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THE PHYSICO-CHEMICAL COMPOSITION OF THE NATURAL ALUMINOSILICATE SORBENTS USED FOR THE PHOSPHORUS EXTRACTION FROM PHOSPHORIC SLIME

Abstract. The research results of the physico-chemical features of initial raw materials of bentonite clay, vermiculite and Lenger clay of the South Kazakhstan fields with definition of chemical and material structures are given in the article.

The mechanism of phosphoric slime formation, technogenic withdrawal of production of the yellow phosphorus which is formed at a phosphorus condensation stage is studied. According to modern representations, phosphoric slime represents the phosphorus emulsion in water, stabilized with fine firm particles.

Considering phosphoric slime as stabilized with highly active pollution of an emulsion in the water, the way of phosphorus extraction is chosen from slimes, with usage firm porous sorbents on the basis of natural aluminosilicates.

The researches on definition of physico-chemical features of initial materials for obtaining from them sorbents were conducted with usage of modern methods of the physico-chemical analysis. The analysis of the scientific results has shown that intensive ranges of absorption are characteristic to fluctuations of valent link of the alumosilicate and hydroaluminate compounds. The microstructure of the studied tests is characterized by prevalence of montmorillonite crystals in bentonite clay and sodium-potassium-calcium minerals of feldspar in the vermiculite. As a result of acid activation of sulfuric acid and heat treatment was reached the high mechanical durability, bloating and bulk density of the received granules.

Keywords: Vermiculite, bentonite, montmorillonite, kaolinite, aluminosilicate, sorbents, hydromica.

Introduction. The production of yellow phosphorus with electrothermal method is large tonnage, material-andpower-intensive production[1-3], necessary for electrothermic treatment production and preparation of phosphorites more than 50%, the sizes 0÷10 mm appear thin details and off-balance phosphatic and siliceous slate stone[4-7]. Besides, during preparation of technological processing, and crushing of metallurgical coke to 20% and more [8-10], the size 0÷5 mm appear thin details. Therefore reusage of production wastes of the phosphoric industry will allow along with the solution of economic problems on improvement of the ecological state [11-13].

The phosphorus-containing slimesappear at the production of yellow phosphorus under the influence of many factors (quality, preparation of raw materials, furnace conditions, etc.) [14-16]. There is a question of utilization of these slimes, processings, considerably, and today topical issue, and not just "new" slimes, and development of the slimes [17-19]., which are saved up for many years, is a problem. Now in devices of cyclonic thermal phosphoric acid by combustion of phosphorus there are remains in the infusion composition not less than 40-50% . However, in the course of combustion of slag,the mineral part of slime is secondary waste[20].

Experimental part. By means of the sorbents obtained from natural aluminosilicates with absorption method and phosphorus-containing slimes are also refinedfrom organic and mineral impurity, allocating from composition pure phosphorus in this article. For preparation of the specified sorbents, are used the aluminosilicatesobtained from the local field, emergence and stabilization of phosphoric slime happens at phosphorus concentration at a stage of free energy at phosphorus-water the interphase borders which are developed for the moment. The adsorptive layers formed phosphorus reduce growth of the emulsion consolidated stabilizers, the drop on the surface of phosphoric drops is adsorbed and creating their liofilization the organic substancesobtained from the phosphoric phase and mineral additives from firm oven are considered as the emulsions stabilizer.

Silicon and fine details of carbon make basis of the phosphoric slime, their small portion is simple phosphorus and create gel like colloidal structure, this disperse environment is yellow phosphorus.

