ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

2 (62)

АПРЕЛЬ – ИЮНЬ 2018 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

UDC 541.183.+ 541.18.053 : 53.096

B. D. BALGYSHEVA[1], H. SEYTKALI[2], SH. G. MACABAY[1], ZH. S. SAMET[1]

Kazakh national University named after al-Farabi, Almaty, Republic of Kazakhstan,
Kazakh national agrarian University Almaty, Republic of Kazakhstan.
E-mail: beikut2013@mail.ru

OBTAINING ZINC-CONTAINING MICROFERTILIZERS METHOD OF MECHANOCHEMICAL ACTIVATION

Abstract. Glauconite by H_3PO_4 was processed in mechanical-thermal and thermal system in different mass ratios. As a result, it was found that the efficiency of MCA-thermal treatment was higher than thermal treatment. IR spectra and x-ray fluorescence analysis were performed.

Key words: thermal, mechanical, glauconite, microfertilization, phosphoric acid.

Now along with fertilizers, mineral micro-fertilizers composed of macronutrients rise high interest in agriculture. If there is no trace element in the soil, the quality of the product will be low and will lead to plant disease. According to the proven scientific and experimental data, low agricultural production is due to the lack of trace elements in the soil [1]. Trace elements play an important role in the normal functioning of enzymatic systems in the physiological processes of plants [2].

Chloride, manganese, molybdenum, zinc, copper and cobalt play an important role in the nutrition and formation of the plant. Trace elements are present in physiological and biochemical processes. Synthesis of proteins, fats, carbohydrates, phosphorus and compounds occurs along with the presence of zinc. Zinc increases vitamin C, carotene in plants. It strengthens the heat resistance and frost resistance of the plant. Deficiency of zinc elements will lead to fine foliage and fruits. Zinc deficiency is strongly felt especially on the plant grown in carbonate soils: vegetables, maize and fruit trees. Because in this soil, there is a low level of zinc sulphate,villemit, calamine, etc. and theyare in the form of compounds. In the soil in theterritory of Kazakhstan zinc is between 47-59 mg/kg per kilogram. Different levels of zinc are associated with soil-forming rocks, their mechanical composition and agrotechnical measures [5].

In General, the soil of Kazakhstan is rich in manganese and boron, but has lack of zinc and molybdenum, although copper is provided in an average degree.

For a plant its useful to have in soil water-soluble compounds of molybdenum and boron, salts of bivalent iron and manganese, as well copper and zinc cations as part of a complex of water-soluble nutrient absorption of soils are useful. When using movable plant typesusually fertilizers of micronutrients absorbing types are used and at the same time their size is counted.

Provision of soils with movable trace elements affects the determination of the size of fertilizers which are used in agricultural crops and the growth of this plants.

In the areas of Northern, Southern, Central Kazakhstan usually have black soil, Matt black and brown soil, brown and black soil, light black soil, copper and cobalt have an average level of provision of movable elements, manganese and boron level is higher, level of movable types of molybdenum and zinc are lower. In Almaty and Taldykorgan regions 5-8 mg per kilogram of dark chestnut soil and 2.5-3.0 mg of immovable copper in Zhambyl and South Kazakhstan regions [6].

Polymicrogyria zinc dark gray, contains 25% zinc, produced in powder form. Used seed treatment (repor t 4 kg per 1 ton of seeds) impregnation into the ground (12-20 kg per hectare in the report)

Scientists from Uzbekistan have proved in scientifically-based experience by usingglauconitic rocks in the industry and agriculture [7, 8].

Based on the results of long – term experiments, the following conclusions were made: $(R_2O + RO)Re_2O_3{\cdot}4SiO_2{\cdot}2H_2O$ glauconite-valuable, traditional, but there are potassium, R_2O-Na_2O and K_2O, RO-MgO, CaO, FeO, ReO, R_2O_3-Al_2O_3 and Fe_2O_3. good effect on plant growth, yield of raw materials. The results of the experiments are good with rice.

