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ИЗВЕСТИЯ

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РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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RESEARCH OF THE POSSIBILITY OF THE USING OF WASTES ENRICHMENT OF GOLD-CONTAINING ORES IN THE PROCESS OF RECEIVING SILICOPHOSPHATE FERTILIZERS BY MECHANOCHEMICAL ACTIVATION

Abstract. The material and phase composition of the wastes enrichment of the gold-bearing ore of the Pustynoye deposit were studied and it was shown that quartz and silicon compounds are their main productive phase, their content in recalculate on silicon dioxide is 75.13 mass.%. With the using of the mechanochemical activation (MCA)method by dry process a silicon-phosphate material was obtained with the component ratio of Karatau phosphorite: enrichment waste = 1: 1. It has been established that mechanically activated phosphorite mixture with wastes of ore enrichment of "Pustynoye" deposit contains 1.4% of water-soluble form of phosphorus pentoxide and 51.7% of citrate-soluble P_2O_5. In this case, the product is completely soluble in citric acid. While the original phosphorus does not contain a water-soluble form of phosphorus pentoxide, and the content of citrate- and citron-soluble forms of P_2O_5 is (rel. %) 8.6 and 58.5, accordingly. Mechanochemical activation of mixtures of natural phosphates with waste of enrichment of gold-bearing ore promotes the appearance in the aqueous extract of assimilable compounds of silicon in the form of monosilicic acid in the amount of 62.5 mg / l, whereas in the original phosphorus these compounds are absent. Also it has been shown that in the silicophosphative-containing product after MCA the fluorine content significantly reduces, from 3.11 to 1.21 wt%. The carried out researches have shown the possibility of using of wastes enrichment of gold-bearing ore of "Pustynoye" deposit in the processes of obtaining silicophosphate fertilizers by the method of mechanochemical activation.

Keywords: silicophosphate fertilizers, wastes of enrichment, mechanochemical method.

Introduction

Over the past century, the population of the Earth has increased from 1.5 to 5.5 billion people and it is expected that by 2020 it will reach 8 milliards. The feed of so many people is the most important problem that has arisen before humanity [1]. Therefore, recently the priority scientific direction in the whole world is the intensification of agricultural production with the using of new science intensive technologies of the application of mineral fertilizers, which are improve the structure of the soil and increasing its fertility and quality of agricultural products. The existing technologies for the production of mineral fertilizers, in particular phosphorus fertilizers, lead to the formation of a huge amount of wastes (phosphogypsum, off-balance ores, waste rock), overphosphating and salinization of soil in the regions of the location of phosphate plants, which lead not only to the loss of a large number of valuable components that remain in the waste, but also it worse the environmental conditions of these areas.

In addition, currently produced single- and two-component mineral fertilizers have a relatively low coefficient of use of nutrients by plants. Thus, the authors of [2-4] showed that the coefficient of nitrogen using of single-component fertilizers does not exceed 40%, phosphorus pentoxide 20%, and potassium

dioxide 50-60%. Consequently, from 1000 kilograms of inputed nutrients from 400 to 850 kilograms pollute the soil, water and atmosphere, and also it increase economic costs for the production of agricultural products.

It should also be noted that with the existing acid methods of natural phosphate raw materials processing, the degree of utilization of fluorine compounds in the production of superphosphate does not exceed 20-50%, and it is even less in the production of complex fertilizers. The content of fluorine in superphosphate reaches 1-1.5, in ammophos 3-5%. On average, with each ton of necessary for plants phosphorus about 160 kg of fluorine is fed to the fields [4]. In addition, in fertilizers, unlike natural phosphate ores, fluorine is in the form of soluble compounds and easily enters the plant. Increased accumulation of fluorine in plants disrupts metabolism, enzymatic activity (inhibits the effect of phosphatase, etc.), negatively affects the photo and biosynthesis of the protein, the development of fruits.

Based on the aforesaid, certain scientific and practical interest in this regard is development of technologies of production of new and effective fertilizers, which are decide question of increasing of soil fertility and improve of the environmental situation of agricultural regions. In our view, a promising technological solution for the production of new phosphoric fertilizers is the mechanochemical activation of natural phosphates with various additives associated with solid-phase reactions in grinding machines [5-10]. This method contains a huge innovative potential, as it provides a comparative simplicity of the process and the ability to conduct reactions in the absence of aggressive liquid reagents - mineral acids, alkalis, which in turn is important from an environmental point of view.