Table 1- Analysis of some samples of slimes of the enterprises on the yellow phosphorus production

Slime composition, %				
Wet			In conversion to dry	
P_4	H.O.	H_2O	P_4	H.O.
35,50	18,70	45,80	25,60	34,40
36,65	21,73	31,62	23,42	31,78
30,50	18,67	40,83	38,45	31,55
14,99	22,53	62,48	29,95	60,05
21,10	35,04	43,86	37,68	62,38
17,95	38,04	44,01	32,06	67,94

Table 2 -The chemical composition of raw materials obtained from different fields

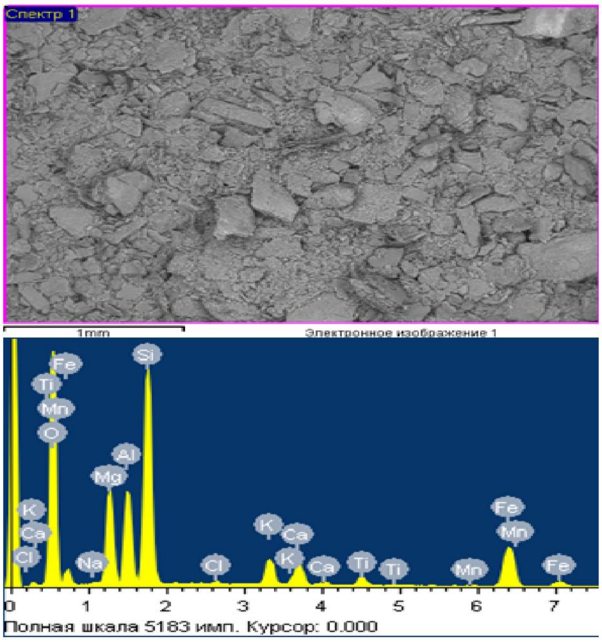
The name of the field	Componenents, %									
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5	ппп
1	2	3	4	5	6	7	8	9	10	11
Kulantau vermiculite	37,65	13,2	3,42	14,72	15,31	1,81	5,16	0,41	-	8,22
Syrdarya bentonite	60,51	16,06	1,95	6,43	3,03	1,27	1,2	2,41	0,12	6,92
Lenger clay	58,29	20,76	2,17	4,16	1,59	0,52	1,16	1,40	1,29	8,56

Raw materials vermiculite is a mineral class of the silicates of layer type relating to hydro mica group when heating they are bent as worms and bulk up to 1,5-2,5 times [7-8]. The biotite belongs to pseudomorphoses. Its colour is brown, yellow, bronze colors, gloss as a glass, hardness -1-1,5MPa very mature, specific weight -2, 4-2, 7 g/cm^3 when burning becomes very easy, both bulk up and does not sink in water. Vermiculite is formed generally at a low temperature the phlogopite and biotite breeds at hydrothermal changes, and sometimes it is formed at slaking biotite. Vermiculite in the burned look is applied in production of wallpaper as warmly-and soundproofing material.

Consumer importance of vermiculite arises when calcinating it is increased and turns into light material with a volume density from 0,06 to 0,15 kg/m^3 a polyfoam. The uniqueness of the increased vermiculite in the adsorption is connected with the increased humidity processes. The vermiculite can absorb and carry out 4-5 times more water more than its body weight.

The vermiculite microstructure obtained from Kulantau field, element structure is given in Pic.1.

