co-activated additive – a humic material (F-NSA-GM) physical tool methods.

4.1. Method of the X-ray phase analysis

Shooting of roentgenograms was made on the X-ray Bruker AXS diffractometer (Germany) on CaK α-radiation at a tension 40 kV and current 40 mA, an interval of coverage of corners 2θ 5-80 ° at a record 0.1 step° and record 2 sec on one step speeds.

The phase structure of initial materials was an object of research. Roentgenograms are submitted in Figs. 1 and 2.

In Fig. 1a the roentgenogram of not burned phosphorite Zhanatas on which apatite lines dominate is submitted. Unfortunately, resolution rentgendifractometre on allows to discriminate lines of various apatites, for example, fluor apatite, hydroxylapatite and francolite in view of proximity of parameters of their elementary cells.

Obviously, at 800 °C there was a thermal disintegration of dolomite according to reaction:

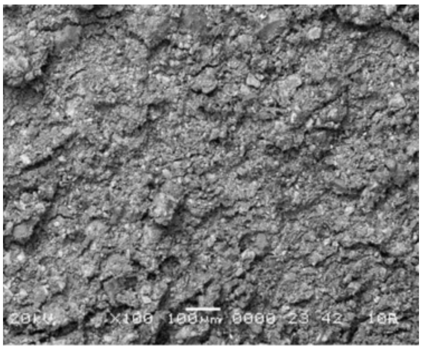
$$CaMg\ (CO_3)_2 = CaO + MgO + 2CO_2 \quad (1)$$

It is remarkable that though and CaO have to be formed by MgO on reaction (1) in equal molar quantities, on the roentgenogram of lines of oxide of calcium is twice more, than lines of a periclase of MgO. We assume that the periclase possesses smaller extent of crystallization in comparison with CaO.

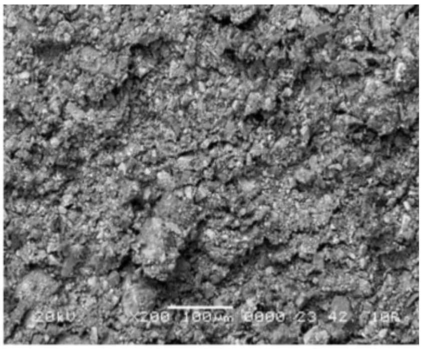
Interpretation of roentgenograms was made in an automatic mode by means of the program EVA complex of the X-ray Bruker AXS diffractometer.

In Fig. 1a the roentgenogram of a sample of mix of 90% of phosphorite Zhanatas and 10% of vermiculite which is burned at 800 °C within 60 min. is submitted, and then activated at a temperature 20 °C within 30 min when using spheres of d = 5 mm and relative spherical loading 10:1. On the roentgenogram crystal phases of apatite (lines much, but they not intensive, brighter reflexes 2θ=25.9 are found; 32; 32.3; 33.1; 34.2; 40; 46.8; 59.6) quartz (intensive lines 2θ = 20.9; 26.7, weak reflexes 2θ=36.6; 40.3; 45.6; 60; 68, etc.) periclase (2θ=42.9; 62.4; 75.6; 78.6) calcium oxide (2θ=24.2; 26.7; 29.9; 39.4; 43.4; 47.6; 48.4) and a new phase dehydrated chabazite $CaAl_2O_4$ (2θ=9.6 – very intensive line, is a lot of others, but all of them are less intensive. It is remarkable that in Fig. 2a of an intensive reflex with the angular coordinate of 2θ=60 here it is not present. Clarification of the reasons of such distinctions of roentgenograms demands further researches.

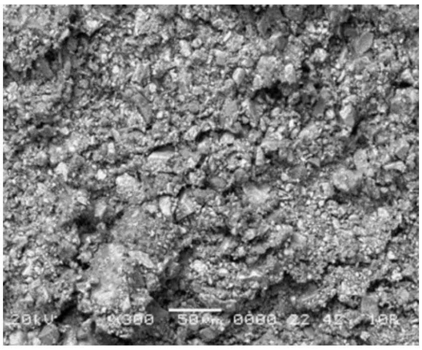
In Fig. 1b the sample roentgenogram – phosphorite mix Zhanatas (80% on weight), vermiculite from Kazakhstan (10% of masses is submitted) and overburden breed of a site Lenger (10%), burned at 800 °C within 40 min.



