UDC 661.632

Andrienko N. I., Plyacuk L. D.,
Chernish E.Yu.
Sumy State University

TECHNOLOGY OF OBTAINING ENRICHED PHOSPHATE MATERIALS WITH REMOVAL OF HEAVY METALS IN WASTELESS PROCESS

У статті запропоновано підхід до безвідходного (маловідходного) процесу виробництва мінеральних добрив. Представлені результати проведених досліджень з утилізації тонкодисперсного високогомогенізованого суспендованого відходу, що утворився при розкладанні фосфоритів азотнокислотном способом з отриманням товарного продукту у вигляді NPK – добрива марки 10:10:10. Технологія отримання збагачених фосфоритів, яка описана в статті, не вимагає спеціального обладнання і може бути реалізована на виробничій лінії отримання суперфосфатів.

Ключові слова: азотнокислотне розкладання, фосфорити, важкі метали, утилізація, малоотходна технологія

В статье предложено подход к безотходному (малоотходному) процессу производства минеральных удобрений. Представлены результаты проведенных исследований по утилизации тонкодисперсного высокогомогенизированного суспензированного отхода, образовавшегося при разложении фосфоритов азотнокислотном способом с получением товарного продукта в виде NPK – удобрения марки 10:10:10. Технология получения обогащенных фосфоритов, которая описана в статье, не требует специального оборудования и может быть реализована на производственной линии получение суперфосфатов.

Ключевые слова: азотнокислотное разложение, фосфорит, тяжелые металлы, утилизация, малоотходная технология

The article focused on the approach to the wasteless process of mineral fertilizers production. There is shown researches of utilization of thin-dispersional high-homogenized liquid waste which is created during nitric-acid method of decomposition phosphorites with receiving of commercial product as fertilizer (N:P:K=10:10:10). Technology of obtaining enriched phosphate which is considered in the article does not require special equipment and can be used on the production line of the production of ordinary superphosphate.

Key words: nitric-acid method of decomposition, phosphorite, heavy metals, utilization, wasteless technology

Problem statement. Effective management of agricultural production based on the timely introduction and in sufficient quantity (quality) of mineral fertilizers, which contain the most important elements for plants nitrogen, phosphorus and potassium. In the absence or lacking of phosphorus in the soil not only reduces crop yields, but also significantly reduces the efficiency of the action of nitrogen and potash fertilizers. The loss of active substances with the crops is depressing factor affecting soil fertility not only in the present, also long-term, and reduces the quality of agricultural products.

Due to numerous problems, among which were and still are the main economic instability and lack of phosphorus own raw material base, is marked by a sharp decline in the production of mineral fertilizers (since 1990). Existing apatite-ilmenite and rare-apatite ores require significant investments in the development and the development of new technologies for their processing. Domestic phosphate rock is complex in terms of technology. For Ukrainian phosphoresces low content of P2O5 and a high content of harmful impurities (mainly acid-soluble oxides). Therefore, recycling of domestic phosphate traditional methods of acid digestion technologically impractical and economically justified. Their use has local regional character [1].

Power plants in Ukraine for the production of phosphate fertilizers are not used by more than 25%. One reason for the low capacity utilization of the industry of mineral Fertilizer is the high cost of imported raw materials, which have traditionally delivered from Russia from the Kola Peninsula, through the supply of Khibiny apatite concentrate. To date, the Russian enterprises themselves are experiencing an acute shortage of phosphate raw materials. All this has led to the inclusion in the phosphate raw materials Ukraine new phosphates including low phosphorus content and is usually a higher content of impurities. The acid phosphate processing most of impurities contained transfer to the solution. These causes increase viscosity of the liquid phase, increase losses during processing (enrichment), reduced nutrient content in the finished product. At the moment, the main suppliers of phosphate raw materials to Ukraine are the countries of North Africa, especially Algeria [2].

Literary review. Algerian phosphates are the product of the enrichment of sedimentary phosphate ores. These ores are relatively young sedimentary rocks and are a mixture of minerals from beige-brown to black colour.

Phosphate substance of phosphate ore is fluoro-apatite minerals containing carbonates: francolite, kurskite, fluorine karbonatapatit. These components are characterized by ore microcrystalline structure, high porosity, and polydispersity of particles, ph 10% aqueous solution varies depending on the batch of 6 to 11.

The density of the Algerian raw material is 1.6-1.7 g / cm^3, to compare the same figure in the Tunisian phosphorite is 2.5 g/cm^3.

