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ON THE PRODUCTION OF PURIFIED DIAMMONIUM PHOSPHATE FROM EXTRACTION PHOSPHORIC ACID BASED ON OFF BALANCE ORES OF THE KARATAU BASIN

Abstract. The problem of utilization of man-made waste from the mining complex has not lost its relevance since the end of the last century. The amount of waste only in the «Central» mine quarry of the Zhanatas field, is about 22 million tons of phosphate-silicon raw materials (PSRM). More than 12 million tons after flotation enrichment were used for acid processing and as commercial phosphates for electro thermal processing. When refining the Zhanatas quarries to the working depth, at least 18-19 million tons of PSRM will be formed [1].

Off-balance ores of internal overburden are represented by three special dumps of the mines "Kokjon", "Koksu", "Tjesay", "Aksay", the volume of which is more than 3.2 million tons with a content of up to 20% P_2O_5.

Mineral fertilizers in the agro-industrial sector of the economy play a key role in improving crop productivity and quality. Given the export orientation of the phosphorus industry, it cannot be considered outside of macroeconomics, as its situation remains complex and unstable.

The practical importance of innovative research to develop technological foundations and technical solutions for the production of diammonium phosphate (DAP) [7], derived from wet-process phosphoric acid (PSRM)balance Karatau phosphorite is no doubt also compiled the original data on the establishment of a pilot plant and the calculated techno-economic assessment of innovative industrial production.

Our proposed technology will reduce the economic costs of processing off-balance raw materials and increase the range of phosphorus-containing products to 10-15%; increase the production of PSRM and DAP to 20-25%; create additional jobs.

The results of innovative scientific research are applicable to the chemical enrichment of man-made waste for target products, which are urgently needed by the agro-industrial complex, to improve the environmental and economic indicators of industrial regions and the welfare of the population of Kazakhstan.

Keywords: Off-balance phosphorites, Karatau basin, diammonium phosphate, extraction phosphoric acid, drum granulator dryer, neutralization, evaporated and non-evaporated PSRM.

Introduction. In world practice, the trademark diammonium phosphate 18:46 has long been established, with a mass fraction of total nitrogen of at least 18 %, and total P_2O_5 of at least 46 %, exported fertilizers usually meet these requirements. In addition, export contracts more strictly regulate the granulometric composition [8]. This requires normalization of the proportion of the size of DAP granules from 2 to 4 mm or from 2 to 5 mm, produced by the largest producers of Russia-JSC "PhosAgro-Cherepovets" and LLC "Balakovskaya mineral fertilizers", which are part of the holding company "PhosAgro" and contain at least 95% of granules from 2 to 5 mm (in practice, from 97 to 100 %) [2].

The composition of the fertilizer DAP includes diammonium phosphate $(NH_4)_2HPO_4$ and monoammonium phosphate $NH_4H_2PO_4$, as well as impurities whose content depends on the chemical composition of the initial phosphoric acid [3].

Diammonium phosphate fertilizer (diammophos, DAP) - a complex fertilizer containing two main nutrients-nitrogen and phosphorus. In accordance with the technical conditions, diammonium phosphate fertilizer, according to its physical and chemical parameters, must meet the technical requirements of TU-113-08-556-93 [4,5].

Commercial innovative product is fire-and explosion-proof. Hazard class-4, maximum permissible concentration (MPC) of DAP dust in the air of the working area-10 mg/m^3 [6].

Compared with ammophos, which contains the predominant amount of monoammonium phosphate (MAP) and diammonium phosphate per unit of P_2O_5 contains twice as much nitrogen, despite the fact that the total content of nutrients in MAP and DAP is the same (about 64 %), in addition, more concentrated fertilizers can be obtained on the basis of DAP [5,14].

In the process of innovative production of DAP, the extraction phosphoric acid is subjected to deeper ammonification, due to the introduction of the cheapest and one of the most concentrated nitrogen – containing components-ammonia-into the fertilizer.

This makes it possible to use a smaller amount of more expensive nitrogen-containing production components (ammonium nitrate or urea) for nutrient balancing [16], which makes it more economically feasible to obtain DAP and fertilizers based on it.

Especially important role of DAP plays in the process of blending. Due to the high concentration of nutrients, its use leads to savings in financial resources for transportation, storage and application of DAP-based fertilizers to the soil [1,12].

