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ИССЛЕДОВАНИЕ ПОВЕДЕНИЯ ТВЕРДОЙ ФАЗЫ В ПРОЦЕССЕ КИСЛОТНОГО РАЗЛОЖЕНИЯ ПОЛПИНСКОГО ФОСФОРИТА

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Рост цен на фосфорные удобрения становится серьезной проблемой для внутреннего рынка России. В настоящее время на территории РФ зарегистрировано около 200 разведанных месторождений бедных фосфоритов, часть из которых обладает достаточными ресурсами для их промышленного использования, но переработка руды из этих месторождений представляет серьезные трудности. Процесс разложения бедных фосфоритов в значительной мере зависит от происхождения руды, её химического и минералогического состава, а также множества других факторов. Различают три типа фосфоритов (карбонизированный, кремнистый и глинистый), поведение которых во время кислотного разложения имеет существенные отличия, что отражается на технологии их переработки. Фосфорит Полпинского месторождения относится к бедному фосфатному сырью кремнистого типа. Руда этого месторождения весьма реакционноспособна из-за содержащихся в ее составе примесей карбонатов. Целью исследования является изучение динамики изменения формы и размера частиц при кислотном разложении представительного образца полпинского фосфорита. Разложение проводили с использованием азотной кислоты с торможением реакции на 0, 10, 30, 60, 300, 600 с эксперимента путем нейтрализации кислоты гидроксидом калия. Поведение твердой фазы исследовали с использованием сканирующего электронного микроскопа с многофункциональным модулем JEOL JSM-6510, а затем полученные микрофотографии обрабатывались специальным программным обеспечением. Анализ количества частиц образца показал, что их общее число для каждого эксперимента практически не менялось, так же, как не менялось со временем количество частиц индивидуальной выделенной фракции. Это позволяет предположить, что фосфатный компонент в фосфорите Полпинского месторождения расположен не только на внешней поверхности частиц, но и внутри пористого альфа-кварца. Было определено, что альфа-кварц образует матричную структуру и не претерпевает существенных изменений в процессе кислотной экстракции, а размер его пор не препятствует кислотному извлечению кальция и фосфора из внутреннего объема.

Ключевые слова: фосфорит, электронный микроскоп, размер частиц

INVESTIGATION OF SOLID PHASE BEHAVIOR DURING PROCESS OF ACIDIC DECOMPOSITION OF POLPINO PHOSPHORITE

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The deficiency and growing price of phosphate fertilizers are becoming a major problem in Russia. Most of more than 200 proved phosphorite deposits have enough recourse to exploit them but processing the ore from these deposits presents severe difficulties, and it can't be effectively implemented at this moment. The result of the decomposition process heavily depends on the origin of the ore, their chemical and mineralogical composition and other factors. Three types of phosphorites (carbonated, siliceous, and argillaceous) can be distinguished, and these types of phosphorites behave differently during the acidic decomposition, which leads to the differences in the conditions and performances in the process of their treatment. Phosphorite from Polpino deposit can be considered poor with total component content P2O5≈15.3%, and by the level of SiO_2 it can be qualified as siliceous type. The stock from this deposit is highly reactive because of the carbonated additions and its mineral structure. The aim of the research is to study the dynamics of particle shape and size change during the acidic decomposition of a representative quartered sample of Polpino phosphorite. The decomposition was performed using nitric acid with temporary inhibition of the reaction at 0, 10, 30, 60, 300, 600 seconds by neutralization of acid with potassium hydroxide. Solid phase behavior was investigated using microscopic analysis (scanning electronic microscopy) with multi-purpose module microscope JEOL JSM-6510, and then obtained micrographs were edited with special software. Analysis of the behavior of the particles shows that their total number was nearly constant for each experiment, and the number of particles for every fraction almost didn't change in time. This leads to assumption that the phosphate component in phosphorite from Polpino deposit is located inside of the porous alpha-quartz. It was determined that alpha-quartz from the phosphorite forms a matrix structure and doesn't undergo changes, and its pore size doesn't prevent acidic extraction of calcium and phosphate from the inner volume.

