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I.A. Tagaev^a, *N.A. Doniyarov*^a, *L.S. Andriyko*^b, *I.N. Murodov*^a, *A.A. Asrorov*^a**ACID TREATMENT AS A BENEFICIATION METHOD FOR PHOSPHORITE WASTE OF KYZYLKUM PHOSPHORITE PLANT**^a Navoi State Mining Institute, Navoi, Uzbekistan^b Chuiko Institute of Surface Chemistry, Kyiv, Ukraine

This article addresses matters relating to the recycling of waste from the Kyzylkum phosphorite plant in the form of phosphorite slimes, the mass of which exceeds 3 million tons at present. The treatment of slime with sulfuric acid having the concentrations from 2 g/l to 40 g/l made it possible to determine the most optimal concentrations (up to 10 g/l), at which the salts of alkali and alkaline earth metals, uranium and other elements are separated. This method permits obtaining a richer fraction of the useful component, phosphorus(V) oxide (up to 19.1%). At the same time, the pH value of the medium remains in the neutral range. Mass spectroscopy showed that such treatment with sulfuric acid having the concentrations up to 10 g/l allows selectively dissolving carbonates without decomposing phosphates. IR spectra of phosphorite slime after acid treatment do not contain absorption bands characteristic of CO₃²⁻ groups. In accordance with the obtained results, a low-cost technological scheme for the phosphorite slime utilization was developed, followed by its introduction into the production process without violating the main technological regulations. The enriched slime fraction corresponds in quality to the burdened phosphorite ore and can be used as an additional product.

Keywords: phosphorite slime, production waste, acid treatment, sulfuric acid, manufacturing scheme.

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Introduction

Over 25 billion tons of industrial waste is accumulated annually world-wide as a result of the mineral resources processing. The dumps occupy vast areas of fertile land, and solid waste clogs the water and air basins. In the Republic of Uzbekistan, special attention is paid to the disposal of man-made wastes as a result of the processing of mineral resources, their involvement in the production and creation of cost-effective methods for their processing, the reduction of the production cost, and development of promising modern technologies [1–5].

Every year, the demand for phosphorus-containing fertilizers increases, and the quantity and quality of currently mined free-milling phosphate ores deteriorates. In this regard, it became necessary to involve ores of inferior quality or production waste in the processing, and to search for effective ways of their beneficiation [3–6].

At the Kyzylkum Phosphate Plant (KPP), the concentrate is obtained by phosphorite ores beneficiation using such methods as separation, dry screening, ore washing for dedusting followed by roasting. After phosphorite ore washing, fine slime wastes are separated, with which 12 to 16% of the useful P₂O₅ component is removed. The chemical and mineralogical composition of the washed fine fractions is identical with phosphorite ore, in which calcite cement and clay aluminosilicates are concentrated [1].

At this point, more than 3 million tons of wastes in the form of phosphorite slimes have accumulated at three tailing dumps of KPP, which were separated in the washing of the burdened phosphorite ores before thermal beneficiation. The main reason for the separation of fine, dusty slime fractions is in the fact that the smallest dusty part of the phosphorite ore during heat treatment (900–1000°C) is carried

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Acid treatment as a beneficiation method for phosphorite waste of Kyzylkum phosphorite plant

away into the atmosphere along with the exhaust gases, and they pollutes the atmosphere immensely. Preliminary separation of slimes identical in composition to phosphorite ores causes large losses of P_2O_5 (more than 15%), and a high concentration of hardness salts formed in process water leads to high consumption of reagents for its softening and reuse.

About 4500 tons of mixed phosphorite ores are processed daily, after their washing only 2200 tons are accumulated, of which 1750 tons are obtained after thermal beneficiation in the form of finished products, and about 450 tons are pumped out as slime wastes to the tailing dump.

Analysis of the literature data on the phosphorite slimes processing showed that little attention is paid to this topic. Research is mainly focused on the phosphorus extraction into solution. However, these processes, first of all, are associated with high energy consumption for slime dissolution, use of scarce solvents, filtration and centrifugation, which are unprofitable under production conditions [4,6,7]. Therefore, the development of methods for separating the maximum amount of unnecessary and harmful impurities into solution, when phosphorus will remain in the sediment, is currently very important.

In this article, we developed a fundamentally new economically profitable method that allows, under the production conditions of KPP, utilizing phosphorite slimes without dumping them at the tailing dump. To implement this technology, reactors made of common ferrous metal are needed with agitators, screws for pulp feeding, devices for diluting sulfuric acid and thickeners in water, allowing separation of the solution from the sediment easily. The slime beneficiated with a useful component can be used to obtain phosphoric fertilizer or to add to the phosphate concentrate.