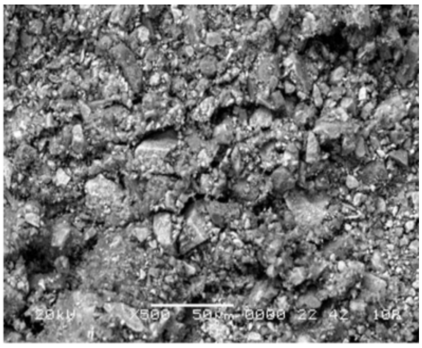
(a) 100 – increase



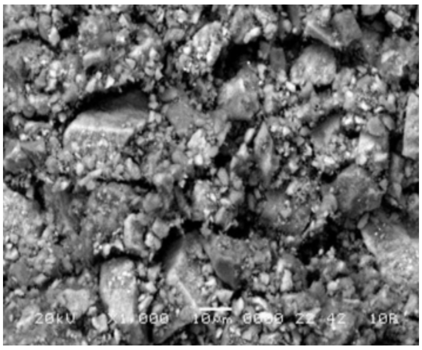
(b) 200 – increase



(c) 300 – increase



(d) 500 – increase



(e) 1000 – increase

Fig. 1. Electronic and microscopic pictures of a phosphorites fines Zhanatas (fraction – 0.16 mm), activated mechanically.

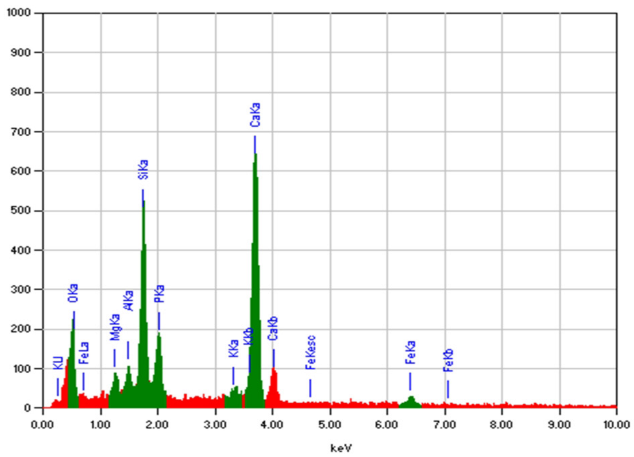


Fig. 2. Energy-dispersive range of a phosphorites fines Zhanatas (fraction – 0.16 m), a mechanically

The description of electronic and microscopic pictures and power dispersive ranges of samples of fertilized of compositions and their ingredients showed that the sample 2 – phosphorite Zhanatas, fraction – 0.16 mm, is activated mechanically. Microphoto of the electronic and microscopic image of this sample (Fig. 4). Comparing this microphoto to Fig. 3 we see that in the microphoto of this sample there are no very large grains, and in the course of activation their average size decreased approximately twice in comparison with a sample 1, and the largest particles in a sample 2 have the size (in the field of the microphoto) 15×30 micron that is caused by crushing large particle in the course of mechanical activation of the material which is present at a sample 1. In a sample 2 in comparison with a sample 1 it is possible to note and particle– instead of shapeless grains of an uncertain configuration in a sample 1 now in a sample 2 we have morphology change particles with more or less expressed flat sides, i.e. in a form particle coming nearer to prismatic or poliedralny bodies. The assumption arises that at grind of grains of apatite in the activator, in apatite the spaynost on sides of prisms is shown. The present small fraction in a sample 2 is larger than similar fraction in a sample 1 on "diameter" of grain approximately twice (on volume – by 8 times), i.e. at activation of a sample 1 integration of dust-like grains of an unknown material probably dolomite takes place. The power dispersive range of a sample 2 is presented in Fig. 4. It is shown that the signals answering to the Ca, Si and O elements amplified, and the signal answering to an element P, weakened that testifies to existence of some structural changes in crystal lattices of the minerals which are present at phosphorite Zhanatas, in the course of mechanical activation of phosphorite (probably, effect of "peening" in the course of impact of grinding spheres of the activator on a powdery material).