As additives that increase the effectiveness of phosphate fertilizers, we proposed to use silicon-containing wastes of the enrichment of ore raw materials of Kazakhstan, since it is known that silica-phosphate fertilizers introduced into the soil significantly improve its structure and increase fertility [12-15]. It is also known that the presence in the soil of available forms of silicon is very important for plants, as it enhances the assimilability of phosphorus, potassium, magnesium, influencing the growth and metabolic processes of the plant, creates conditions for expanding the feeding zone, strengthening drought resistance, increases resistance to frost, radiation, toxic substances, pest damage [11]. It is also known that the presence in the soil of available forms of silicon is very important for plants, as it enhances the assimilability of phosphorus, potassium, magnesium, influencing the growth and metabolic processes of the plant, creates conditions for expanding the feeding zone, strengthening resistance to frosts, increases resistance to frost, radiation, toxic substances, pest damage [11].

Methods

The research objects in this work are Karatau phosphorites (phosphate component) and wastes of enrichment of gold-bearing ore of the “Pustynoye” deposit, which are a light-yellow material without any inclusions. A study of the material composition of the enrichment wastes and the initial Karatau phosphorites was carried out by electron-probe analysis with using of electron microscope of JEOL-733 firm with X-ray analyzer. The phase composition was studied by X-ray diffractometric analysis, which was carried out on an automated diffronometer DRON-3 with CuK_{α} radiation, β-filter. X-ray phase analysis on the semi-quantitative basis was carried out according to diffractograms of powder samples using the method of equal weights and artificial mixtures. Quantitative ratios of crystalline phases were determined. Interpretation of the diffractograms was carried out using the ICDD file data: powder diffractometry database PDF2 (Powder Diffraction File) and diffractograms of minerals free of impurities.

Results

The average material composition of Karatau phosphorites and ore wastes from the "Pustynoye" deposit are presented in Tables 1-2, and the results of semi-quantitative X-ray phase analysis of crystalline phases of the objects of investigation are given in Tables 3-4.

Table 1 – The average material composition of the initial phosphatites of Karatau

Content of component in reculculations on oxides, wt.%										
F	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	MnO	FeO	total
3.17	4.14	3.53	20.83	25.17	0.94	1.12	38.58	0.47	2.05	100.00

From the results it follows that the wastes of the gravity concentration of the ore at the "Pustynoye" deposit are mainly represented by silicon compounds, whose content in terms of SiO_2 is 75.13% by weight. There are no harmful impurities (plumbum, cadmium, arsenic, antimony, barium) in the wastes studied, which allows us to recommend them as an initial silicon-containing component for the production of silicophosphate fertilizers.

Table 2 – The average material composition of wastes of gravitational enrichment of gold-bearing ore of the “Pustynoye” deposit

Content of component in reculculations on oxides, wt.%								Total
Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	
2.13	0.74	12.22	75.13	3.19	2.11	0.58	3.90	100.00

Table 3 – Results of semi-quantitative X-ray phase analysis of Karatau samples

Phase name	Chemical formula	Content, wt.%
Fluoropatite	$Ca_5(PO_4)_3F$	51.6
Quartz	SiO_2	20.0
Dolomite	$CaMg(CO_3)_2$	22.9
Albite	$Na(AlSi_3O_8)$	2.0
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	2.1
Calcite	$CaCO_3$	1.3

Table 4 – Results of semi-quantitative X-ray phase analysis of crystalline phases of wastes of gravity concentration of gold-bearing ore of "Pustynnoe" deposit

Mineral	Chemical formula	Content, wt.%
Quartz	SiO_2	79.1
Albite	$Na(AlSi_3O_8)$	9.4
Calcite	$CaCO_3$	6.9
Mica	$KAl_2(AlSi_3O_{10})(OH)_2$	4.6

Silicophosphate fertilizers were obtained by the dry process by mechanochemical activation of mixtures of initial phosphorites with silicon-containing wastes with the ratio of components 1: 1. The activation was carried out in a planetary ball mill of the "Activator 2S" type for 5 minutes. For comparison, a known fertilizer, phosphorite flour, was used. The phosphorus content available for plants (water-soluble, citrate- and citric-soluble P_2O_5) was carried out in accordance with standard methods [16]. Extraction of the assimilable silicon compounds was carried out with distilled water with stirring and a ratio S: L = 1: 100. The concentration of monosilicic acids in the filtrates was determined by a known method [17]. The results are shown in Table 5.

