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OFF-BALANCE PHOSPHATE RAW MATERIALS OF THE ZHANATAS DEPOSIT: COMPREHENSIVE STUDY OF COMPOSITION AND STRUCTURE

Abstract. The article presents the results of physicochemical studies of the composition and structure of off-balance raw materials from the Zhanatas deposit, located in the phosphorite-containing depression Karatau (South Kazakhstan). For the study, modern instrumental methods of physical and chemical analysis were used. The elemental-material composition is determined by the method of chemical analysis in accordance with the rules of regulatory documents and standards. The results of these studies are of practical importance for their further processing into phosphorus-containing products.

Mineral fertilizers, including diammonium phosphate and off-balance phosphate raw materials in the agro-industrial sector of the economy play a key role in increasing the yield and quality of agricultural crops. Therefore, given the export orientation of the products of the phosphorus industry, it cannot be considered outside of macroeconomics, information is provided on the mineral petrographic analysis and the chemistry of the process of obtaining DAP based on the results of X-ray phase analysis obtained by IRS and on a scanning electron microscope. Filming was carried out on a D8 Advance (Bruker) apparatus, Cu-K_a, tube voltage 40 kV, current 40 mA. The processing of the obtained data of diffraction patterns and the calculation of interplanar distances were carried out using the EVA software. Sample decoding and phase search were carried out using the Search / match program using the PDF-2 powder diffractometric data base (ICDD).

Key words: phosphorite, IR spectrum, elemental analysis, mineralogy, extraction phosphoric acid.

Introduction. In production conditions, part of the mineral raw materials becomes unusable and leads to a decrease in the quality of raw materials, as well as to an increase in production costs. Currently, one of the main factors of economic prosperity of developing countries is its mineral resource base. Kazakhstan, which is one of the largest countries in terms of territory area, is one of the leading countries in terms of the variety of its minerals [1]. Currently, in many countries, along with the decline in the quality of mineral raw materials, the unsuitability of extracted minerals is observed [1, 2]. In this regard, it is obvious that the growth in the consumption of raw materials creates a number of barriers to providing working enterprises with high-quality raw materials [3].

Due to the decline in the quality of raw materials, research has recently begun on the enrichment of low-quality ores in order to improve their suitability. Among them are phosphorites [4]. The composition and structure of phosphorites depend on their location and origin. Currently, open-pit and underground methods of mining phosphorite deposits are widely used [5-6].The Karatau phosphorite-bearing basin in Kazakhstan is one of the largest deposits of this type of raw material on earth. The Sholaktau and Zhanatas deposits, located in the Karatau basin, are among the phosphorite ores extracted underground [7].

According to the content of the main component P_2O_5, these deposits belong to the middle groups (25-27%). In this regard, the low-quality concentrates produced have a low demand on the world market [8]. This situation actualizes the need to study the problem of enrichment and search for new methods of utilization of poor deposits. There are a number of studies on the use of ordinary and low-grade phosphorites. Among them are the production of WPA (wet-process phosphoric acid) and the production of feed phosphates [9, 10].

The purpose of this work is a comprehensive study of the composition and structure of off-balance phosphate raw materials of the Zhanatas deposit for its full assessment of suitability in the production of phosphorus-containing products.

Materials and methods. The raw material used for the research was low-grade phosphorite from the Zhanatas deposit (Karatau basin). The study of its elemental, mineralogical and structural composition was carried out by modern instrumental methods of analysis:

- elemental analysis was studied by chemical analysis using various regulatory documents (GOST);
-the mineralogical composition was studied using a MIN-8 metallographic microscope;
- The Avatar 370 CsI infrared Fourier spectrometer was used to study the IR spectra of raw materials;
- X-ray phase analysis was performed on a D8 Advance diffractometer (Bruker). The decryption of the received data is made in the PDF-2 database.

