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To the question of using of low-grade phosphate rock from Synycheno-Yaremivske field of the Iziumskyi district

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To the question of using of low-grade phosphate rock from Synycheno-Yaremivske field of the Iziumskyi district

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Abstract. The article is devoted to the study of low-grade phosphorites of the Synycheno-Yaremivske deposit in the Iziumskyi district of the Kharkiv region. The possibility of enrichment of this ore by three methods is considered: mechanical, thermal and chemical, carried out in laboratory conditions. The qualitative and quantitative composition of phosphorite has been determined using X-ray fluorescence analysis and electron microscopy with an attachment for energy dispersive analysis. Both natural and enriched raw materials have been studied. Based on the data obtained, it is possible to concentrate this ore with a subsequent increase in the P_2O_5 content, despite the abnormally large amount of iron.

1. Introduction

Stable operation of the chemical industry, producing mineral fertilizers, is possible only with the smooth supply of raw materials quality regulated [1].

The use of mineral fertilizers is one of the main criteria for increasing yields in agriculture. Complex fertilizers, which contain both nitrogen and phosphorus, are of particular importance. To provide agriculture with domestic complex fertilizers, technologies based on the use of phosphorus-containing raw materials, which are located in Ukraine, are promising [2, 3]. Phosphorites are used not only in the chemical industry, but also in metallurgy [4-9], therefore it is necessary to conduct exploration and development of new phosphorite deposits, as well as little-studied phosphorite deposits.

Ukrainian phosphorites belong to the class of low-grade [10, 11], so their composition is the main criterion for different efficiency in their direct use [12-14]. Therefore, the development of a universal technology for the enrichment and processing of phosphorus-containing raw materials into mineral fertilizers is of particular practical interest.

Considering the above and knowing that enrichment is a set of sequential operations, the purpose of which is to increase the content of nutrients, the first and mandatory stage of the technology is crushing the phosphorus-containing ore with its subsequent classification.

The Kharkiv region has always been an industrial and agricultural region. The work [15] describes the phosphorite deposits of the Kharkiv region. In particular, phosphorites occurring in the Iziumskyi, Barvinkivskyi and Lozivskyi district. These deposits are represented by chemogenic, nodular and nodular-slab types (table 1).

Table 1. Deposits of low-grade phosphorites of the Kharkiv region.

Name of the phosphorite deposit	Kind of minerals	Content of the P_2O_5, no more %
Kremenetske (Iziumskyi district)	Nodular and nodular-slab phosphorites	13
Malokomyshuvakhske Viaziv Yar	Nodular in marls, phosphorite slab, nodular in quartz-glauconite sand	14.4 17.8
Synycheno-Yaremivske	Nodules in marl	19.0

The main phosphorus-bearing horizon of the Kharkiv region is the Cenomanian, which is most widespread in the Iziumskyi and Lozivskyi district. The P_2O_5 content in phosphate rock varies from 3.5 to 11.4 %. The component composition is represented mainly by fluorochlorohydroxylapatite, with impurities of phosphate, glauconite, calcite and quartz. According to the data of radiological studies of the Kharkiv sanitary and epidemiological service, the content of natural radionuclides of uranium, thorium, cesium and potassium in these deposits is within normal limits. Therefore, unlike foreign ones, the phosphorites of the Iziumskyi district are distinguished by their ecological purity. Conditions for carrying out hydrogeological exploration are favorable, in particular: a layer of phosphorite and chalk lies above the aquifer, the relief of the area makes it possible to get rid of surface waters. Finishing the review of local phosphorites, the author insists on the need for further study of the deposits of the Iziumskyi district.

It is known that the Izium nodular phosphorites, from the point of view of mineral and petrographic characteristics, are sandy. A feature of these phosphorites is a significant content of P_2O_5 in a lemon-citrate-soluble form and a low content of R_2O_3 is about 3 % [16].

Also, from the literature data, the characteristics of the chemical composition of the phosphorite-bearing layer of the deposits of the Iziumskyi district are known, presented in table 2.

Table 2. Deposits of phosphorites of the Iziumskyi district.