IR-research was carried out on IR-Fourier a spectrometer: NEXUSTM E.S.P. (Thermo Nicolet, the USA) by a pressed of hinge plates of samples weighing 1–1.5 mg on 500 mg of the powder KBr received by crushing of monocrystals of KBr, with the subsequent press fitting in one monolithic tablet.

Research of IR spectrums was conducted on samples of not activated and activated apatite Zhanatas, the humate of the materials received from brown coal (Kazakhstan) and breeds Lenger, and also compositions apatite – a humate.

The received IR spectrums are presented on Figs. 3–5.

On IR spectrums of not activated and activated phosphorite Zhanatas the following frequencies (more precisely – wave numbers, cm^{-1}) fluctuations of apatite, carbonates of calcium and magnesium, quartz are shown.

Analysis of a range of dolomite. Observed frequencies 1454, 1425 cm^{-1} – valent fluctuations of C-O of communication 875, 381, 727 cm^{-1} – angular and deformation fluctuations of CO_3^2 of groups.

Analysis of a range of quartz. Observed frequencies 1170, 796, 781, 693, 573, 472, 400, 371 cm^{-1}.

The cm^{-1} line 3620 – possibly characterizes OH-group of a clay mineral.

Analysis of a range of apatite. Observed frequencies: 1039, 1044, 970 cm^{-1} answer valent and angular fluctuations of communications of P-O, P-O-P.

The received result, is probably caused by impact of mechanical activation of phosphorite on an oscillatory range of RO_4 – of group as a part of apatite and allowing to assume that mechanical activation not only crushes a material, but also deforms a crystal lattice of apatite, i.e. creates structural changes at nuclear and molecular level. This assumption demands the additional researches lying outside a perspective of this work.

Research of disperse composition of not activated and activated phosphorite Zhanatas.

Research was conducted for the purpose of obtaining additional information on the nature of the processes happening at mechanical activation of phosphorites.

The technique of research consisted in the following.

Test of a phosphoritic fines of an ore field Zhanatas (200 g) was crushed manually in a porcelain mortar (for the purpose of the minimum mechanical impact on the crushed material) before passing through a sieve with a cell size 0.16×0.16 in mm then a test half (100 g) was subjected to mechanical activation at the following parameters of process – 140 rpm; 30 min.; loading of spheres 15:1; ø 5 mm.

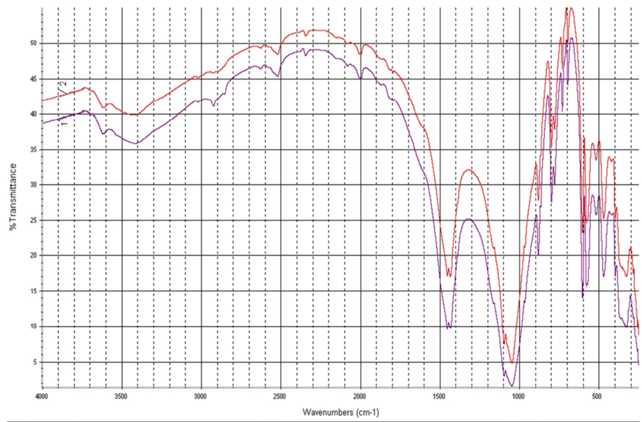
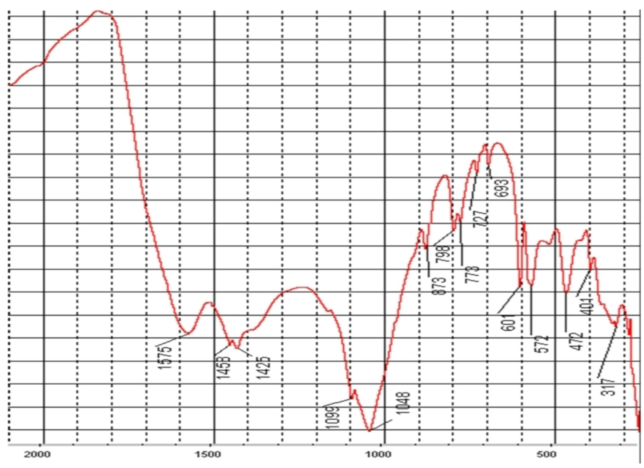
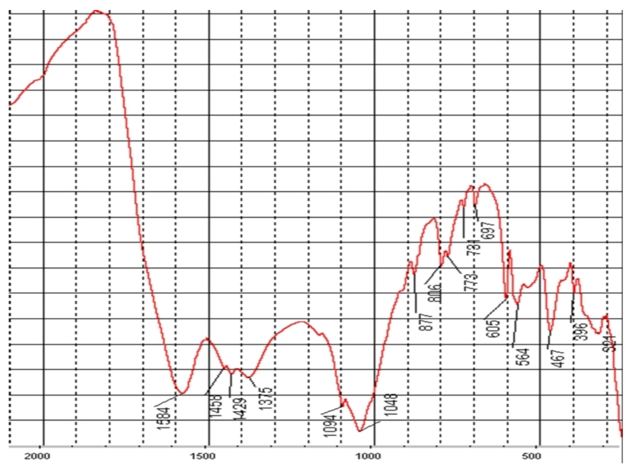