Currently, ammonium phosphates with a nutrient concentration (P2O5+N) of more than 60% are obtained in the CIS countries from Apatite concentrates and high-quality phosphorites of North Africa.

Production of highly concentrated fertilizers from phosphorites of the Karatau basin of the Republic of Kazakhstan requires deeper enrichment, with the production of concentrates containing more than 30% P_2O_5 and MgO less than 1% [3,7], or additional purification of extraction phosphoric acid from impurities, and especially from magnesium and fluorine, since iron and sulfur can play the role of micro-fertilizers.

The production of phosphorus and other mineral fertilizers in Kazakhstan is mainly carried out by three enterprises: - «Kainar» LLP, with a capacity of 240 thousand tons per year (Shymkent) and the «KazAzot» LLP plant (Aktau), where there are production facilities nitrogen fertilizers and liquid ammonia with a capacity of 1600 thousand tons per year, Taraz branch of «Kazphosphate» LLP mineral fertilizer plant (MFP), with a capacity of 150 thousand [19] tons per year. However, they do not fully satisfy the need of the Republic of Kazakhstan for fertilizers.

Therefore, establishing the mechanism of the influence of impurities, in particular compounds of fluoride and magnesium on the physico-chemical and physico-mechanical properties of purified DAF are necessary conditions for the creation of a hardware-technological scheme of the innovative technology of obtaining the target product (DAP) from natural phosphate rock of the Karatau basin and industrial wastes [16], stored in the dumps of the Zhanatas, Aksay and Kokjon mines.

In the course of research on the innovative process of obtaining DAP, the main attention is paid to the chemistry, kinetic dependencies and hardware design of the main technological stages, as well as to the quality of the finished product: such as caking, granule strength, and dust formation [18]. In the literature, the influence of the concentration of phosphoric acid, the impurities contained in it, and the hardware design of the process on the properties of the finished product, as well as the mechanism and chemise of this influence are not sufficiently developed, which is the goal of an innovative research work [8], which has relevance.

The difference between the innovative technology offered by us and the existing ones is the use of evaporated and unpaired extraction phosphoric acid from raw resources of domestic balance and off balance ores.

The production of mineral fertilizers from local raw materials will allow involving low-grade phosphorites and man-made waste in the new technology of enrichment.

DAP, obtained using phosphoric acid with a lower concentration than traditional technology, has lower physical and mechanical properties, increased hygroscopicity and traceability [10]. To preserve the quality of DAF during transportation and storage the moisture content of the finished product shall be not more than 2.0 %; for this purpose– exposure of the product to produce at least 2 hours and the temperature of the shipment is maintained in accordance with the requirements of normative technical documentation.

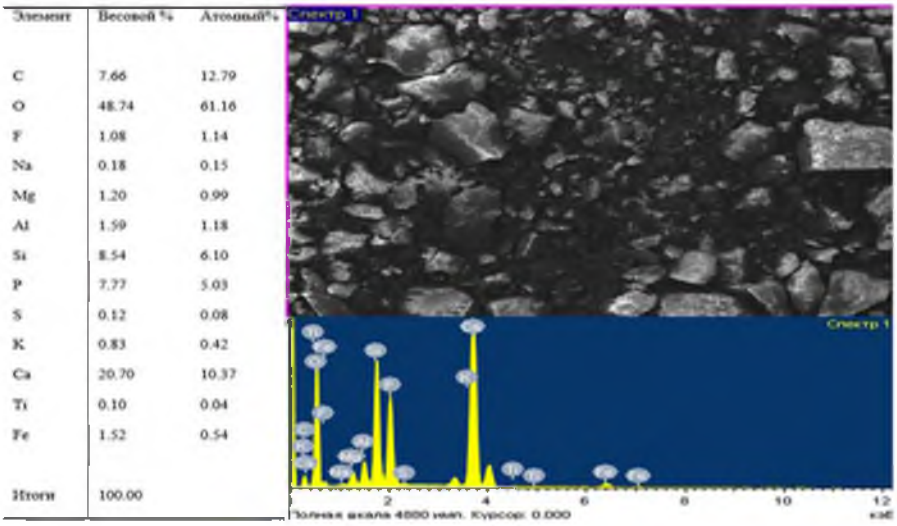
Materials and Methods. In connection with the rise of the economy of the Republic of Kazakhstan on the basis of innovative and industrial development and its transfer from a raw material to a competitive commodity-producing state, there is a need to develop new and improve existing technologies in all sectors of the economy [7].