Name of the phosphorite deposit	Chemical composition, wt%									
	P_2O_5	R_2O_3	R_2O_5	CO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	not specified
Kremenetske (Iziumskyi district)	13.20-19.32	4.36-6.51		4.38-5.28						30.45-39.83
Malokomyshu-vakhske	14.00-18.00				30.00-40.00	2.47-3.78	1.60-4.94	20.58-37.94	0.14-0.86	26.34-37.18
Synycheno-Yaremivske	13.20-19.00		7.35					22.65-35.15		30.37

It is known that in the 1925-1954 the phosphorites of the Kamyshuvakhske and partially Synycheno-Yaremivske deposits were used for the production of phosphate rock. But after the discovery of deposits on the Kola Peninsula, domestic deposits remained unclaimed. Now, when there has been a depletion of foreign resources, our priority task is to restore these deposits in order to involve them in industrial production in full.

Based on all of the above, as well as based on the data in table 2, we found that the least studied are the phosphorites of the Synycheno-Yaremivske deposit, therefore the purpose of this work is to further study them.

2. Methods

Having carried out preliminary preparation of raw materials by crushing with subsequent classification, we visually determined that this ore is iron-containing, as indicated by the characteristic color. Therefore, we decided to carry out not only a chemical study, but also several physical ones, in order to accurately establish the composition of these phosphorites.

The first stage in the study of the phosphorus-containing ore of the Synycheno-Yaremivske deposit was a chemical analysis for the determination of iron. The result was up to 30 % of the mass.

The next step was to establish the elemental composition using X-ray fluorescence analysis, as one of the modern spectroscopic methods [17, 18]. The result of X-ray fluorescence analysis is shown in figure 1.

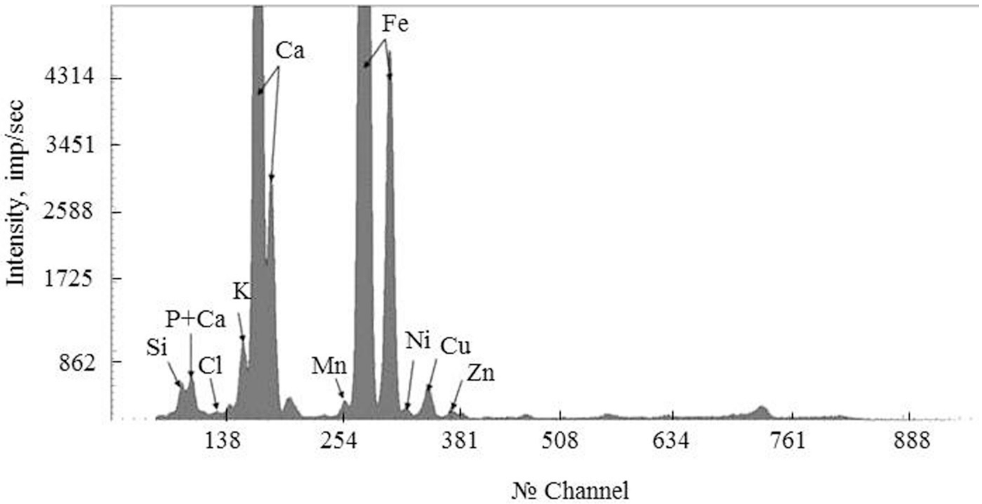

Figure 1. The qualitative composition of the phosphorus-containing ore of the Synycheno-Yaremivske deposit.

From the X-ray diffraction pattern of the phosphorus-containing ore of the Synycheno-Yaremivske deposit, obtained by X-ray fluorescence analysis, it can be seen that the highest content is in calcium and iron. In addition to these elements, the ore contains phosphorus, silicon, potassium, manganese, nickel, copper, zinc and chlorine.

In order to more accurately establish the qualitative composition, an analysis was carried out using electron microscopy with an attachment for energy dispersive analysis, especially since this analysis also shows the quantitative composition. The results are presented in table 3.

Table 3. The qualitative and quantitative composition of the phosphorus-containing ore of the Synycheno-Yaremivske deposit.