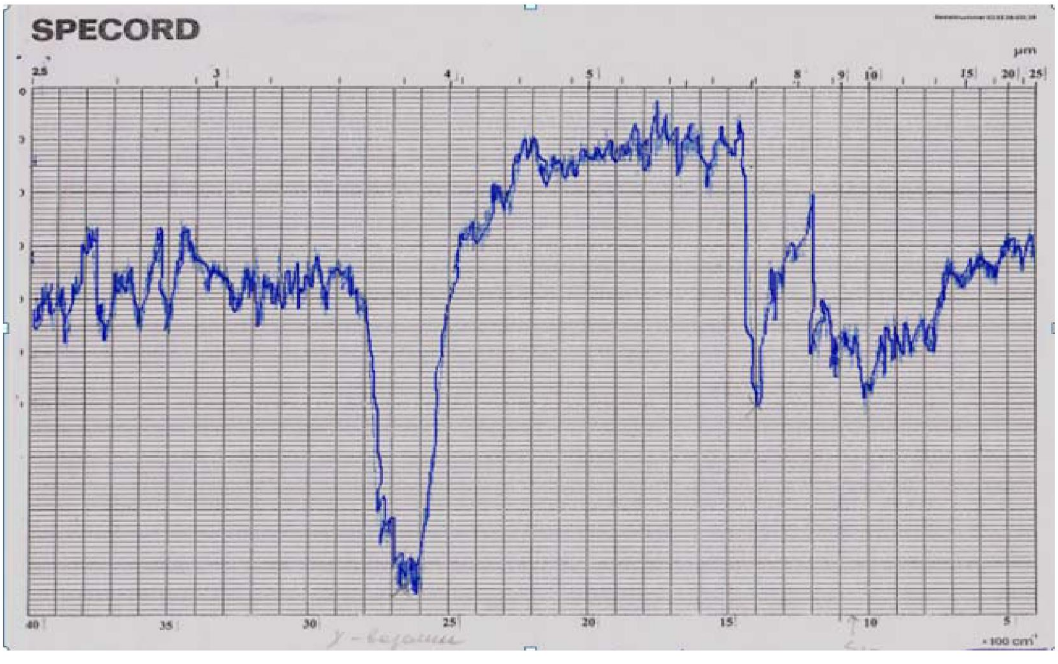
Elements	Weight%
O	46.73
Na	0.15
Mg	8.62
Al	7.69
Si	17.27
Cl	0.24
K	2.83
Ca	2.45
Ti	1.23
Mn	0.08
Fe	12.71



Picture 1- Ultimate composition and microstructure of the vermiculite obtained from Kulantau field

Unique properties of vermiculite can be used as a sorbent for absorption of mineral and organic compounds at extraction of phosphorus from phosphorus-containing slimes.

Now raw materials of vermiculite have loose weight and are friable adjournment which consist from the closed cover of feldspar, mica and amfibold. IR spectrum of the vermiculite received from the Kulantau field is given in the picture 2.



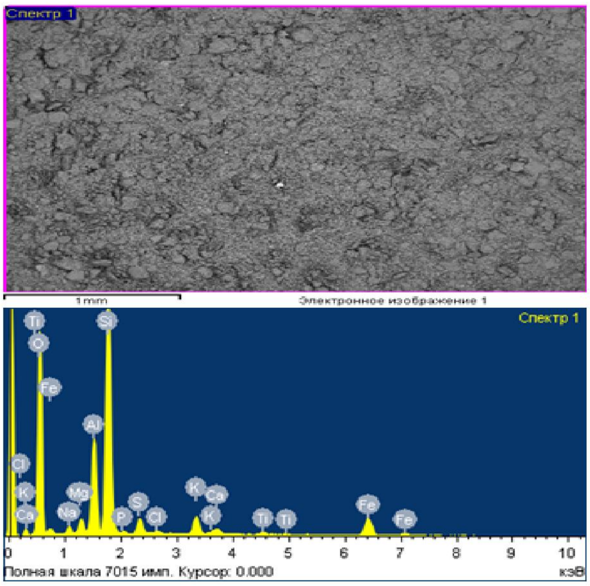
The picture 2 - IR Spectrum of the vermiculite obtained from the Kulantau field υ * cm^2

For Kulantau vermiculites are characteristic 700-1500sm-1 length of waves of a range of the absorption territory. Poorly intensive 600-650sm^{-1} and 70-850^{-1} ranges of absorption α and β characterizes modifications AI–O compounds, and on average intensive waves 830-850 cm^{-1} characterizes alumocalcium compounds Ca-AI-O. on 980-1010 cm^{-1} of the territory intensive absorption range Si-O valent linked compounds and on 1380 cm^{-1}, territories show-OH valent groups, on 3180-3250 cm^{-1} and 3500-3730 cm^{-1} territories characterizes ranges of absorption of O-group magnesium (Mg^{+2}) and (Fe^{+2}, Fe^{+3})compounds of iron hydrate.