Table 5 – Results of analytical determination of phosphorus and silicon compounds assimilated by plants in silicophosphate fertilizers, obtained by dry method MCA

Composition of fertilizer	The content of assimilable forms of P_2O_5, rel.%			Content of assimilable silicon compounds, mg / l
	water-soluble	citrate-soluble	citron-soluble	
The initial phosphorite of Karatau (phosphorus)	0.0	8.6	58.5	0.0
Mechanoactivated Phosphorite of Karatau	1.2	30.5	65.8	20.5
Mechanoactivated mixture of phosphorite with wastes of ore enreachment of "Pustynoye" deposit with component ratio 1: 1	1.4	51.7	100.0	62.5

From the obtained results, it follows that the mechanically activated phosphorite mixture with the ore enreachment wastes of "Pustynoye" deposit at component ratio equal to 1: 1 contains 1.4% by weight of the water-soluble form of phosphorus pentoxide and 51.7% by weight of citrate-soluble P_2O_5. In this case, the product is completely soluble in citric acid. While the original phosphorus does not contain a water-soluble form of phosphorus pentoxide, the content of citrate- and citron-soluble forms of P_2O_5 is (rel.%) 8.6 and 58.5, respectively. In mechanically activated phosphoryte, a water-soluble form of P_2O_5 (1.2 rel.%) appears, the content of citrate-soluble form increases 3.5 times and the content of citrate-soluble phosphates slightly increases. The main difference between the mechanically activated phosphorite mixture and the wastes of ore ereachment of "Pustynoye" deposit from mechanoactivated and initial phosphorite is the presence of assimilable silicon compounds 62.5 mg/l in the form of monosilicic acid, whereas in the original phosphate flour these compounds are absent, and after mechanochemical activation their content in the aqueous extract is 20.5 mg / l. In addition, as follows from the results of the physical analysis of the mechanically activated (MCA) mixture of the Karatau phosphorite with wastes of gold-containing ore enrichment of "Pustynoye" deposit (Table 6), the fluorine content decreased significantly from 3.11 to 1.21 mass.% in the silicon phosphate product.

Table 6 – The average material composition of mechanically activated (MCA) Karatau phosphorite and its mixture with wastes of enrichment of gold-bearing ore of "Pustynoye" deposit

Content of component in reculculations on oxides, mass.%											
	F	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	MnO	FeO	TiO_2
MCA phosphorite	3.11	3.82	2.53	25.53	24.06	0.90	0.97	36.82	0.39	1.82	0.0
MCA mixture of phosphorite with wastes	1.21	2.98	8.84	46.87	12.49	0.51	2.50	10.12	0.27	2.28	0.36

Thus, the conducted studies showed that the mechanochemical activation of mixtures of Karatau phosphorites with wastes of gold-containing ore enrichment of "Pustynoye" deposit leads to destruction of the initial phosphorite, accompanied by defluorination of MCA products and the appearance in the solution of not only assimilable forms of P_2O_5, but also the formation of silicon compounds assimilated by plants. In addition, involving large-tonnage siliceous wastes from the enrichment of ore raw materials into the production of silicophosphate fertilizers will not only expand the range of phosphate fertilizers, but it will also solve the problem of solid waste storage and environmental protection.

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Discussion

The carried out researches have shown the possibility of using wastes of enrichment of gold-bearing ore of "Pustynoye" deposit in the processes of obtaining of silicophosphate fertilizers by the method of mechanochemical activation. In this process, natural phosphates are degraded, resulting in the reduction in the fluorine content of the final product. Acid-free method of used ultrafine grinding allows obtaining completely soluble in citric acid silicophosphate materials containing water (1.4% by weight) and citrate-soluble (51.7 rel.%) forms of P_2O_5, as well as plants assimilated by silicon compounds (62.5 mg/l).