Element	Conditional concentration	Intensity	Weight, %	Weight (Sigma), %	Atomic, %	Content, %	Formula	Number of Ions
Na K	0.07	0.7437	0.19	0.11	0.22	0.26	Na_2O	0.01
Mg K	0.22	0.7045	0.62	0.09	0.68	1.03	MgO	0.04
Al K	0.18	0.7328	0.48	0.03	0.47	0.91	Al_2O_3	0.03
Si K	4.39	0.9026	9.70	0.19	9.10	20.75	SiO_2	0.59
P K	2.49	1.2435	3.99	0.14	3.40	9.15	P_2O_5	0.22
S K	0.08	0.9240	0.17	0.07	0.14	0.43	SO_3	0.01
K K	0.61	1.1175	1.09	0.11	0.74	1.32	K_2O	0.05
Ca K	5.36	1.0532	10.15	0.22	6.67	14.20	CaO	0.43
Mn K	0.16	0.8496	0.37	0.18	0.18	0.59	MnO_2	0.01
Fe K	15.61	0.8659	35.92	0.50	16.95	51.35	Fe_2O_3	1.10
O			37.30	0.46	61.45			4.00
Result			100.00					

Analyzing the results of electron microscopy with an attachment for energy dispersive analysis, it can be concluded that the qualitative composition of the phosphorus-containing ore of the Synycheno-Yaremivske deposit is represented by such elements as sodium, magnesium, aluminum, silicon, phosphorus, sulfur, potassium, calcium, manganese, iron and oxygen. All elements were recalculated to chemical formulas, after which the ore has the following quantitative composition, %: Na_2O – 0.26,

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MgO – 1.03, Al_2O_3 – 0.91, SiO_2 – 20.75, P_2O_5 – 9.15, SO_3 – 0.43, K_2O – 1.32, CaO – 14.20, MnO_2 – 0.59, Fe_2O_3 – 51.35.

Based on the quantitative composition of the phosphorus-containing ore of the Synycheno-Yaremivske deposit, it follows that it is iron-containing (as evidenced by the Fe_2O_3 content of 51.35 %). According to our assumptions, iron is in the α-Fe_2O_3 modification (hematite), since the magnetic field applied by us during the laboratory experiment did not act on it. The presence of calcium in the ore, which is the second component in terms of its abundance (14.2 %), is not difficult, since there are a number of ways to remove it.

Knowing the exact qualitative and quantitative composition of phosphorites, we decided to subject them to thermal and chemical enrichment in order to increase the proportion of nutrients.

The first stage of beneficiation consisted in calcining the ore in a muffle furnace at a temperature of 680 °C. Then, according to the method of determining the iron in the ore by boiling the latter in concentrated HCl, the content of ferrous and ferric iron was determined. As a result, the Fe_2O_3 content was obtained equal to 32.43 wt%, and FeO equal to 5.57 wt%. Accordingly, the total iron content in the ore is 38 % of the mass.

At the second stage, ore concentration was carried out using nitric, sulfuric, hydrochloric acids, as well as their mixtures.

The first laboratory experiments were carried out with a mixture of nitric and sulfuric acids. The concentration of nitric acid (HNO_3) was 56 %, and sulfuric acid (H_2SO_4) was 40 %. The acids were taken in the ratio HNO_3: H_2SO_4, equal to 75:25.

The essence of the experiment was as follows: 1 g of ore was calcined in a muffle furnace at a temperature of 680 °C, after which decomposition was carried out with a mixture of acids at different temperatures and interaction times. Further, the resulting aqueous solution of acids was filtered and a purified solution was obtained, from which the required amount was taken for further determination of Fe_2O_3 and P_2O_5. The results are presented in table 4 and 5.

Table data 6 were obtained by laboratory experiments with hydrochloric acid of various concentrations. The essence of the experiment is similar to the experiments from table 3 and 4. But instead of a mixture of nitric and sulfuric acids, HCl was used with a concentration of (20 and 30) % of the mass.

The purified aqueous solution obtained by enriching the ore with 20% HCl was analyzed for the P_2O_5 content. The results are presented in table 7.