Fig. 3. Phosphorite IR spectrums Zhanatas activated mechanically (a curve 1) and not activated (a curve 2) in range of wave numbers of 465–4000 cm^{-1}. Frequencies of 605 and 568 cm^{-1} – answer deformation fluctuations of PO_4 – of group in not activated prosphorite and 597 and 580 cm^{-1} – in mechanically activated phosphorite.

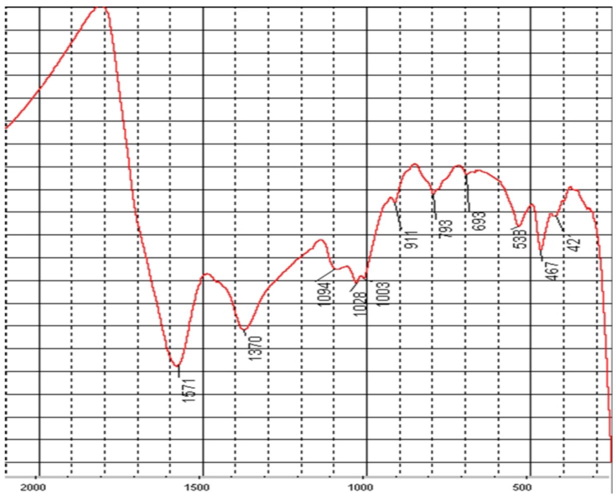


G1+F1

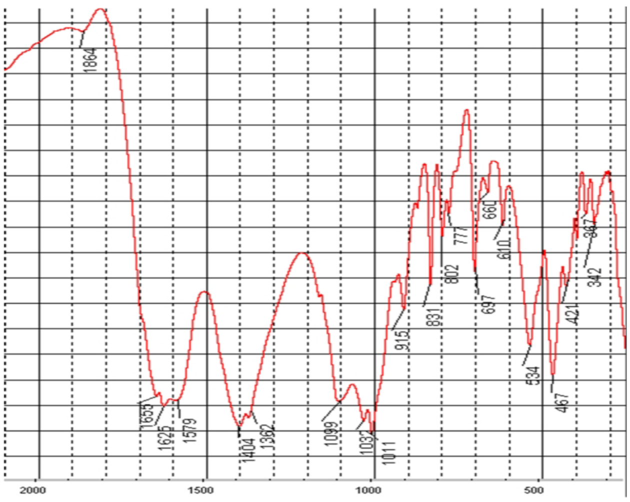


G1+F2

Fig. 4. The developed comparison of IR spectrums of compositions phosphorite humate in low-frequency area 475–2700 cm^{-1}. Designations: G1+F1 – a humate of brown coal on the activated phosphorite Zhanatas; G1+F2 – too on not activated phosphorite Zhanatas.



G1



G2

Fig. 5. The developed comparison of IR spectrums of the humates received by leaching by means of 10% KOH solution of a sample of brown coal (G1) and overburden breed Lenger (G2) in low-frequency area.