Experimental research is traditionally the most objective method. Therefore, the main method of the proposed work is a free associative instrumental method of experiment, one of the most accessible and effective ways to develop a number of scientifically based physical, chemical, technological and technical solutions for the synthesis of competitive domestic DAP with an optimal ratio of paired and non-paired PSRM [9,11].

This will ensure compliance with the principles of scientific ethics and their use in the creation of technology for the synthesis of DAP in BGS using unpaired and evaporated PSRM and ammonia gas [17].

To conduct experiments, samples of phosphate raw materials from various deposits "Chulaktau", "Zhanatas" and "Kokjon" were studied on a raster electron microscope (SEM) for the content of P_2O_5 . The results of the study are shown in figures 2,4 and 6.figures 1,3 and 5 show the appearance of a large and crushed sample of phosphorites taken for experiments.

Figure 1 - Coarse and crushed phosphorite sample taken from «Chulaktau» field



Элемент	Весовой %	Атомный%
C	7.66	12.79
O	48.74	61.16
F	1.08	1.14
Na	0.18	0.15
Mg	1.20	0.99
Al	1.59	1.18
Si	8.54	6.10
P	7.77	5.03
S	0.12	0.08
K	0.83	0.42
Ca	20.70	10.37
Ti	0.10	0.04
Fe	1.52	0.54
Итоги	100.00	

Figure 2 - Elemental composition and electronic image by electron microscopic examination of a phosphorite sample taken from the «Chulaktau» deposit

Figure 3 - A large and crushed phosphorite sample taken from the «Zhanatas» field

Элемент	Весовой %	Атомный%
C	19.55	28.42
O	43.65	49.38
Mg	8.06	5.79
Al	0.49	0.32
Si	1.53	0.95
P	8.18	7.10
K	0.20	0.09
Ca	17.93	7.81
Fe	0.41	0.13
Итоги	100.00	

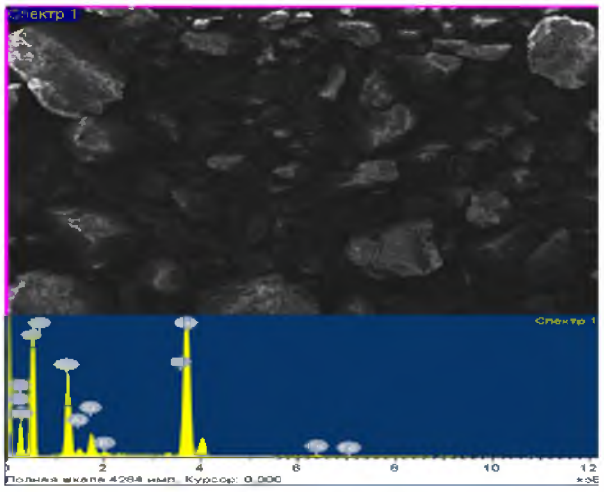


Figure 4 - The elemental composition and the electronic image are shown according to the results of an electron microscopic study of a phosphorite sample taken from the «Zhanatas» deposit

Figure 5. Coarse and crushed phosphorite sample taken from «Kokjon» deposit.

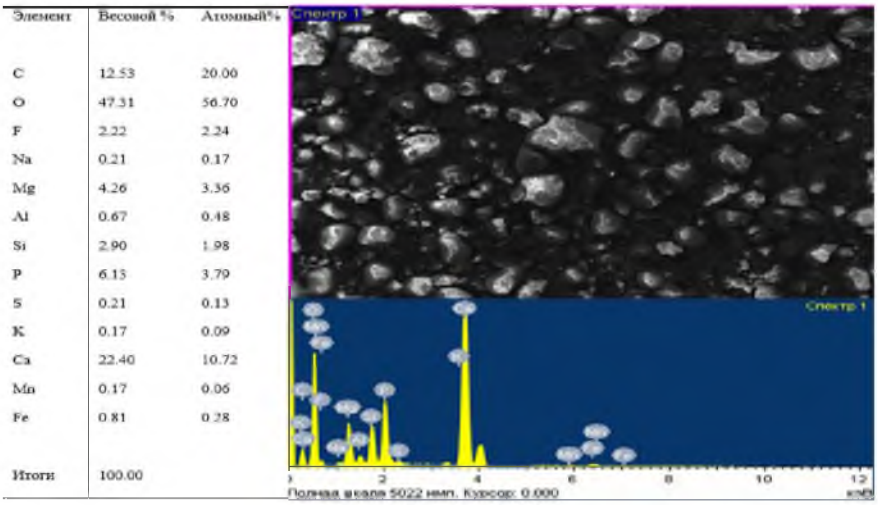


Figure 6 - The elemental composition and the electronic image are shown according to the results of electron microscopic examination of a phosphorite sample taken from the «Kokjon» deposit

Results and discussion. The chosen method, with its own individuality of the Association process, has common reference points of contact between individual participants of collective research, as well as with respondents offering various DAP production technologies [13].