Experimental

The chemical composition of phosphorite slimes was determined by mass spectroscopy method (Table 1), that confirmed the similarity with the chemical composition of phosphorite ores, with the exception of the fractional composition fineness, and the amount of the useful component P_2O_5 corresponded to the amount of layer 2 of the deposit.

Chemical analysis showed that phosphorite slimes contain calcium oxide (CaO) in a maximum amount of 42 to 48.1%. The interaction of calcium oxide with carbon dioxide (8–15%) leads to the formation of mineral calcite, which is presented in the form of carbonates $CaCO_3$. The maximum amount of such carbonates can be up to 28% in phosphorites of the Dzheroi-Sardara deposit. That

Table 1

Chemical composition of the Central Kyzylkum phosphorite slimes

Substance	Content (%)
P_2O_5	15.10
Al_2O_3	1.5–3.0
SiO_2	6.0–8.0
CaO	42–48.1
MgO	2.5–3.5
Fe_2O_3	0.6–0.8
CO_2	8–15
U	0.0032
ΣREE	0.04–0.089
Fluorine	1.8–3.2
SO_3	2.5–3.5
H_2O	10.0
organic matter	2.8–3.0
insoluble residue	8.0–8.2

in turn leads to an increase in the alkalinity of phosphorite ores. The content of phosphorus(V) oxide (P_2O_5) is 15.1%. The amount of silicon oxide SiO_2 ranges from 6.0 to 8.0%. It was detected a small amount of aluminium oxide (1.5–3.0%). Sulfuric anhydride SO_3 (2.5–3.5%) binds to the organic residue and ranges from 2.8 to 3.0%. Fluorine, in the amount of 1.8 to 3.2 %, was found mainly in the francolite composition, fluorapatite and organic matter, forms a cement substance, that includes up to 70% phosphorus. Iron and magnesium, apparently of organic origin, in the form of Fe_2O_3 (0.6–0.8%) and magnesium oxide MgO (2.5–3.5%) are also found in the slime waste. The amount of the radioactive element U was 0.0032%, and the amount of rare earth elements (REE) ranged from 0.04 to 0.089%. Insoluble residues (8.0–8.2%) are represented by separate rock-forming and accessory minerals in the form of quartz, feldspar, dickite, kaolinite, ilmenite and zeolite.

The mineralogical composition of phosphorite slimes (Table 2) also corresponds to the phosphorite ore composition, where a large proportion is represented by the complex mineral francolite and reaches to 56%. Francolite can include not only P_2O_5 (more than 70%), but also uranium compounds and rare earth elements. In quantitative terms, the mineral calcite is in second place (22.5%). Quartz is presented in the form of sand in an amount of 7.5 to 8.0%. Hydromicaceous minerals and feldspars are in the amount of 4.0–4.5%.

10 samples of 100 g of phosphorite slime after burdening were taken from the KPP tailing dump.

Table 2

Average mineralogical composition of the Central Kyzylkum phosphorite slimes

Mineral	Chemical formula	Content (%)
Francolite	$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{F}, \text{O})$	56.0
Calcite	CaCO_3	22.5
Fluorapatites, hydroxylapatites	$\text{Ca}_4(\text{CaF})(\text{PO}_4)_3, \text{Ca}_4(\text{CaOH})(\text{PO}_4)_3$	4.0
Quartz	SiO_2	7.5–8.0
Hydromicaceous minerals and feldspars	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot (\text{Na}, \text{Ca}, \text{Ba})$	4.0–4.5
Gypsum	$\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	3.5
Goethite	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	1.0
Zeolites	Tetrahedron fragments SiO_4 and AlO_4	<1.0
Organic substance	Oxalates	~0.5
ΣREE	REE	0.03

Table 3

Variants of sulfuric acid concentrations

Sample number	1	2	3	4	5	6	7	8	9	10
H_2SO_4 solution (g/l)	Ph S initial	2	4	6	8	10	15	20	30	40

Under laboratory conditions, special mixing reactors with built-in impellers were designed, in which phosphorite slime samples were successively treated with aqueous solutions of sulfuric acid (Table 3) in the ratio solid (S) to liquid (L) S:L=1:10.

The solutions were prepared in the following way. Distilled water was added to concentrated sulfuric acid (2, 4, 6, 8, 10, 15, 20, 30 and 40 g/l) and the volume was adjusted to 1000 ml (Table 3). While stirring for 30 minutes at a temperature of 20°C, suspensions were obtained, which were washed and filtered in a Buchner funnel with an area of 0.0064 m². Then the washed samples were dried at 70°C in a drying oven for one hour. The filtrate was analyzed for phosphorus content according to the state standard GOST 20851.2-75.