The thermal analysis of the provided samples was carried out using the STA 449 F3 Jupiter synchronous thermal analysis device. Before heating, the furnace space was pumped out (the achieved vacuum level is ~ 92%) and then purged with an inert gas for 5 minutes. Heating was carried out at a speed of 10^0C/min. in an atmosphere of highly purified argon. Cooling was carried out at a speed of 12^0C/min. The total volume of the incoming gas was kept within 100 ml/min. The results obtained with the STA 449 F3 Jupiter were processed using the NETZSCHProteus software.

Results. The chemical analysis of the composition of the studied raw materials is presented in Table 1.

Table 1. Chemical analysis of the feedstock

Element / Compound	Content, %
B	0.03
K / K_2O	0.51 / 0.15
Ca	36.50
Mg / MgO	1.30 / 4.76
Mn	0.09
As	0.01
F	0.004
P / P_2O_5	7.50 / 17.40
Insoluble residue	30.29

Based on the table data, it can be seen that the content of the main component P_2O_5 is at an extremely low level and is about 17.40%. In addition, there are impurity elements in the form of fluorine, arsenic, boron. The high content of the insoluble residue indicates the comparative characteristics of this type of raw material.

For a complete study of the mineralogical composition of phosphorite, the method of metallographic microscopy was used [11]. The results of the studies are shown in Figure 1.

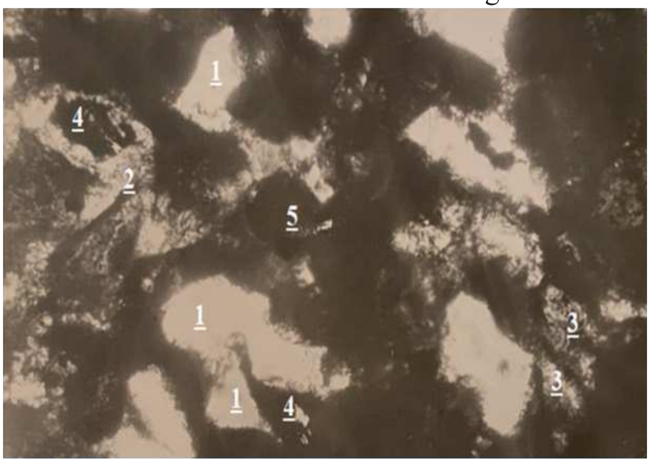

Fig.1. Mineralogical composition of Zhanatas phosphorite: 1-SiO_2 (quartz); 2- SiO_2 (chalcedony); 3-$CaCO_3$ (calcite); 4- $Ca_5(PO_4,CO_3)_3F$ (francolite); 5-FeS_2 (pyrite)

The surface of the test sample is characterized by uniformity. They are largely represented by black carbonaceous shales. The structure of the sample is oolitic, there is the presence of organic matter. The francolite in the sample under study is arranged in the form of oolites. There is a significant amount of quartz and less often chalcedony. Pyrite is represented in the form of cubic crystals. The percentage of basic substances,%: phosphorite-47.9; dolomite-12.25; calcite-5.04; quartz-22.8.

When performing the IR spectroscopic analysis, the following peaks were obtained (Figure 2):