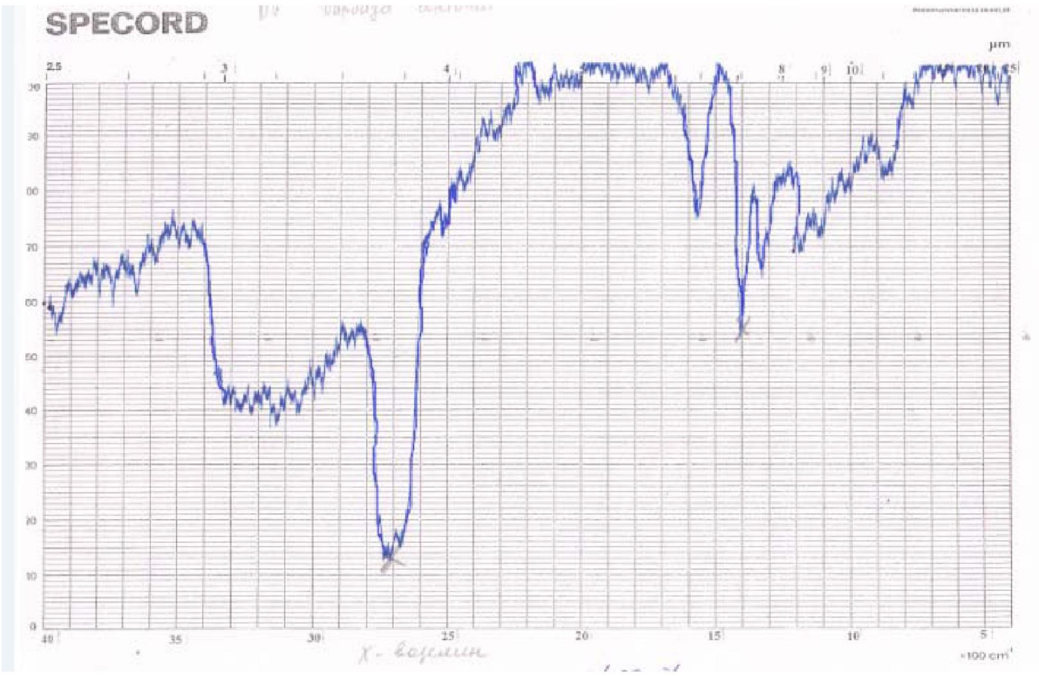
Bentonites are formed as a result of chemical decomposition of volcanic ashes, tuff and lavas in sea water or at land aeration (generally from granules it is lower than 0,001 mm). He doesn't conduct heat and sound as light filler of concrete, etc.It is applied to production of construction materials and products. Bentonites are fire resistant 1350-1430 °C, fusion point is 900 - 950 °C. Chemical formula (Mg, Fe+2, Fe+3) 3 [(S i, Al) 4O10] • (OH)2•4H2O.

The microstructure of the bentonite obtained from Syrdarya field the element and chemical composition and IR spectrum are provided in the picture 3,4.

Elements	Weight%
O	52.08
Na	1.31
Mg	1.48
Al	8.87
Si	23.00
P	0.32
S	1.78
Cl	0.34
K	2.48
Ca	0.93
Ti	0.54
Fe	6.87



The picture 3 - The microstructure of the bentonite obtained from Syrdarya field the element and chemical composition