Sugar in the Rostov region, the experiment was done on sugar beet, the productivity of culture according to GJI increased by 14-18 t/ha. The results of the experiment with potatoes went well.

Talking about the requirements for glauconite: the requirement of glauconite is still not approved by GOST. The recommendation was presented by the Rostov and Uzbek geologists, also by group of chemists.

In a certain area of production of glauconite and the possibility of application in many worksare provided [9].

Summing up the results of the literature review, current problem is to use glauconitefertilizers, especially produsing new types of glaukopis and glucocare by using production technology can be rational consideration.

Information about the scientific work under glaukonit conversion at high temperature is very rare.

Therefore, the aim is to produce fertilizers by activating glaukonit phosphoric acid and Zn^{2+} salts.

EXPERIMENTAL PART

As a source of raw materials in Kostanay region Sokolov-Sarbai mine used glauconite $K{<}1(Fe^{3+},Fe^{2+},Al,Mg)2\text{-}3[Si_3(Si, Al)O_{10}][OH]2{\cdot}nH_2O$.

As an additive to Glauconite, 40% of orthophosphoric acid was used. Glauconite (G) and 40% phosphoric acid (H_3PO_4) was produced by spraying through batcher in 1:1, 2:1, 3:1, 4:1 mass communication.The ratio of mass of Ball and other ingridientsare 25:1, reaction duration is 15 minutes mechanical; rotation frequency is 300 rpm.

Mechanochemical processing of glauconite is made by – modern 2SL brand planetary dirmode in two reels.

Favorable conditions of firing the process were obtained: T=450 ºC, t=45 min.

Heat treatment was carried out in a volume of 45 min mass of the sample.

For the study of fertilizer properties $ZnSO_4{\cdot}7H_2O$ salt was used.

Glaukonit modification was considered in two ways: thermal and mechano-thermal processing (heat treatment and MOSS). The modification was carried out according to the specific methodology.

To detect changes of modified characteristics of the glauconite, structural and electronic microscopic method, x-ray analysis, infrared spectroscopy method, x-ray fluorescence analysis (elemental analysis), differential thermal analysis and atomic absorption analysis methods were used.

Zn^{2+} salt solution 60 μg/ml, 500 μg/ml, 1000 μg/ml concentration solutions were prepared in three models. In a flask with 200 ml of the prepared solutions on the filling cone, 2g were placed in each three cone kobas. The flask is stoppered and fixed by cone mixer machine for 60 min. At the end of sorption of solutions, are filtered by paper filter of d=12 cm "blue ribbon". Chemical analysis were made. As part of the filtrate Zn^{2+} ion concentration of is determined by the atomic absorption analysis method.

RESULTS AND ANALYSIS

The mixture of Glauconite and phosphoric acid obtained by thermal and chemical, mechanochemical way after processing were conducted by a special methodology (tables 1, 2).

Glauconite-H_3PO_4 (40%) of $ZnSO_4{\cdot}7H_2O$ system, obtained by the results of various characteristics after heat treatment of the product salt concentration of Zn^{2+} ions 60; 500; 1000 mg/ml P_2O_5cit in low concentrations falls. It's also seen obviously during mechanochemical and chemical treatment.P_2O_5cit.men's. G. significance of the Supreme size is: H_3PO_4 =1:1 mass relationship of Zn^{2+} ions of 60 μg/ml of P_2O_5 concentration is observed, the size of 32,07% was revealed (table 2).

Table 1 – Heat treated samples P_2O_5 size

The ratio of the sample	C_0 (Zn^{2+}), mkg/ml	P_2O_5 total, %	P_2O_5 the citrate solution, %	$K_{decompose}$, %
G: H_3PO_4 =1:1	60	29,85	22,73	76,14
	500	18,81	13,92	74,00
	1000	12,97	8,86	68,30
G: H_3PO_4 =2:1	60	30,46	20,53	67,39
	500	14,26	9,37	65,70
	1000	14,02	9,16	65,30
G: H_3PO_4 =3:1	60	23,03	15,43	66,99
	500	11,99	8,90	66,99
	1000	11,89	7,28	61,22
G: H_3PO_4 =4:1	60	12,14	6,70	55,18
	500	11,78	5,13	43,54
	1000	12,01	5,82	45,96