Solubility Algerian ores in 2% citric acid, 15-30% and in 2% formic acid, this component is 13-74%, which characterizes their high reactivity.

Algerian phosphorite is completely resistant to the product of environmental conditions [5,6].

Table. 1, 2 shows the main characteristics of the Algerian raw materials affect to the recycling process. For comparison, the performance of phosphate raw materials Khibina (Kirov apatite) and Tunis fields.

Processing of high-Mg phosphate rock in a number of traditional technologies on phosphoric acid and fertilizer difficult or even impossible. In particular, the processing of phosphate raw materials with a high content of magnesium phosphoric acid decreases the coefficient of acid decomposition and the resultant phosphoric acid was not concentrated to the concentration of 50% or higher. In this regard, the processors phosphate rock phosphate concentrates manufacturers impose strict requirements on the content of MgO. High phosphate varietal MgO usually contain no more than 0.7%. These restrictions apply to other impurities, such as heavy metals. After the processing of phosphate rock with a high content of Cd in the fertilizer enters the bulk of the pollutant. The subsequent use of such a product entails the accumulation of heavy metals in soil and food, and later on in the human body, thereby leading to disease.

Table 1

The chemical composition of Algeria phosphate

№	Index Unit	Phosphorite of Algerian	Phosphorite of Tunis №213	Kirov apatite
1	2	3	4	5
1	P_2O_5, %	30	29,3	39
2	MgO, %	1,22-2,0	0,2	0,3
3	$Fe_2O_3 + Al_2O_3$, %	0,78	0,61	1,3
4	Cl, %	0,06	0,07	0,014
5	$CO_{2,\ \%}$	4,4	5,85	0,2
6	H_2O, %	0,53	1,5	0,56
7	CaO, %	47,62	47,4	52
8	$SiO_{2,\ \%}$	3,5	3,75	1,4
9	F, %	3,3	3,49	3,0
1	2	3	4	5
10	Sr, %	0,27	0,03	2,3
11	Na_2O, %	1,22	1,57	0,9

12	K_2O, %	0,1	0,053	0,1
13	Cd, mg/kg	16,1	22	0,1
14	Pb, mg/kg	2,8	2	1,8
15	As, mg/kg	2.8	3,9	2
16	Sieve residue01K, %	85	94	-
17	The total efficiency of natural radionuclides Bq / kg	848	442	130

Table 2

Granular composition of phosphate rock

Phosphates	Mass fraction of particles, % the size in mm							
	>2,5	>1	0,63-1,0	0,315-0,63	0,2-0,315	0,1-0,2	0,063-0,1	<0,063
Algerian phosphorite	0	2,5	0,2	21,3	19,7	44,8	6,5	5,0

Nitric acid decomposition method is promising, due to the lower solubility of impurities, and the resulting extract than in sulfur – and phosphate solutions.

Almost complete degradation of phosphorite is achieved within 20-30 minutes at 45-50 °C. First decompose containes in phosphate raw material carbonates of calcium and magnesium, causing a rapid churning pulp, thereby severely complicating the conduct of the process. As there is a gradual decomposition of phosphate rock with nitric acid neutralization of the solution and the accumulation of reaction products. As a result of the decomposition process is gradually slowing down.

To prevent the inhibition of the reaction process is normally carried out at 2-5% excess of nitric acid to waste including the decomposition of carbonates. In some cases an excess of nitric acid is increased to 20-50%, if necessary subsequent processing operations of the solution obtained fertilizer.

As a result, decomposition of nitric acid phosphorite formed pulp, the solid phase which is composed mainly of insoluble compounds on silica. Liquid phase pulp nitric acid extract contains various amounts of nitrogen, phosphoric acid, fluorosilicic acid and nitrates.

Contained phosphorites organic compound and ferrous compound interacting with the nitric acid to form nitrogen oxides. This causes a loss of nitric acid, and moreover, a danger of air pollution by oxides of nitrogen production facility.

The degree of decomposition of phosphate rock phosphate, the ratio of the P_2O_5 passed into the solution to the amount of P_2O_5 in the raw material, at a rate of nitric acid is substantially less than the stoichiometric rate of acid. Interaction with phosphorites average concentrations of nitric acid occurs rapidly, and most of the phosphate mineral is dissolved during the first 15-30 minutes. The process speed is almost independent of the concentration of nitric acid in the range of from 45 to 55% HNO_3. With increasing acid concentration decreases and the amount of water increases the concentration of salts in the solution.