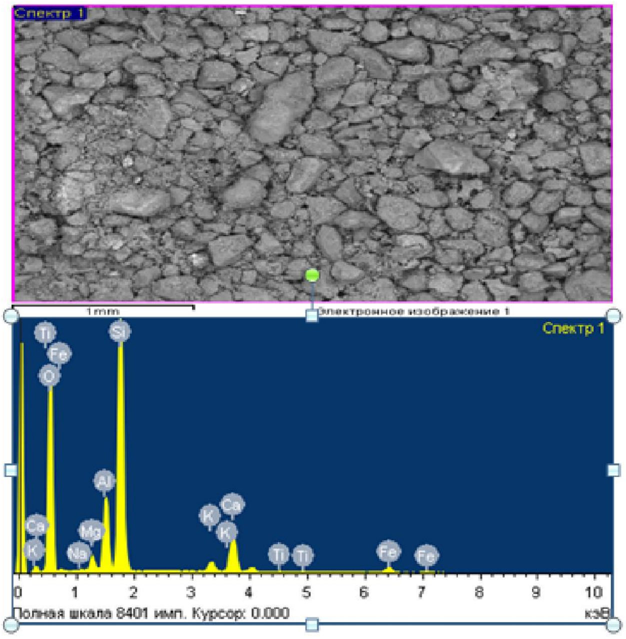


The picture 4 - IR spectrum of the bentonite obtained from Syrdarya field, υ * cm

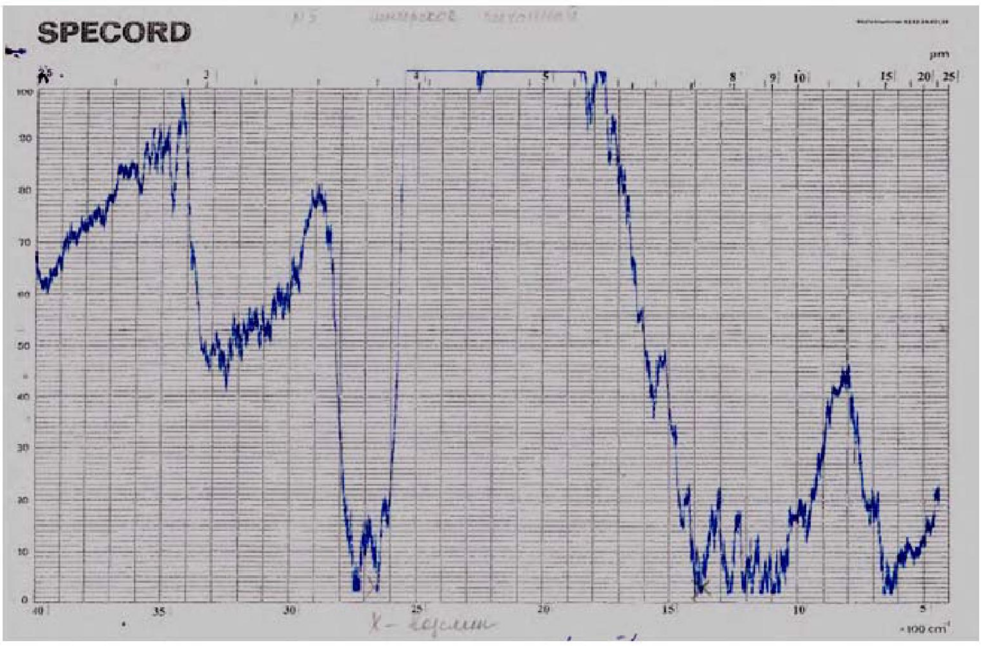
Absorption spectra of Syrdarya bentonites is characterized by length of waves in the territories of 1400 cm^{-1} and 1570sm^{-1}. weak intensive lines of absorption in the territory of 430-500 cm^{-1} Si-O - Fe characterizes strain stress state. In the territory of 930-1010 cm^{-1} is characteristic to wavelength of oscillations Si-O valent link. In the territory of 1320-1400 cm^{-1} ranges of intensive absorption is characteristic on OH-groups to diffraction oscillations.In the territory 3050-3230 cm^{-1} oscillations in wavelength characterizes absorption spectra H-OAI, H-OFe^{+3} group.

The microstructure of high-melting clays of Lenger, element composition and roentgenogram are given in pictures 5,6.