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МЕХАНОХМИЯЛЫҚ АКТИВАЦИЯЛАУ ТӘСІЛМЕН КРЕМНЕФОСФАТТЫ ТЫҢАЙТҚЫШТАР АЛУ ҮРДІСІНДЕ АЛТЫН ҚҰРАМДЫ КЕНДЕРІНІҢ БАЙЫТУ ҚАЛДЫҚТАРЫН ҚОЛДАНЫЛУ МҮМКІНДІГІН ЗЕРТТЕУ

Аннотация. Берілген жұмыста «Пустынное» кенорының алтын құрамды кенін байыту қалдықтарының заттық және фазалық құрамы зерттелген және олардың негізгі фазасы - кварц пен кремний қосылыстары (кремний диоксидіне қайта есептегенде 75.13 масс.%) болып келетіні дәлелденген. Механохимиялық активациялау әдіс (МХӘ) қолданумен Қаратау фосфориті:байыту қалдықтары компоненттердің 1:1 тең қатынаста кремнийқұрамды фосфаттық материал алынған. Фосфорит және «Пустынное» кенорындағы алтынқұрамды кенінің байыту қалдықтарынан тұратын механобелсендірілген қоспада фосфор пентаоскиді суда еритін түрінде 1.4 сал.% және цитрат ерігіш түрінде 51.7 сал.% P_2O_5 бар. Алынған өнім лимон қышқылында толық ериді. Алайда бастапқы фосфорит үні пентаоксидтің суда еримейтін формалар жоқ, ал P_2O_5 цитратты- және лимонды-ерігіш формалары (сал.%) 8,6 және 58,5 сәйкесінше құрайды. Табиғи фосфаттары мен алтынқұрамды кенінің байыту қалдықтарының қоспаларды механохимиялық активациялау кезінде сулы сүзіндіде монокремний қышқылы 62,5 мг/л мөлшерде болатын кремнийлі сіңірімді қосылыстар пайда болады, ал бастапқы фосфоритті үнда бұл қосылыстар жоқ. Сонымен қатар, МХА-дан кейін кремнефосфатты өнімдегі фтордың мөлшері айтарлықтай – 3,11-ден 1,21 масс.%-ға дейін азаяды. Жүргізілген зерттеулер «Пустынное» кенорының алтын құрамды кенін байыту қалдықтарын механохимиялық активация арқылы кремнефосфатты тыңайтқыштар алу үрдісінде қолданылу мүмкіндіктері көрсетілген.

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ИССЛЕДОВАНИЕ ВОЗМОЖНОСТИ ИСПОЛЬЗОВАНИЯ ОТХОДОВ ОБОГАЩЕНИЯ ЗОЛОТОСОДЕРЖАЩИХ РУД В ПРОЦЕССЕ ПОЛУЧЕНИЯ КРЕМНЕФОСФАТНЫХ УДОБРЕНИЙ МЕХАНОХИМИЧЕСКИМ СПОСОБОМ

Аннотация. В работе изучен вещественный и фазовый состав отходов обогащения золотосодержащей руды месторождения «Пустынное» и показано, что их основной продуктивной фазой являются кварц и соединения кремния, содержание которых в пересчете на диоксид кремния составляет 75.13 масс.%. С использованием метода механохимической активации (МХА) сухим способом получен кремнефосфатный материал с соотношением компонентов фосфорит Каратау:отходы обогащения = 1:1. Установлено, что механоактивированная смесь фосфорита с отходами обогащения руды м. «Пустынное» содержит 1,4 отн.% водорастворимой формы пентаоксида фосфора и 51,7 отн.% цитратнорастворимой P_2O_5. При этом продукт полностью растворим в лимонной кислоте. Тогда как исходная фосмука не содержит водорастворимой формы пентаоксида фосфора, а содержание цитратно- и лимоннорастворимой форм P_2O_5 составляет (отн.%) 8,6 и 58,5 соответственно. Механохимическая активация смесей природных фосфатов с отходами обогащения золотосодержащей руды способствует появлению в водной вытяжке усвояемых соединений кремния в виде монокремниевой кислоты в количестве 62,5 мг/л, тогда как в исходной фосмуке эти соединения отсутствуют. Также показано, что в кремнефосфатном продукте после МХА существенно снижается содержание фтора – с 3,11 до 1,21 масс.%. Проведенные исследования показали возможность использования отходов обогащения золотосодержащей руды м. «Пустынное» в процессах получения кремнефосфатных удобрений способом механохимической активации.

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