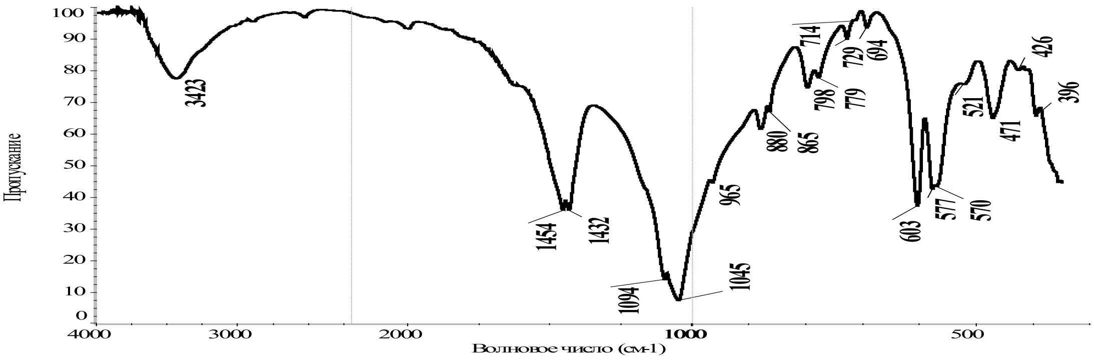

Fig.2. IR spectra of Zhanatas phosphorite

From the above figure, it is determined that the wave numbers 1049-965 cm^{-1} and 603-570 cm^{-1} are characterized by the phosphorite $Ca_5(PO_4)_3F$. The absorption spectra in the range 798-694 and 521-396 cm^{-1} represent silicate compounds. The presence of dolomite in the absorption region of 1454-729cm^{-1} is also noted. In addition, the possibility of the presence of calcite and siderite in the areas of 1432-714 cm^{-1} and 1432-865 cm^{-1}, respectively, was established [12].

The results of the X-ray phase analysis study allowed us to determine the main compounds in the studied composition of the feedstock (Figure 3).

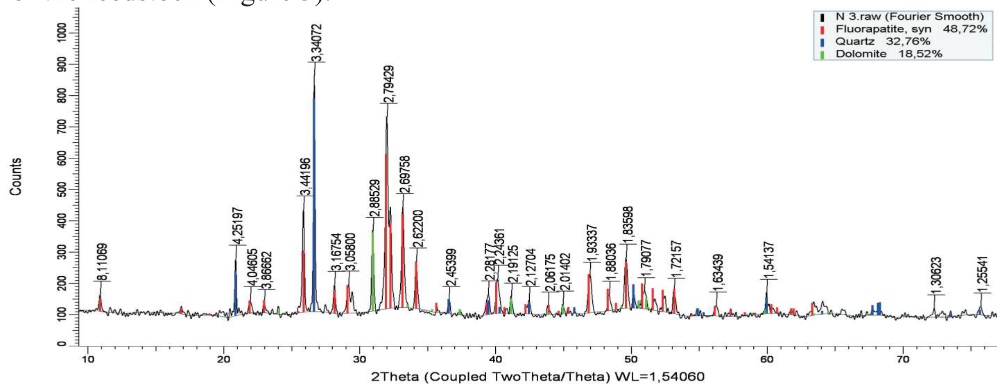

Fig.3. X-ray phase analysis of Zhanatas phosphorite

The data in Figure 3 clearly indicate the presence of the main compounds in the composition of the phosphorite of the Zhanatas deposit. As shown in the XRD results, the main compound with a significantly predominant compound is phosphorite with a content of 48.72%. Silicate minerals in the form of quartz (SiO_2) are also largely present, where its percentage is 32.76%. In addition, there are dolomite compounds with a fraction of 18.52% [13].

The DTA curve (Figure 4) showed endothermic effects with maximum development at 727^{0}C and 829.5^{0}C. Additional endothermic effects are recorded on the DTA curve. Their extremes were at 175.1^{0}C, 275.1^{0}C, 564.5^{0}C, 633.2^{0}C, 763.5^{0}C. On the same curve, an exothermic effect was observed with a peak at 994.9^{0}C. The DTG curve shows lows at 273.9^{0}C, 719.3^{0}C, 821.9^{0}C, 1072^{0}C, as well as activity in the 627^{0}C region.