Elements	Weight %
O	57.24
Na	0.09
Mg	1.37
Al	6.84
Si	25.02
K	1.41
Ca	5.53
Ti	0.18
Fe	2.32



Picture 5 - Microstructures of high-melting clays of Lenger, element composition



Picture 6 - IR spectrum of high-melting clays of Lengerυ * cm^2

The choice of activization method of their porosity of sorbents mechanically determines acid surface areas, the absorption volume and development. Chemical activation of sorbents is their processing average acids at a different temperature.The increase in absorption properties of acid activation of natural clays is considered in the article. For obtaining sorbents is used burned porous vermiculite, bentonite and refractory clays of Lenger.

Mechanical cleaning and fractional sifting on the vibrosieve (0,13 mm) was carried out for this purpose. The method applied when crushing directly influences chemical activity of the received product. At Vibro and spherical crushing granulation happens on the surface of clay particles and granulation process significantly influences properties of absorption sorbents. The sorbents on the sphericalmill are stirred for production of the granulated clays then it is necessary to mix with a speed about 40-60 v/m in the optimum volume of water is at 5-10 minutes. The granulations of sorbents occurs on the plate granulator in the diameter of d=3-1,5 mm.

The granulated sorbents are dried constantly on air and undergo to heat treatment. Heat treatment of the granule is carried out in the mode: T = 473-773K within 1-4 hours in the muffle furnaces on the certain temperature and at the scheduled time.The samples of sorbents were determined with usage of real kerosene density, by means of Le-Chatelie's device.

The processing of clay minerals with hot acids, their catalytic and adsorptive properties of sorbents was known that their activity sharply increases at a research.

Result and its discussion.Theprocessings and influence on the structure of sorbents and the adsorptive properties with hot sulfuric acid is considered in this article. The last in temperature volume 700 - 1100°C for 4 hours, firm and liquid phase in T:I in the correlation = 1:5 in the ratio 25% $H_2SO_4$are activated.: G.C=1:10 in the ratio, in others similar conditions, have been investigated also influence of the adsorptive properties 5,10, 15, 20, 25 of % of H_2SO_4 [19].

Table 3 - Test volumes after activation

Probe numbers, №	Temperature, ^{0}C	The diameter of granules before thermo treatment,mm	The diameter of granules after thermo treatment,mm			
			1 hour.	2 hour.	3 hour.	4 hour.
1.High-melting clays of Lenger	700	8-11	9-11	9-12	11-12	12-13
	900		10-12	11-13	12-15	14-17
	1100		10-13	12-14	13-16	15-18
2.Kulantau vermuculite	700	8-11	8-12	11-12	11-13	12-13
	900		9-11	10-12	11-12	12-13
	1100		9-12	11-14	15-17	16-19
3.Syrdarya bentonite	700	8-10	10-11	10-13	11-13	10-13
	900		10-12	11-13	12-13	12-14
	1100		10-12	12-13	12-15	14-16

In this scientific research were studied initial raw materials i.e. Kulantau vermiculite, the obtained bentonites of the Syrdarya field and physical and chemical characteristics of refractory clays from Lenger and Syrdarya areas have been investigated.

During the research on the absorption method for phosphorus extraction from slime, the granulated raw materials in the technological plan sorbents in the composition of aluminosilicates of natural minerals, high-quality technologies have been developed.

Such process of sorbents absorption of organic and mineral impurity with effective and during lifetime therefore stability on phosphorus water is broken.

In the structure of phosphorus extraction from phosphoric slimes, porosity directly influences porosity of minerals as a part of which there are aluminosilicates. Such bentonites can belong to refractory clays from Lenger and bentonite raw materials and vermiculite. The method of absorption is provided by cleaning of technogenic waste in the nature from impurity. Therefore the production technology of sorbents of mineral raw materials is “a new theme”.