Table 2 – Glauconite-H_3PO_4 (40%) system $ZnSO_4{\cdot}7H_2O$ MOSS concentration of various salts-characteristics obtained after heat treatment of the product

The ratio of the sample	C_0 (Zn^{2+}), mkg/ml	P_2O_5total, %	P_2O_5 the citrate solution, %	$K_{descompose}$, %
G: H_3PO_4 =1:1	60	36.22	32.07	88.54
	500	21.00	17.92	85.33
	1000	16.58	13.86	83.60
G: H_3PO_4 =2:1	60	24.15	19.53	80.86
	500	18.36	16.37	78.82
	1000	13.01	10.46	72.50
G: H_3PO_4 =3:1	60	21.38	18.32	76.33
	500	14.99	11.90	74.42
	1000	11.89	9.28	77.27
G: H_3PO_4 =4:1	60	15.14	11.70	75.29
	500	12.78	10.13	63.00
	1000	8.01	7.82	60.17

IR spectroscopic results of the study:

Phosphoric acid 40% raw glauconite glauconite activated mechanochemically in respect of samples and infrared spectroscopy Specord-M80 installation tabledesign 4000,0 KBr-450,0 cm^{-1}. Identification of the samples was performed by comparison with data debating.

Glaukonit primary $\delta(O_3PO)$ in the area of deformation vibrations of when the IR spectrum in this area 471,12 oscillation frequency, cm^{-1}, which look line. A frequency at 875.17, 779.28, 797.13, 713.12 cm^{-1}) line γ (P-OH) and describes the relationship of oscillations (figure 1).

However, 1630.69, 1429.17 cm^1 line δ (P-OH)was characterized by oscillations. And the frequency of 2513.55, 3434.93 cm^{-1} vibrations of OH groups in the structure of minerals, which characterize the line of interflooroverlappings. The IR spectrum of the frequency fluctuations of securities, the visible 520.06, 648.85, 608.79 cm^{-1} vibrations sistery $PO_4{}^{3-}$ ions, are described. But in contrast to the phosphate ions it is possible to trace lines. The frequency of oscillations 460, 471 cm^{-1}, which are composed of silica-oxygen bond quartz, characterizing the line looks dynamic. This line of Si-O fluctuations characterizes the valence bonds. And the frequency 648.85, 694.74, 713.12, 779.28, 797.13, 875.17 cm^{-1}) lines of the Si-O-Si vibrations and characterizes the figure 1. Glauconite primary any IR spectra

Glauconite δ, thermally processed (O_3PO) in the zone of deformation vibrations of the IR spectrum of the curve 471.12 oscillation frequency, cm^{-1} lines were visible. A frequency 779.08, 797.13 cm^{-1}) line γ (P-OH) and describes the relationship of oscillations (figure 2).