After mechanical activation in test of phosphorite there is a fraction with a size of particles of 0.05–2.0 microns, and the maintenance of fraction of 5–50 microns, prevailing in not activated material, decreases, that is at mechanical activation of a powdery material of phosphorite the maintenance of larger fraction decreases, and small fraction increases (that is natural and it isn't surprising). The selective increase in number of narrow small fraction of the size of 5–10 microns is unusual.

Measurement of a specific surface of not activated and activated phosphorite Zhanatas used to measurements applied the PSH-8A device determined a specific surface of powders by the Kozeni-Karmana method, based on measurement of hydraulic resistance of a layer of a powdery material at a filtration of a stream of air through it under the lowered pressure.

Characteristics of samples and the received results are shown in Table 5.

Table 5

Measurement of a specific surface of not activated and activated phosphorite Zhanatas on the PSH-8A device

Composition	Parameters	Specific surface, m^2/g
Phosphorites fines Zhanatas not activated	L = 10.6 mm M = 273.5 τ = 355 mp	0.24
Phosphorites fines Zhanatas activated	L = 13.1 mm M = 471 τ = 1562 mp	0.87

The analysis of tables showed that in the course of fraction activation – 0.16 mm phosphorite Zhanatas his specific surface increases from 0.24 m^2/g to 0.87 m^2/g, i.e. by 3.5 times.

5. Conclusions

1. The carried out laboratory research connected with the acid-free production of polycomponent mineral fertilizers with application of mechanical, thermal and chemical activation of phosphorites of the Zhanatas and Chulaktau deposits with addition of brown coal, the Lenger overburden rocks and vermiculite has shown positive results.

2. Physicochemical and physicomechanical researches of the Zhanatas phosphorite and the compounds have been performed with use of the following methods and devices:

- chemical analysis for determination of phosphate ions' specific activity;
- X-ray phase analysis;
- scanning electronic microscopy for determination of energy-dispersion spectra of the material's grains;
- IR-spectroscopy;
- laser determination of materials' dispersion;
- the method of nonactivated and activated Zhanatas phosphorite's specific surface determination.

It is established that the chemical composition of Zhanatas and Chulaktau phosphorites is practically identical. Phosphorite fines and the given phosphorites contain microelements such as Ti, Mn, Cr, Fe, Ni, Co, Cu, Ba, Zr and therefore they are of interest to the fertilizer manufacture not only as raw materials but also as a source of microelements.

3. The optimum parameters of mechanochemical activation of Zhanatas and Chulaktay phosphorite fines have been determined. The mechano-thermo-chemical activation allows essentially

increasing a relative content of assimilable phosphorus in the phosphorite fines from 16−17% to 30−37%.

4. The application of brown coal, ammonium sulphate and ammonium nitrate additives in the charges given in a mechanical activator (a spherical mill) allows increasing transition degree of phosphate-ion of the phosphorite fines in the assimilable citric-acid-soluble form. It is found, that the internal overburden rocks formed at the mining brown coals and the vermiculite don't increase, and somewhat reduce relative phosphorus activity in the NPK-fertilizer. It means that these components should be added after carrying out of mechanical activation, i.e. at the stage of mineral fertilizers mixing.

5. The research of IR-spectra of nonactivated and activated humate-containing phosphatic raw materials have shown, that:

- in the dolomite at the frequencies of 1454, 1424 cm^{-1} can observe valence vibrations of C-O bonds, and at 875, 384 and 727 cm^{-1} − angular and deformation vibrations of CO_3^{2-}
- in the phosphatic part the observed frequencies of 1039, 1044 and 970 cm^{-1} correspond to valence and angular vibrations of P-O and P-O-P bonds; the frequencies of 605 and 568 cm^{-1} correspond to deformation vibrations of PO_4^{3-} group in the nonactivated phosphorite and 597 and 580 cm^{-1} – in the mechanically activated phosphatic substance. It is defined, that the mechanical activation allows not only to improve the material, but also to deform the phosphorite crystal lattice creating atom-molecule structural changes.