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ФОСФОР ШЛАМЫНАН ФОСФОРДЫ БӨЛІП АЛУ ҮШІН ҚОЛДАНЫЛАТЫН ТАБИҒИ АЛЮМИНОСИЛИКАТТЫ СОРБЕНТТЕРДІҢ ФИЗИКА- ХИМИЯЛЫҚ ҚҰРАМЫ

Аннотация. Мақалада Оңтүстік Қазақстан аумағындағы жергілікті кен орындарынынан алынған шикізаттар бентонит, вермикулит және Ленгірдің қиын балқитын саз-балшығының химиялық және материалдық композицияларын анықтау арқылы физикалық және химиялық ерекшеліктерін зерттеу нәтижелері келтірілген.

Фосфордың конденсациясы кезеңінде пайда болатын фосфор шламы, сары фосфор өндірісінің антропогендік қалдықтарын түзу механизмі арқылы зерттеледі. Қазіргі заманғы тұжырымдамаларға сәйкес, фосфор шламы майда шашыраңқы қатты бөлшектермен тұрақтандырылған судағы фосфор эмульсиясы болып табылады.

Фосфор шламын суда эмульсияның жоғары белсенді ластануымен тұрақтандырылғаны ретінде қарастыра отырып, табиғи алюмосиликаттар негізінде қатты кеуекті сорбенттерді қолдану арқылы фосфор шламынан фосфорды бөлу әдісі таңдалды. Сорбенттерді өндіру үшін табиғи шикізаттың физико-химиялық сипаттамаларын анықтау бойынша зерттеулер, физика-химиялық талдаудың заманауи әдістерін қолдана отырып жүргізілді.

Алынған нәтижелерді талдау көрсеткендей, қарқынды сіңіру спектрі алюмосиликат пен гидролю-минат қосылыстарының валенттік байланысының діріліне тән. Зерттелген үлгілердің микроқұрылымы вермикулиттегі, бентонит балшықтарындағы монтморилонит кристалдарының және натрий калий-кальцийлі дала шпаттарының минералдарының басым болуымен сипатталады. Күкірт қышқылы мен термиялық өңдеу арқылы қышқылды белсендірілу нәтижесінде алынған түйіршіктердің интенсивті және тығыздығы жоғары механикалық беріктікке ие болды.

Түйін сөздер: Вермикулит, бентонит, монтмориллонит, каолинит, алюмосиликаттар, сорбент, гидрослюдалар.

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ФИЗИКО- ХИМИЧЕСКИЙ СОСТАВ ПРИРОДНЫХ АЛЮМИНОСИЛИКАТНЫХ СОРБЕНТОВ ИСПОЛЬЗУЕМЫХ ДЛЯ ИЗВЛЕЧЕНИЯ ФОСФОРА ИЗ ФОСФОРНОГО ШЛАМА

Аннотация. В статье приведены результаты исследований физико-химических особенностей исходных сырьевых материалов бентонитовой глины, вермикулита и Ленгерской глины месторождений Южного Казахстана с определением химического и вещественного составов.

Изучен механизм формирования фосфорного шлама, техногенного отхода производства желтого фосфора, образующегося на стадии конденсации фосфора. В соответствии с современными представлениями, фосфорный шлам представляет собой эмульсию фосфора в воде, стабилизированную тонкодисперсными твердыми частицами.

Рассматривая фосфорный шлам как стабилизированную высокоактивными загрязнениями эмульсии в воде, выбран способ выделения фосфора из шламов, с использованием твердых пористых сорбентов на основе природных алюмосиликатов.

Исследования по определению физико-химических особенностей исходных материалов для получения из них сорбентов, проводились с использованием современных методов физико-химического анализа. Анализ полученых результатов показал, что интенсивные спектры поглощения характерны колебаниям валентных связей алюмосиликатных и гидроалюминатных соединений. Микроструктура исследуемых проб характеризуется преобладанием кристаллов монтморилонита в бентонитовой глине и натрий-калий-кальциевыми минералами полевого шпата в вермикулите. В результате кислотной активации серной кислотой и термической обработки достигнута высокая механическая прочность, вспучиваемость и насыпной плотность полученных гранул.

Ключевые слова. Вермикулит, бентонит, монтмориллонит, каолинит, алюмосиликаты, сорбент, гидрослюды.