An increase in temperature accelerates the decomposition of phosphate with nitric acid by reducing the viscosity of the solution and to improve the diffusion of the reactants. However, at temperatures above 50 °C increases the corrosion of equipment. Therefore, the process is usually conducted at 40-50 °C.

Technical requirements for phosphate cheeses, due to technological feasibility and economic viability of processing it in phosphate fertilizers and other products.

The object and aim of the study. The object of the study was phosphate raw materials.

The aim of this work was to obtain a phosphate raw materials to meet the basic requirements for higher quality cheeses. Further processing of the latter in the fertilizer and the full utilization of

the by-product of enrichment. Thus, objective of this work next: selective expansion of the Algerian phosphate rock with nitric acid.

Experimental part and results obtained. Chosen nitric acid move the selective thermal decomposition of carbonates included in the dolomite, nitric acid, wherein, removal of materials soluble magnesium compounds and reducing the content of heavy metals (cadmium) in the product and to minimize the passage of phosphates in the liquid phase, provides enrichment of phosphorite. All this takes the original Algerian phosphorite at a higher level trade.

Together with the Institute of fertilizers and pigments developed technology for rich phosphorite AZTN-acid method. By varying the proportions of components and process parameters investigated the conditions and the optimal parameters the process of getting rich phosphorite.

The experiment was based on the use of magnesium-containing phosphate rock deposits of the Algerian El Jebel brand BPL. Which is characterized by a significant carbonate content (4 to 8%).

Carbonates in phosphorus present in the form of minerals calcite $CaCO_3$ and dolomite $(Ca_nMg_{2-n})(CO_2)$, and are part of the phosphorus-containing minerals, the high content of magnesium (MgO 1.2 - 2%) and cadmium (Cd =10-18 mg/kg).

Table 3

The chemical composition of Algeria phosphate used in the experiment

The original Algerian phosphorite	P_2O_5, %	CaO, %	H_2O, %	MgO, %	CO_2, %	F, %	Cd, mg/kg	Pb, mg/kg	As, mg/kg
	30	47,62	0,53	1,22	7,2	3,3	16,1	2,8	2,8

The main element of enrichment technology is the grinding of phosphate rock phosphate rock, after mining and washing with water clay and carbonate rocks. Next, the resulting wet weight laundered phosphorus containing high content of magnesium compounds and heavy metal is transferred to the chemical enrichment.

Decomposition of nitric acid phosphate is a complex process, it can be represented as follows.

In the initial stages of amino acid decomposition of phosphorite most actively manifest themselves admixture of calcite and dolomite.

$$CaO_3 + 2HNO_3 + 3H_2O = Ca(NO_3)_2 + 4H_2O + CO_2 \quad (1)$$

$$(Ca,Mg)(CO_3)_2 + 4HNO_3 = Ca(NO_3)_2 + Mg(NO_3)_2 + CO_2 + H_20 \quad (2)$$

The liberated by the reaction rapidly (1,2) CO_2 foam forms on the surface of the reaction mass. Due to the presence of impurities in the phosphorites of organic matter and clay particles of foam can be stabilized.

Acid digestion fluorapatite in the extractor proceeds as with the initial formation of monocalcium, since the bulk of the liquid phase of the reaction slurry solution of nitric acid.

$$Ca_{10}(PO_4)_6F_2 + 20HNO_3 = 10Ca(NO_3)_2 + 6H_3PO_4 + 2HF \quad (3)$$

Decomposition frankolita nitric acid is also carried out by the reaction with the formation of monocalcium phosphate.

$$Ca_{10}[(PO_4)_{5,2}(CO_3)_{0,8}F_{0,8}]F(OH) + HNO_3 = \\ = 10Ca(NO_3)_2 + 0,8\ CO_2 + 1,8HF + 1,8H_2O \quad (4)$$

In consequence of the reaction (6) isolation of the reaction mass of CO_2 practically up to the moment of complete decomposition of the phosphate rock.

Along with the basic chemical reactions accompanied by the decomposition of phosphorite reaction with acid impurities, resulting in the composition of the liquid phase alkali compounds pass (Na_2O, K_2O), sesquioxides (Al_2O_3, Fe_2O_3), magnesium oxides and heavy metals.