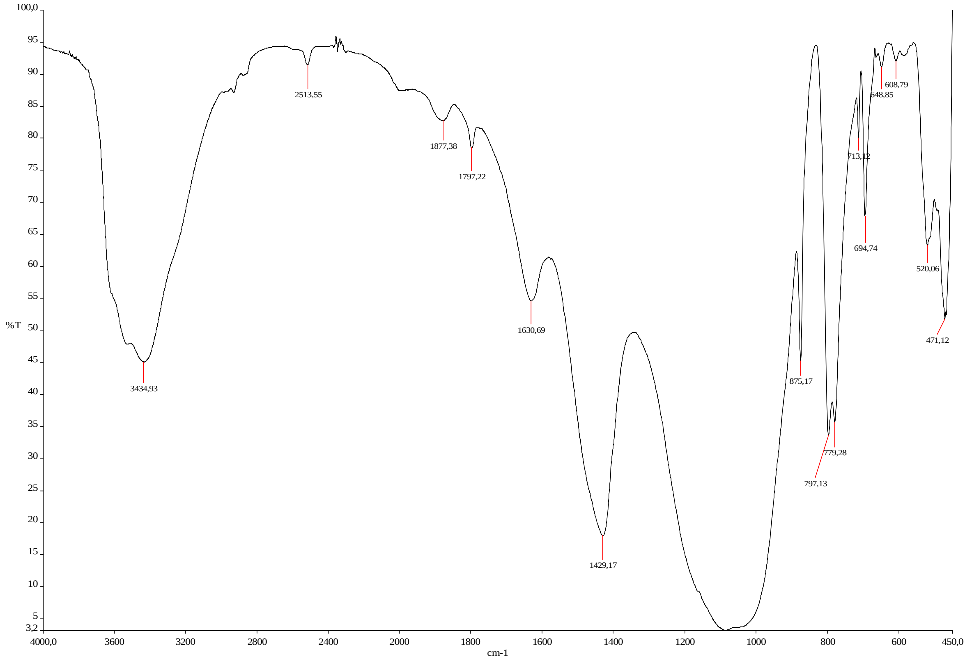

Figure 1 – Glauconite primary any IR spectra

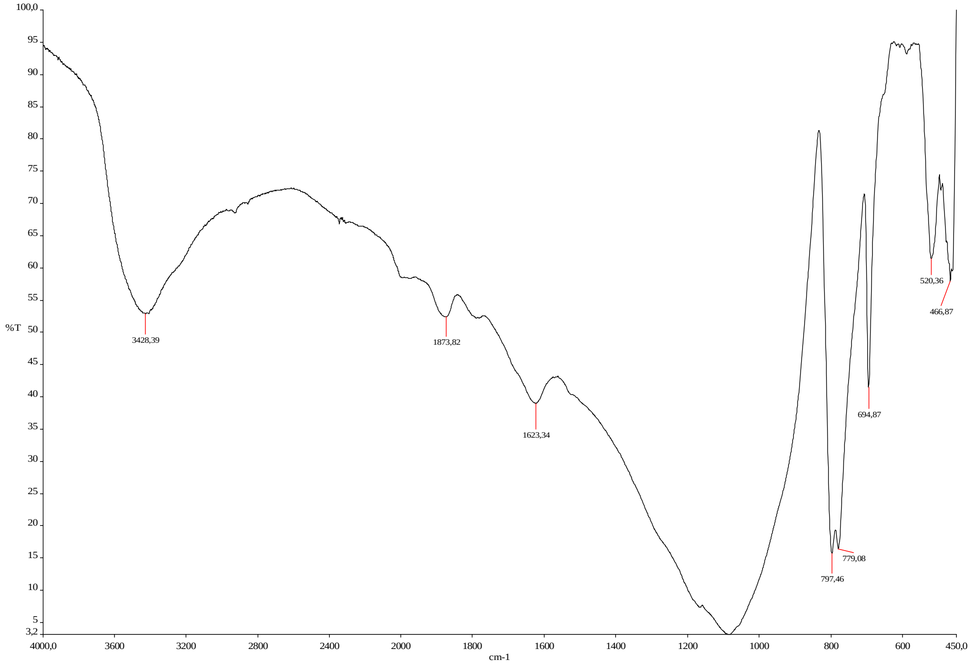

Figure 2 – Glauconite: H_3PO_4 (40%) = 1:1 system Zn^{2+} ions 60 µg/ml,
the concentration of the sample after thermal treatment IR spectrum

However, 1623.34 cm^{-1} line δ(P-OH) and was characterized by oscillations. 520.30 oscillation frequency, 466.87 cm^{-1} vibrations sistery PO_4^{3-} ions, are described. Lines characterize Si-O-Si vibrations. But in contrast to the phosphate ions it is possible to trace lines. Activated mechanochemically has samples IR spectroline 407.66 oscillation frequency, cm-1 line, it was evident that glauconite $\delta(O_3PO)$ was characterized by the deformation vibration of connection with the area (figure 3).