Key words: phosphorite, electronic microscopy, particle size

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INTRODUCTION

Domestically utilized raw phosphate base is characterized by predominance in its structure the apatite ore reserves, which are locally concentrated at Kola Peninsula and are very far from functional processing plants and agricultural regions [1]. This factor increases logistic part in the final price of mineral fertilizer. Constantly growing demand in phosphorus-containing mineral fertilizer and exhausting of rich operational raw deposits already require either import of standard phosphate materials or involving of domestic unused poor and off-balance reserves of phosphate ores into effective processing [2, 3]. More than 200 phosphorite deposits are proved to be in Russia. Majority of these deposits have enough reserves to use them as a base for producing standardized products.

However, about 75% of total reserves of phosphate ores in our country are considered unusable and existing methods of concentrating and processing can't be effectively implemented for now [4]. It is usually connected to the origin of phosphate ores, their chemical and mineralogical composition, petrographic characteristics. Virtually always ores from different deposits require individual approach to study and valuation of technological and economical efficiency of their processing in phosphorus-containing fertilization products [5-7]. Carbonated, siliceous, and argillaceous (clay) phosphorites can be distinguished, mostly based on the nature of main inclusions. These types of phosphorites behave differently during the acidic decomposition, and that defines the difference in the conditions and performances in the process of their treatment [8].

Kinetics and degree of decomposition of phosphate raw materials depends on the dynamics and behavior of mineral grains, which differs for different types of phosphorite. Models of acidic decomposition of phosphate stock particles usually based on the principle of complete destruction of particles and gradual uniform decrease of the size of the presumably spherical particles. Intercrystalline bonds between impurities and phosphate minerals are destroyed in case of carbonate and argillaceous types of ore [9, 10]. But the mechanism of the change in the size and shape of the particles during the acidic decomposition of high-silica phosphorites is not completely clear, although the impurity mineral there (SiO_2) is inert to acids which are used to decompose the phosphate stocks. The exception is a fluorine-containing phosphate raw material, where one of the decomposition products is a hydrofluoric acid, which reacts with silica oxide [11, 12].

SAMPLE SELECTION

Earlier the qualitative change of samples of phosphorite solid phase in the acidic decomposition process was shown by us using the element mapping method: phosphate part of solid phase of phosphorite was quickly extracted (half-reaction time 8-9 s), and undissolved residue (u.r.) is almost pure alpha-quartz. Such high reactivity of Polpino phosphorite is determined by carbonated additions and mineral structure, which allows performing acidic decomposition at the atmospheric temperature, and thus providing a power efficient processing technology [13].

Current work examines the dynamics of particle shape and size change for fine-dispersed fraction of phosphorite ore during the process of acidic decomposition. This study utilizes scanning electron microscopy for the purpose of obtaining micrographs of solid phase particles in time.

Test subject of the research is a representative quartered sample of phosphorite from Polpino deposit. The chemical composition of the sample is represented by the table 1. Judging by the target component content ($P_2O_{5total} \approx 15.3\%$), which was determined by photocalorimetry, this feedstock can be characterized as poor, and by the level of SiO_2 it can be qualified as siliceous type. Note that almost all undissolved residue is a silica oxide. Polpino phosphorite consists of four minerals: hydroxycarbonate apatite $Ca_{10}(PO_4)_3(CO_3)_3(OH)_2$ (55.7%), alpha-quartz α-SiO_2 (32.5%), montmorillonite $(Na)(Fe,Mg)_2(Si,Al)_4O_{10}(OH)_2{\cdot}nH_2O$ (7.2%), and bonshtedtite (4.6%) [14].