Table 4. The content of Fe_2O_3 in the purified aqueous solution obtained by enriching the ore with a mixture of HNO_3 and H_2SO_4.

Experience number	Interaction temperature, °C	Interaction time, min	Fe_2O_3 content, wt%
1	25	120	3.20
2	50	60	4.00
3	60	30	4.51

Table 5. Content of P_2O_5 in a purified aqueous solution obtained by enriching ore with a mixture of HNO_3 and H_2SO_4.

Experience number	Interaction temperature, °C	Interaction time, min	P_2O_5 content, wt%
1	25	120	9.00
2	50	60	9.41
3	60	30	11.00

Table 6. The content of Fe_2O_3 in the purified aqueous solution obtained by enriching the ore with HCl.

Experience number	HCl concentration, % mass	Interaction temperature, °C	Interaction time, min	Fe_2O_3 content, wt%
1	20	108	20	26
2	30	90	20	30

Table 7. Content of P_2O_5 in the purified aqueous solution obtained by enriching the ore with 20% HCl

Experience number	HCl concentration, % mass	Interaction temperature, °C	Interaction time, min	P_2O_5 content, wt%
1	20	108	20	9.4

Next, laboratory experiments were carried out to enrich the ore with sulfuric acid H_2SO_4, with a concentration of 1: 1. The results are presented in table 8.

Table 8. The content of Fe_2O_3 in the purified aqueous solution obtained by enriching the ore with H_2SO_4, with a concentration of 1:1.

Experience number	Interaction temperature, °C	Interaction time, min	Fe_2O_3 content, wt%
1	60	20	14
2	boiling	20	27

Experiments on the purification of an aqueous solution from Fe_2O_3 were carried out using an ion-exchange resin KU-2. The essence of the experiment was as follows: an aqueous acid solution obtained by the interaction of ore with 20% HCl was passed through an ion-exchange resin KU-2, after which it was analyzed for the content of Fe_2O_3 and P_2O_5. The results of the experiments are presented in table 9.

Table 9. The content of Fe_2O_3 and P_2O_5 in the purified aqueous solution obtained by enriching the ore with 20% HCl, after purification with ion-exchange resin.

HCl concentration, % mass	Interaction temperature, °C	Interaction time, min	P_2O_5 content, wt%	Fe_2O_3 content, wt%
20	108	20	11.00	0.05

3. Results and discussion

The studies carried out show that this ore is of industrial interest, both from the point of view of the P_2O_5 content in it, and from the point of view of the Fe_2O_3 content, and also lends itself to beneficiation, as evidenced by the studies performed.

Based on the laboratory experiments, it follows that the use of ion-exchange resins is effective for acidic solutions, both for purification from Fe_2O_3 and for increasing the proportion of P_2O_5. Comparative characteristics of the content of P_2O_5 and Fe_2O_3 in an acid solution obtained during the decomposition of ore with 20 % HCl, before and after the application of the KU-2 ion-exchange resin is presented in table 10.

Table 10. Comparative characteristics of the content of P_2O_5 and Fe_2O_3 in the purified aqueous solution obtained by enriching the ore with 20% HCl.

Content of components in a purified aqueous solution	The use of ion exchange resins	
	Without use	Using
P_2O_5 content, wt%	9.4	11.0
Fe_2O_3 content, wt%	26.0	0.05

Summarizing all of the above, it follows that the phosphorus-containing ore of the Synycheno-Yaremivske deposit requires the use of various chemical and physicochemical enrichment methods to increase the proportion of nutrients and to remove unwanted impurities.

4. Conclusions

It has been confirmed that the studied ore is consistent with the data on the composition of the Izium phosphorites, with the exception of an anomalously large amount of iron.

The studies carried out indicate the possibility of enrichment of the P_2O_5 content in the ore.

The high iron content was determined and confirmed by three methods of analysis, and ranged from 38 % by weight to 51.35 % by weight.

It was found that the removal of Fe_2O_3 occurs most completely when using cation exchangers.

The data obtained indicate the possibility of using phosphorites of the Synycheno-Yaremivske district in the production of mineral fertilizers and metallurgy.

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