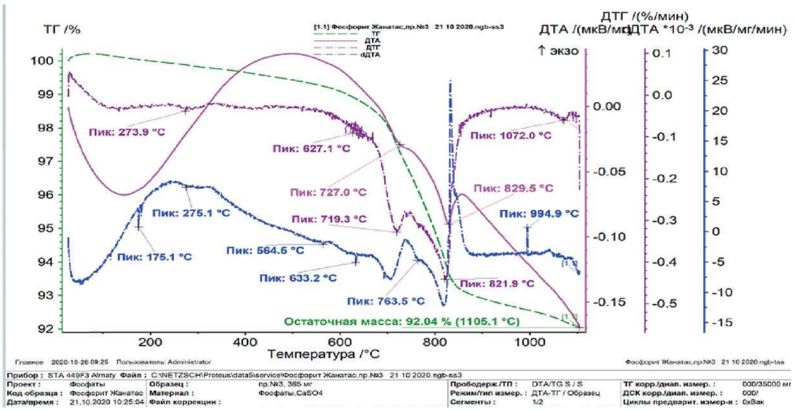

Fig.4. Results of thermal analysis of Zhanatas phosphorite

Judging by the elemental composition applied to the sample under study, the main phase is apatite. This phase is thermoinert, so it is not determined by thermal analysis. You can only assume that it exists. Separately considering the endothermic effect with an extremum at 727^0C on the DTA curve, we can assume the presence of carbonatapatite (dallite) $Ca_{10}[PO_4]_6CO_3$.

Discussion. The combination of the endothermic effect with the extremum at 7270C and the endothermic effect with the extremum at 829.5^0C on the DTA curve can be interpreted as a manifestation of dolomite. The presence of calcite in the overlay is not excluded (effect 829.5^0C, DTA). The combination of the endothermic effect with an extremum at 727^0C on the DTA curve, the endothermic effect with an extremum at 763.5^0C on the dDTA curve, and the endothermic effect with an extremum at 829.5^0C on the DTA curve is due to the manifestation of ankerite carbonate $Ca(Mg,Fe)\,[CO_3]_2$. The presence of chantite carbonate $CaMg_3\,[CO_3]_4$ is not excluded. Its manifestation reflects a combination of a weak endothermic effect with an extremum at 633.2^0C on the DTA curve and an endothermic effect with an extremum at 829.5^0C on the DTA curve. In addition, the endothermic effect with an extremum at 727^0C on the DTA curve is also a manifestation of lazulite phosphate $(Mg,Fe)Al_2[PO_4]_2(OH)_2$.All of the above effects are accompanied by a decrease in the weight of the suspension. They correspond to the minima on the DTG curve (activity in the area of 627^0C, 719.3^0C, 821.9^0C). The minimum at 273.9^0C on the DTG curve may reflect the dehydration of impurity iron hydroxides [14, 15]. The minimum at 1072^0C on the DTG curve can be considered as a manifestation of dehydration of the mica mineral biotite $K(Mg,Fe)_3[AlSi_3O_{10}](OH,F)_2$.

A weak endothermic effect with an extremum at 564.5^0C on the dDTA curve is characterized by the manifestation of quartz inversion. In addition, the transition of $AlPO_4$ to a tridymite-like form is also possible here. The combination of the endothermic effect with an extremum at 727^0C on the DTA curve and the exothermic effect with a peak at 994.9^0C on the DTA curve can be interpreted as a manifestation of a small amount of augelite phosphate–$Al_2[PO_4](OH)_3$.

Conclusion. In the course of IKS studies and X-ray phase analysis, the petrographic, mineralogical and chemical composition of the off-balance phosphate-siliceous rocks of the Zhanatas deposit was revealed. It was found that the phosphate substance consists of fluorapatite, quartz, calcite, dolomite and siderite with the following content Fluorapatite, $Ca_5(PO_4)_3F$, Quartz, SiO_2, Dolomite, $CaMg(CO_3)_2$, respectively.

Thus, the results of the physical and chemical studies carried out confirm the suitability of the off-balance raw materials of the Zhanatasskoye deposit for the production of phosphorus-containing industrial products. The data obtained confirm the applied significance of these results when planning the use of Zhanatas phosphorites as raw materials. The results of the above studies complement each other and prove the presence of basic and impurity compounds in the composition of the feedstock.