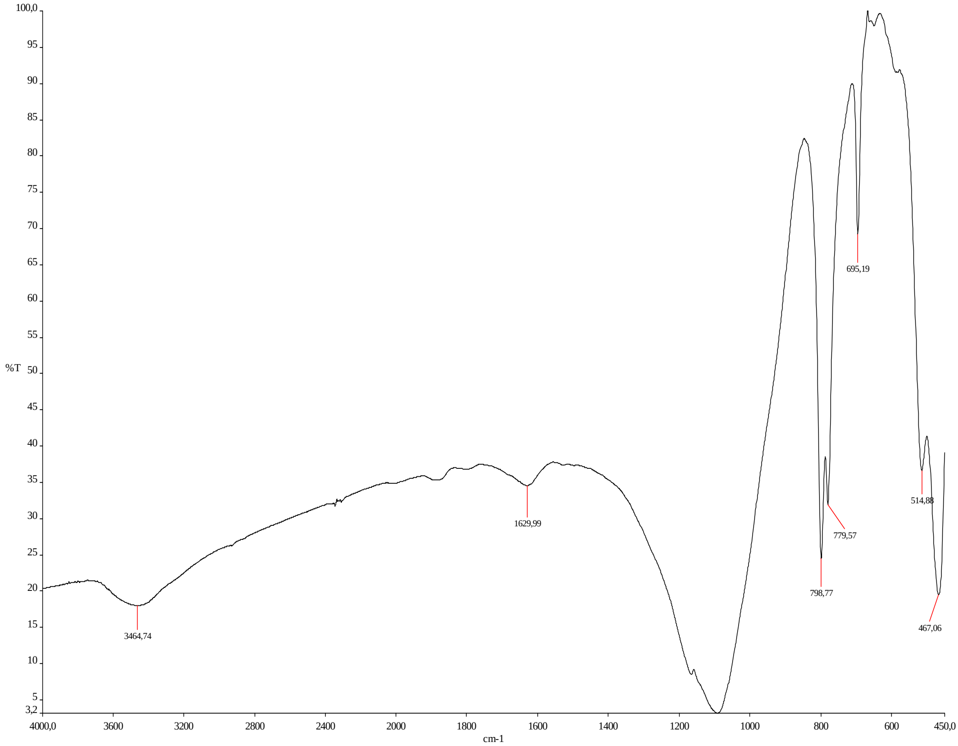

Figure 3 – Glauconite: H_3PO_4 (40%) = 1:1 system Zn^{2+} ions of 60 µg/ml and the concentration of the sample after the heat treatment of MOSS IR range

Figure 3 mechanochemical samples activated IR oscillation frequency spectroline 779.57, 798.77 cm^{-1}) lines of γ(P-OH) fluctuations, characterizes the connection. However, 1629.99 cm^{-1}) of the δ(P-OH) line was characterized by oscillations. 514.88 oscillation frequency, 605.19 cm^{-1} vibrations sistery PO_4^{3-} ions, are described. But in contrast to the phosphate ions it is possible to trace lines. Frequency 779.08, 798.77 cm^{-1}) linescharacterize the Si-O-Si vibrations. Here you can see that fluctuations in these indicators primary glauconitegilcher. As well as the Silicon-oxygen bond, the relevant abatacept phosphate ions, characterizing the intensity increases the vibration frequency of the oscillation frequencies of floors with lines in the water. Posts (sodium dihydrotes-veils) the concentration of water in the composition of interflooroverlappingsazip share annually, mostly glauconite, as well as interflooroverlappings that characterize 3464.74 water, cm^{-1} frequency of the oscillation intensity decreases. The floor of the water and the phosphate ions may be the chemical interaction between two. Each reduction in the size of glauconite in the composition of the mixture, mainly in the IR spectrum of water, reduces the intensity of the lines characterizing interflooroverlappings. Starting glauconite IR spectrum of vibrations than after heat treatment and the frequency of mechanochemical Vik-range looks like reduced frequency. Hence, there were chemical interactions. That is, as a result of penetration into the structure of glauconite mechano-chemical activation of sodium dihydrophosphate, phosphate ions bind with glauconite water in the composition.