Table 1

The averaged chemical composition of Polpino phosphorite

***Таблица 1.* Усредненный химический состав полпинского фосфорита**

P_2O_5, %	15.30
CaO, %	27.42
MgO, %	0.23
Fe_2O_3, %	2.97
Al_2O_3, %	0.00
F, %	0.008
Cl, %	0.001
CO_2, %	5.00
н. о., %	32.90

Table 2

Fraction composition of Polpino phosphorite

***Таблица 2.* Фракционный состав полпинского фосфорита**

Fraction, mm	Fraction yield, %	P_2O_5, %	u.r., %
> 5.0	2.23	13.58	35.79
5.0 – 3.0	5.07	14.52	35.96
3.0 – 2.0	7.92	15.26	34.33
2.0 – 1.0	11.39	17.14	33.38
1.0 – 0.5	17.03	15.50	34.85
0.50 – 0.355	10.81	17.31	33.11
0.355 – 0.315	4.19	15.44	35.42
0.315 – 0.18	13.83	15.64	37.78
0.18 – 0.09	17.62	12.61	47.18
0.09 – 0.071	3.07	12.48	48.31
< 0.071	6.84	15.77	39.26

Earlier [13] we divided a representative quarter sample into 11 fractions and performed a chemical analysis of each fraction. Part of the results of this work is presented in the table 2. It was shown that the chemical composition of Polpino phosphorite depends on the particle size very slightly. It was demonstrated that the reactivity of Polpino phosphorite almost doesn't depend on the particle size as well. Based on these two facts we chose the most highly dispersed fraction of phosphorite (<0.071 mm) as a test subject since it is the most convenient for microscopy analysis.

METHODS

Nitric-phosphoric acid decomposition of Polpino phosphorite was performed in the thermostated three-neck flask equipped with a stirrer. We adapted a known method for inhibiting the reaction which is a neutralization of the sample of nitric acid extract with potassium hydroxide (C_{KOH} = 0.02N) [12]. This technique provides effective and quick fixation of surplus protons. Dilute solution of alkali allows using larger quantities (in comparison with sample volume) of solutions and thus avoiding alkali gradient in the sample. The volume of potassium hydroxide solution and its concentration were calculated with the intention of covering a given pH value in the range of 3-4. The reaction inhibiting was performed after fixed periods of time (0, 10, 30, 60, 300, 600 s), and the suspensions were separated by filtration after that. Solid phases were dried and analyzed three times with multi-purpose module microscope JEOL JSM-6510, which combines scanning electronic microscope with energy dispersive x-ray analyzer. As a result, 18 micrographs were obtained, which then were processed using ImageJ software (open source) to estimate the particle sizes. Processing of micrograph included scaling of the images, selection of optimal brightness and contrast values, conversion of grey image to black-and-white, inversion, and evaluation of particle sizes and counting their number.

RESULTS AND DISCUSSION

As an example there is one of three micrographs of initial sample of Polpino phosphorite (with decomposition time 0 seconds) at the main stages of image processing (fig. 1-4).

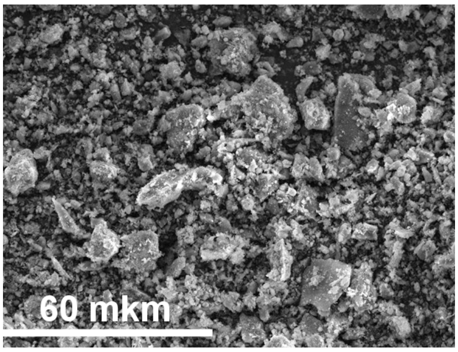

Fig. 1. Original micrograph of Polpino phosphorite
Рис. 1. Исходная микрофотография полпинского фосфорита

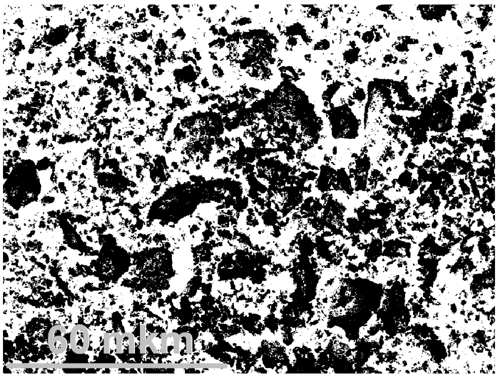

Fig. 2. Micrograph of Polpino phosphorite, conversion to black-and-white and inversion
Рис. 2. Микрофотография полпинского фосфорита, перевод изображения в черно-белое и инвертирование