Table 1 shows the content of P_2O_5 (%) in the phosphate feedstock of the «Chulaktau», «Zhanatas» and « Kokjon» deposits.

Table 1 - P_2O_5 content (%) in the phosphate feed of the «Chulaktau», «Zhanatas» and « Kokjon» deposits

Type of phosphate material	Content P_2O_5,%	
	Weight %	Atomic %
Chulaktau	7,77	5,03
Zhanatas	8,18	7,10
Kokjon	6,13	3,79

Comparison of the results of research of samples of phosphate raw materials from various deposits «Chulaktau», «Zhanatas» and «Kokjon» for the content of P_2O_5 shows that the best quality is characterized by the phosphorite of the Deposit "Zhanatas", containing P2O5 -8.18% [12].

The presence of harmful impurities and low P_2O_5 content make it necessary to enrich the phosphorous ore [1,15]. To do this, in our opinion, it is possible to use the flotation method of enrichment. At present, fine - milled fosmuka is obtained from carbonate ores and flotation phosphorous concentrate is obtained from it. Flotation phosphate concentrate is usually used as a raw material for the production of phosphorous-containing and complex mineral fertilizers, phosphoric acid.

Conclusion. Experimental data and technological schemes can be used to obtain diammonium phosphate from substandard phosphate raw materials. The aim of the research is to develop and create an innovative technology for obtaining high-quality diammonium phosphate in a drum granulator dryer from a mixture of evaporated and unpaired extraction phosphoric acid with a predominant share of unpaired EFC extracted from off-balance phosphorites of the Karatau basin. From the conducted research of samples of phosphate raw materials of various deposits, «Chulaktau», «Zhanatas» and «Kokjon», the best was the phosphorite of the" «Zhanatas» Deposit, containing P_2O_5 - 8.18%.

Scientific research and experimental work was carried out using modern laboratory equipment equipped with computer technology. The analysis of the raw materials, the resulting product and materials was performed using physical and physico-chemical methods of research on modern raster microscope JSM 6390 LV, DRONE, IR spectroscopy, etc., and comparative analysis was performed using mathematical processing of research results [4.19].

The results of the conducted research of bidit are applied in the development of technological bases and technical solutions for the innovative process of diammonium phosphate production using BGS from unpaired extraction phosphoric acid obtained from phosphorites of the Karatau basin.

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ҚАРАТАУ БАССЕЙНІНІҢ БАЛАНСТАН ТЫС КЕНДЕРІ НЕГІЗІНДЕ ЭКСТРАКЦИЯЛЫҚ ФОСФОР ҚЫШҚЫЛЫНАН ТАЗАРТЫЛҒАН ДИАММОНИЙФОСФАТ АЛУ

Аннотация. Тау-кен өндіру кешенінің техногендік қалдығын пайдага жарату мәселесі өткен гасырдың соңынан бастап өзектілігін жогалтпай келеді. Жаңатас кен орны «Центральный» карьеріндегі қалдық мөлшері 22 млн. тоннага жуық фосфат-кремний шикізатын (ФКШ) құрайды. Флотаңиялық байытудан кейін 12 млн. тоннадан астам қышқылды өңдеу үшін электротермиялық өңдеуде тауарлық фосфорит ретінде пайдаланылган. «Жаңатас» карьерін жұмыс тереңдігіне дейін жетілдіру кезінде кемінде 18-19 млн. тонна ФКШ пайда болады [1].

Ішкі аршыма тау жыныстарының баланстан тыс кендері «Көкжон», «Көксу», «Тьесай», «Ақсай» сынды үш арнайы үйінді арқылы ұсынылды, көлемі 3,2 млн. тоннадан астам, құрамында 20% P2O5 бар.