The analysis Rentgen fluorescent glauconite 40% of the samples processed in accordance with the legislation established the elemental composition phosphorus limited mechano-chemically vertical mixing change proportionally. During activation the oxidation of some components and we can say that in connection with mechano-chemical flight was in lesser extent.

Conclusion.

1. G(glauconite) – H_3PO_4 (40%) of the system $ZnSO_4{\cdot}7H_2O$ as a result, identify the optimum temperature for heat treatment. In 450 ^{0}C colors were turned into light brown beige, also was left free .

2. It was determined by rule that G(glauconite)-mass tinasteride system H_3PO_4(1:1; 2:1; 3:1; 4:1) $ZnSO_4{\cdot}7H_2O$ salt (60; 500; 1000 μg/ml) whileare increasing the size of the P_2O_5 is decreasing.

3. Were determined the favorable conditions: G: H_3PO_4 =1:1 mass relationship of Zn2+ ions of 60 mcg/ml concentration 450 ^{0}C. Kadyrow, 76,14%.

4. G(glauconite) – H_3PO_4 (40%) of the system $ZnSO_4{\cdot}7H_2O$ in the treatment compared to heat treatment with salt K MOSS, 88.54% revealed that.

REFERENCES

[1] Stefan V.K. Life of plants and fertilizers. M., 1981.

[2] Artjushin A.M., Derzhavin L.M. Brief Dictionary on Fertilizers. 2nd ed. M., 1984.

[3] The fundamentals of farming and plant growing. 3rd ed. / Ed. Niklyaeva V.S. M., 1990.

[4] Journal of Chemistry and Business. 2001. N 46.

[5] Agrochemistry / Edited by prof. A.S. Yagodina. M.: The Ear, 1982.

[6] Journal Chemistry and Life – XXI century. 1998. N 4.

[7] Nabiev M.N., Kasymova M.A., Sat "Mineral and Organo-mineral Fertilizers, Structure Formers of Soils and Herbicides". Tashkent: FAN, 1967.

[8] Vigdorovich V.I., Tsygankova L.E., Nikolenko D.V., Protasov A.S Sorption purification of flowing solutions from copper (II) concentrate glauconite GBMTO // Sorb. and chromatography. Processes. 2013. 13, # 4. P. 442-448. (Rus.).

Резюме

Б. Д. Балгышева, Н. Сейтқали, Ш. Ғ. Мағабай, Ж. Самет

ҚҰРАМЫНДА Zn-БАР МИКРОТЫҢАЙТҚЫШЫН
МЕХАНОХИМИЯЛЫҚ АКТИВТЕУ АРҚЫЛЫ АЛУ

Глауконит – H_3PO_4 жүйесінің әртүрлі массалық қатынастары термиялық, механохимиялық-термиялық өңдеуден өткізілді. Нәтижесінде термиялық өдеуге Қарағанда МХА-термиялық өдеудің тиімділігі анықталды. ИК-спектрлер мен рентгенфлуоресцентті талдау жүргізілді.

Түйін сөздер: термиялық, механохимиялық, глауконит, микротыңайтқыш, фосфор қышқылы

Резюме

Б. Д. Балгышева, Н. Сейтқали, Ш. Ғ. Мақабай, Ж. Самет

ПОЛУЧЕНИЕ Zn-СОДЕРЖАЩИХ МИКРОУДОБРЕНИЙ
МЕХАНОХИМИЧЕСКИМ СПОСОБОМ

Проведена термическая и механохимическая обработка в системе глауконит – H_3PO_4 в разных массовых соотношениях. В результате химического анализа установлено, что механохимическая обработка более эффективна, чем термическая.

Приведены результаты исследований ИК-спектроскопии и рентгенофлуоресцентные.

Ключевые слова: термический, механохимический, глауконит, микроудобрения, фосфорная кислота.