After completion of the initial interaction of the components resulting slurry is separated into a fine suspension which is largely transferred compound of magnesium, calcium and heavy metal preferably thickened and aggregated particles enriched phosphorite.

The slurry containing particles phosphorite filtrate washed first, then with water, thereby making it more environmentally friendly technology, using the principle of circulating water. The washed sediment-rich phosphorite is dried in a dryer.

After drying, the product turned phosphorite trade marks B and C (TU U 24.1 1-14005076-065-2003). For phosphorite grade A further calcination is carried out (calcination) of the product enrichment, partial leaching of water $Ca(OH)_2$, $Mg(OH)_2$, and final drying.

The dried enriched filtrate is used as a raw material for the production of fertilizers and phosphoric acid or shipped to the customer.

Enriched phosphate rock contains 32 $\pm$ 1% what is 103.3 $\pm$ 110% P_2O_5 and less than 0.7% MgO, which is 43% less than the original phosphorus.

The content of environmentally-controlled element cadmium per 1 kg of P_2O_5 enriched in phosphorus 30-40% less than the original. A by-product of enrichment, a fine suspension is directed to produce fertilizers, the use of which should be used in an area adjacent to the processing plant. To give the products of satisfactory utilization of physical, mechanical and chemical properties of soluble compounds convert the suspension. Recycle slurry are as follows. In fine suspension of the additive potassium sulphate and conduct their conversion processes such as:

$$Ca(NO_3)_2 + K_2SO_4 = CaSO_4 + 2KNO_3 \quad (5)$$

$$Mg(NO_3)_2 + K_2SO_4 = MgSO_4 + 2KNO_3 \quad (6)$$

When administered potassium supplements sulfate molar ratio of the mixture was maintained within HO_3^{-1}: K_2SO_4 1 : (0,14 + 0.18). Thus obtained NPK-pulp, which is the main nutrient content close to balanced.

During the granulation and drying, chlorine-free NPK-brand ydobpenie 10:10:10. containing 10 $\pm$ 1% of each feed component.

Conclusions. This technology is getting rich phosphorite requires no special equipment and can be performed in-line production of simple superphosphate.The developed technology allows the production of enriched phosphorite:

- Expand the raw material base of production of mineral fertilizers.
- To obtain a quality product – enriched phosphorite, wherein the phosphorus content increased to 3 - 10% in terms of P_2O_5, which can be used in the production of phosphate fertilizers.
- To reduce the content of heavy metals, especially cadmium by 30-40%, compared to the starting material.
- This technology allows you to work with high magnesia raw materials, reducing the magnesium oxide content of 43%, translating to a higher competitive level.
- To provide a balanced product for fertilizer blends, with a ratio of P_2O_5 : CaO as 1:1.
- Obtaining chlorine-free NPK-fertilizer grade 10:10:10 containing 10 + 1% of each nutrient component.
- Get the environmental and economic benefits using the principle of water recycling. (Closed cycle of production).
- Get the environmental and economic benefits through the use of low-cost locally available raw materials and the cultivation of environmentally friendly products, by making the soil better fertilizers.
-

References

1. Брагин Ю. Н. Зернистые фосфориты Украины / Ю. Н. Брагин. – Симферополь: ИПП «Таврия», 2000. – 134с.

2. Захаренко В. А. Мировые тенденции производства и использования минеральных удобрений / В. А. Захаренко // Агрохимия. – 2000. – №5. – С. 14-15.

3. Карпович Е. А.Химическое обогащение фосфоритов в сочетании с проблемами эклогии / Е. А. Карпович, С. В. Вакал, Н. И. Малий, Г. В. Силич, Н. И. Андриенко // XIII Международная научно-техническая конференция Экология и здоровье человека. Охрана водного и воздушного бассейнов. Утилизация отходов. Сборник научных статей, том II, Харьков. – 2005. – С 145-148.

4. Пляцук Л. Д. Методы переработки природных фосфатов /Л. Д. Пляцук, С. В. Вакал, Н. И. Андриенко // Вісник СумДУ.– 2006. –№5(89). – С. 108-116.

5. Технические условия «Суперфосфат гранулированный из зарубежных фосфоритов» ТУУ6 – 14005076.048 – 97. Введен 25.11.97. – Сумы: ГосНИИ «МинДиП», 1997 – 49 с.

6. Технические условия «Фосфорит зарубежный»ТУУ614005076. 052 – 98. Введен01.09.98 – Сумы: ГосНИИ «МинДиП», 1998. – 69 с.