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ЖАҢАТАС КЕН ОРНЫНЫҢ БАЛАНСТАН ТЫС ФОСФАТ ШИКІЗАТЫ: ҚҰРАМЫ МЕН ҚҰРЫЛЫМЫН КЕШЕНДІ ЗЕРТТЕУ

Аннотация. Мақалада Қаратау (Оңтүстік Қазақстан) фосфориттік бассейнінде орналасқан Жаңатас кен орнының балансттан тыс шикізатының құрамы мен құрылымын физика-химиялық зерттеу нәтижелері ұсынылған. Зерттеу жүргізу үшін физика-химиялық талдаулардың заманауи аспаптық әдістері қолданылды. Элементтік-заттық құрам нормативтік құжаттар мен стандарттардың ережелеріне сәйкес химиялық талдау әдісімен анықталған. Бұл зерттеулердің нәтижелері оларды одан әрі фосфоры бар өнімдерге қайта өңдеу үшін практикалық маңызы бар.

Минералды тыңайтқыштар, оның ішінде диаммонийфосфаты мен баланстан тыс фосфат шикізаты экономиканың агроөнеркәсіптік секторындағы ауыл шаруашылығы дақылдарының өнімділігі мен сапасын арттыруда шешуші рөл атқарады. Сондықтан фосфор өнеркәсібі өнімдерінің экспорттық бағдарын ескере отырып, оны макроэкономикадан тыс қарастыруға болмайды, алынған рентгендік фазалық талдау нәтижелері бойынша минералды петрографиялық талдау және ИКС және сканерлеуші электронды микроскопта ДАФ алу процесінің химиясы туралы ақпарат берілген. Түсірілім D8 Advance (Bruker) $Cu\text{-}K_a$ аппаратында жүргізілді, құбыр кернеуі 40 кв, ток 40 ма. Алынған дифракциялық заңдылықтардың мәліметтерін өңдеу және жазықаралық қашықтықтарды есептеу EVA бағдарламалық құралын қолдану арқылы жүзеге асырылды. Үлгіні декодтау және фазалық іздеу PDF-2 (ICDD) ұнтақ дифрактометриялық деректер базасын пайдалану арқылы Search/match бағдарламасының көмегімен жүзеге асырылды.

Түйінді сөздер: фосфорит, ИК-спектр, элементтік талдау, минералогия, экстракциялық фосфор қышқылы.

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ЗАБАЛАНСОВОЕ ФОСФАТНОЕ СЫРЬЕ МЕСТОРОЖДЕНИЯ ЖАНАТАС: КОМПЛЕКСНОЕ ИЗУЧЕНИЕ СОСТАВА И СТРУКТУРЫ

Аннотация. В статье представлены результаты физико-химических исследований состава и структуры забалансового сырья месторождения Жанатас, расположенного в фосфорит содержащей впадине Каратау (Южный Казахстан). Для исследования использовались современные инструментальные методы физико-химического анализа. Элементно-вещественный состав определяется методом химического анализа в соответствии с правилами нормативных документов и стандартов. Результаты этих исследований имеют практическое значение для их дальнейшей переработки в фосфорсодержащие продукты.

Минеральные удобрения, в том числе диаммоний фосфата и за балансового фосфатного сырья в агропромышленном секторе экономики играют ключевую роль в повышении урожайности и качества сельскохозяйственных культур. Поэтому, учитывая экспортную направленность продукции фосфорной отрасли, ее нельзя рассматривать вне макроэкономики. Приведены сведения по минерального петрографическому анализу и химизму процесса получения ДАФ на основе результатов полученных ИКС рентгенофазового анализов и на растровом электронном микроскопе. Съемка производилась на аппарате D8 Advance (Bruker), Cu-K_a, напряжение на трубке 40 кв, ток 40 ма. Обработка полученных данных дифрактограмм и расчет межплоскостных расстояний проводились с помощью программного обеспечения EVA. Расшифровка проб и поиск фаз проводились по программе Search/match с использованием базы порошковых дифрактометрических данных PDF-2 (ICDD).

Ключевые слова: фосфорит, ИК-спектр, элементный анализ, минералогия, экстракционная фосфорная кислота.

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