6. The researches connected with determination of the activated and nonactivated phosphorites specific surface have been carried out. It is found, that the mechanical activation positively influences on the opening of phosphatic substance; in the phosphorites with particle size of 0.16 mm and less the specific surface of the activated phosphatic substance has increased in 3.5 times (from 0.24 m^2/g to 0.87 m^2/g).

7. On the basis of the received results the obtaining polycomponent fertilizer samples and their agrochemical tests have been planned.

References

[1]. A.S. Saparov. Fertility of soils and efficiency of cultures. – Alma-Ata, - 2006. - 244 p. (in Russian).

[2]. I.E. Fischer, V.M. Filonov. Some results of agrochemical inspection of soils // Sb. "State and prospect of development of soil science". Alma-Ata. - 2005 (in Russian).

[3]. Innovative patent No. 27474. Way of receiving organic mineral fertilizer. Published on 15.10.2013 bulletin No. 10 (in Russian).

[4]. K.T. Zhantasov, Sh.M. Moldabekov, V.K. Bishimbayev, Zh.U. Myrkhalykov, M.K. Zhantasov. Works of ISPC "Auezov Readings-11": Kazakhstan on a way to society of knowledge: The innovative directions of development of science, education and culture" – Shymkent, 2012. t.65, 149–155 p. (in Russian).

[5]. K.T. Zhantasov, K.N. Bazhirova, Z.D. Toltebayeva, D.M. Zhantasov, I.A. Petropavlovskiy, I.A. Pochitalkina. Himicheskaja promyshlennost' segodnja [Chemical Industry Today] 5 (2013) 4–6 (in Russian).

[6]. I.A. Petropavlovskiy, I.A. Pochitalkina, V.K. Bishimbayev, K.T. Zhantasov, K.N. Bazhirova. Himicheskaja promyshlennost' segodnja [Chemical Industry Today] 2 (2013) 15–18 (in Russian).

[7]. M.K. Zhantasov, Zh.M. Altybayev, M.K. Zhantasov, M.M. Eskendirova, B.A. Lavrov, L.Kh. Frangulidi. Eurasian Chemico-Technological Journal 4 (2013) 351–355.

[8]. Ch.B. Kovoleva, E.A. Solovyova. Use of natural coals for the solution of ecological tasks. // col. Environmental problems of mining. - M, 1993. – P. 149–157 (in Russian).

[9]. V.K. Smolyakov, O.V. Lapshin, V.V. Boldyrev. Int. J. Self-Propag. High-Temp Synth. 8 (1) (2008) 20–29 (in Russian).

[10]. T.I. Golikov Logical bases of planning of experiment. M: Metallurgy, 1981 (in Russian).

[11]. Yu.P. Adler, E.V. Markova, Yu.V. Granovsky, Experiment planning by search of optimum conditions. M: Science, 1976 (in Russian).

[12]. I.G. Zedginidze, Planning of experiments for research of multicomponent systems. M: Science, 1976 (in Russian).

[13]. E.V. Boldyreva, V.V. Boldyrev. Mechanochemistry and mechanical activation of solids. Part I // In: Experimental and Theoretical Studies in Modern Mechanochemistry (Ed. G. Mulas & F. Delogu) 2010, Transworld research network: Kerala, p. 1–19.

[14]. V.Z. Brodsky, L.I. Brodsky, T.I. Golikova etc. Tables of plans of experiment for factorial polynomial models. M: Metallurgizdat, 1982 (in Russian).

[15]. Kh. Usmanov, R. Chernyakova, U. Dzhusipbekov. Perspectives of Innovations, Economics & Business. International Cross-Industry Journal. 6 (3) (2010) 131–133.

[16]. E.V. Markova, A.N. Lisenkov. Combinatory plans in problems of multiple-factor experiment. M: Science, 1979 (in Russian).

[17]. S.M. Ermakov, V.Z. Brodsky, A.A. Kozlov, M.B. Malyutov etc. Theory of mathematical planning of experiment. M: Science, 1983 (in Russian).

[18]. S.L. Akhnazarova, V.V. Kafarov. Methods of optimization of experiment in chemical technology. M: The higher school, 1985 (in Russian).

[19]. S.M. Ermakov, A.A. Zhiglyavsky, Mathematic theory of optimum experiment. M. Nauka, 1987 (in Russian).