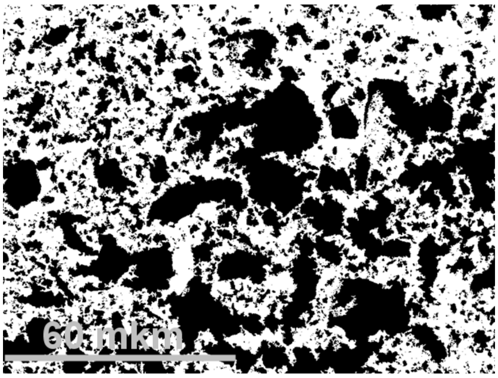

Fig. 3. Micrograph of Polpino phosphorite, filling out large particles outlines
Рис. 3. Микрофотография полпинского фосфорита, заполнение контуров крупных частиц

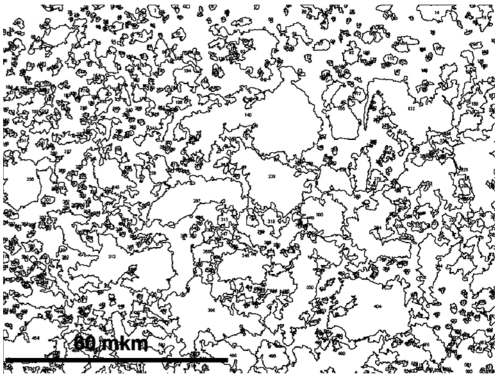

Fig. 4. Micrograph of Polpino phosphorite, contouring and calculating
Рис. 4. Микрофотография полпинского фосфорита, оконтуривание и подсчет частиц

The values were averaged after counting the number of particles and estimating their sizes, and the results were combined in the table 3.

Analyzing the dynamics of change in the number of particles from different fractions during the process of decomposition of phosphorite, it is worth noting that it is nearly constant. This fact allows to make an assumption that the phosphate component in

Table 3

Averaged number of solid phase particles, registered on micrographs at the set time during the process of nitric acid decomposition of Polpino phosphorite

Таблица 3. **Усредненное количество частиц твердой фазы, зарегистрированных на микрофотографиях в заданные моменты времени азотнокислотного разложения полпинского фосфорита**

Fraction, µm	Decomposition time, s					
	0	10	30	60	300	600
< 0.5	82	94	94	107	105	83
0.5 – 1.0	97	88	80	88	81	80
1.0 – 1.5	40	48	39	51	47	38
1.5 – 2.0	20	22	22	25	33	39
2.0 – 3.0	27	30	30	40	46	52
3.0 – 5.0	24	26	39	24	34	53
5.0 – 9.0	24	34	26	33	28	40
> 9.0	78	69	71	62	67	71
Total	392	411	401	430	441	456

Polpino phosphorite is located inside of porous alpha-quartz and not presented in form of separate particles. Therefore, silica oxide, being a part of Polpino phosphorite, is in fact a natural matrix with significantly large pores that don’t prevent the extraction of phosphorite from them. Sedimentary genesis of phosphorite doesn’t contradict our assumption.

CONCLUSIONS

Distribution of particles by sizes was obtained and the change in the particle size during the process of nitric acid decomposition of Polpino phosphorite was estimated for fraction < 0.071 mm of a representative quartered sample using electronic microscope and ImageJ software. It was demonstrated that the particle size during the process of decomposition almost doesn’t change, and, based on this, the assumption of phosphate component being located in the pores of undissolved residue was made. That means that alpha-quartz component of Polpino phosphorite represents a natural matrix.

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