Экономиканың агроөнеркәсіптік секторында минерал тыңайтқыштар ауылшаруашылыгы дақылдары-ның өнімділігі мен сапасын арттыруда маңызды рөл атқарады. Фосфор саласының экспорттық багытын ескере отырып, оны макроэкономикадан тыс қарастыруга болмайды, өйткені оның жагдайы күрделі және тұрақсыз болып қалады.

Диаммонийфосфат (ДАФ) өндірісінің технологиялық негізі мен техникалық шешімін әзірлеу бойынша инновациялық зерттеулердің практикалық маңыздылыгы [7], Қаратау теңгерімдік фосфориттерінен экстракциялық фосфор қышқылынан (ЭФК) алынатын, сондай-ақ тәжірибелік-өнеркәсіптік қондырғы құруға бастапқы деректер жасалган және өнеркәсіптік инновациялық өндірісті техникалық-экономикалық багалау жұмысы есептелген.

Біз ұсынып отырган технология теңгерімнен тыс шикізатты қайта өңдеуге, экономикалық шыгынды азайтуга және құрамында фосфор бар өндірілетін өнім сұрыптамасын 10-15%-га, ЭФК және ДАФ өндіріс көлемін 20-25%-га дейін жогарылатуга, қосымша жұмыс орындарын құруга мүмкіндік береді.

Инновациялық гылыми зерттеулер нәтижесі агроөндірістік кешен аса қажетті, мақсатты өнімдерге техно-гендік қалдықтарды химиялық байытуда, өнеркәсіптік аймақтардың экологиялық-экономикалық көрсеткіштерін және ҚР халқының әл-ауқатын жақсартуда қолданылады.

Түйін сөздер: баланстан тыс фосфориттер, Қаратау бассейні, диаммонийфосфат, экстракциялық фосфор қышқылы, барабанды түйіршіктегіш кептіргіш, бейтараптандыру, буланган және буланбаган ЭФК.

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О ПОЛУЧЕНИИ ОЧИЩЕННОГО ДИАММОНИЙ ФОСФАТА ИЗ ЭКСТРАКЦИОННОЙ ФОСФОРНОЙ КИСЛОТЫ НА ОСНОВЕ ЗАБАЛАНСОВЫХ РУД БАССЕЙНА КАРАТАУ

Аннотация. Проблема утилизации техногенных отходов горнодобывающего комплекса не теряет свою актуальность с конца прошлого столетия. Количество отходов только по карьеру «Центральный», месторождения Жанатас составляет около 22 млн. тонн фосфатно-кремниего сырья (ФКС). Более 12 млн. тонн после флотационного обогащения использовано для кислотной переработки и как товарные фосфориты при электротермической переработке. При доработке карьеров «Жанатас» до рабочей глубины образуется не менее 18-19 млн. тонн ФКС [1].

Забалансовые руды внутренней вскрышной породы представлены тремя спецотвалами рудников «Кокжон», «Коксу», «Тьесай», «Аксай», объем которых составляют более 3,2 млн. тонн с содержанием до 20% P_2O_5.

Минеральные удобрения в агропромышленном секторе экономики играют ключевую роль в повышении урожайности и качества сельскохозяйственных культур. Учитывая экспортную направленность фосфорной отрасли, ее нельзя рассматривать вне макроэкономики, так как ее обстановка остается сложной и неустойчивой.

Практическая значимость инновационных исследований по разработке технологических основ и технических решений производства диаммонийфосфата(ДАФ)[7], получаемого из экстракционной фосфорной кислоты (ЭФК) балансовых фосфоритов Каратау не вызывает сомнений, также составлены исходные данные на создание опытно-промышленной установки и рассчитана технико-экономическая оценка промышленного инновационного производства.

Предлагаемая нами технология позволит снизить экономические затраты на переработку забалансового сырья и увеличить ассортимент выпускаемых фосфорсодержащих продуктов до 10-15%; увеличить объем производства ЭФК и ДАФ до 20-25%; создать дополнительные рабочие места.

Результаты инновационных научных исследований применимы при химическом обогащении техногенных отходов на целевые продукты, в которых остро нуждается агропромышленный комплекс, в улучшении эколого-экономических показателей промышленных регионов и благосостояния населения РК.

Ключевые слова: забалансовые фосфориты, бассейн Каратау, диаммонийфосфат, экстракционная фосфорная кислота, барабанный гранулятор сушилка, нейтрализация, упаренная и неупаренная ЭФК.

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