During acid treatment, in parallel with the slime sediments beneficiation, it was supposed to extract uranium and a certain amount of alkali and alkaline earth metals into solution. The sediment is planned to be further processed into a phosphorus fertilizer, and uranium can be extracted with selective ion-exchange resins from the solution.

The determination of the total P₂O₅ content was carried out using a Shimadzu UV-1280 spectrophotometer (spectral range 190–1100 nm, slit width 5 nm, error ±1 nm, and reproducibility ±1 nm).

Chemical analysis of solutions was performed on an ICP MS Agilent 7500 mass spectrometer No. IP51202494, verification certificate No. 0907633. Sensitivity: concentrations up to 10⁻¹⁰% in solutions and 10⁻⁶% in solid phase, concentration measurement error ±0.02%, measurement range Li, Be, Sc, Ga,

Rb, Sr, Nb, Mo, Cd, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Bi, Th and U. Characteristic of the measurement error at a confidence level P=0.95 to 0.5 ppm inclusively $\pm\Delta=0.50 \cdot C_{\text{Me}}$ (or 0.00005%), from 0.5 ppm to 20 ppm inclusively $\pm\Delta=0.41 \cdot C_{\text{Me}}$ (or 0.000041%), and from 20 ppm to 4000 ppm inclusively $\pm\Delta=0.38 \cdot C_{\text{Me}}$ (or 0.000038%).

A neutron activation analysis was carried out by using a heterogeneous submersible nuclear reactor (RG-1m) and a pulsed solution reactor IIN «Hydra» in a stationary mode. The microscopic structure study of the mineral components of phosphorites was conducted on a binocular microscope of the NLCD-307B brand with digital modeling and with a monitor based on the android OS «Ningbo optics» (PRC). IR spectroscopic studies of the samples were performed on an IR-Fourier spectrometer IRTracer-100, Shimadzu, 8×26 mm tablets weighing 10–12 mg with KBr, 1:100. The absorption bands of infrared light correspond to antisymmetric wavelengths in the range from 400 to 4000 cm⁻¹. For a quantitative study of the solubility degree, the initial sample mass and the final mass after filtration and drying of sediments were measured.

Results and discussion

The method of neutron activation analysis permit to determine more than 45 elements in the composition of thin washed phosphorite slime. The obtained results (Table 4) correspond to the composition of phosphorite ores extracted from 1, 2 and 3 layers from the Tashkurinskoye deposit. 1 and 2 layers are used in the production process. After

Table 4
Content of main elements in phosphorites (Tashkurin deposit) (g/t)

Elements	I layer	II layer	II layer dark brown	Slime
Ca (%)	31.0	31.5	29	27
Fe	6200	1700	4300	9500
Na	4200	4500	5400	4400
K	1900	2300	1800	5500
Sr	2200	1600	2000	1300
Mn	320	240	280	450
Ni	300	100	300	380
Cr	140	130	120	260
Zn	100	68.0	110	130
Ba	40	580	–	80
Mo	2.0	33.0	17	30
As	6.7	3.7	13	4.9
Br	5.8	6.1	8.3	11
U	57	62	52	59
Se	4.2	66	12	19
Rb	–	6.7	11	42
Co	3.6	1.8	3.0	5.0
Sb	2.4	2.0	2.7	3.2
Cs	1.5	1.3	1.0	3.8
Hf	0.95	0.88	1.2	1.6
Ta	–	–	0.37	0.4

washing the ore and forming slimes, all the elements included in the composition of phosphorite ores were found. The calcium amount in the slime was more than 27%. Further, iron (9500 g/t) was in second place, followed by sodium (4400 g/t) and potassium (5500 g/t). A fairly high amount of strontium (1300 g/t) was also found in the slime.

With a gradual increase in the sulfuric acid concentration from 2 to 40 g/l, the pH value of the medium changes quite smoothly from 8.17 to 6.61 (Table 5). Such a slight deviation of pH from the

neutral level is due to the decomposition of calcium carbonates and the formation of $\text{Ca}(\text{OH})_2$ hydroxides. Analysis of the quantitative content of P_2O_5 showed that low concentrations of sulfuric acid did not lead to significant P_2O_5 dissolution. This useful component, during sulfuric acidic treatment from 2 to 40 g/l, passed into the solution in the amount of 0.096–0.227%. It is known that after washing the phosphorite mixture, thin, very fine fractions of waste are formed, where the main amount of P_2O_5 is concentrated in small shells. The maximum P_2O_5 content (up to 19.1%) in sediments can be obtained by processing waste with weak concentrations of sulfuric acid (6 and 8 g/l).

Treatment with the use of low H_2SO_4 concentration of 2 and 3 g/l, led to a decrease in the initial mass (100 g) to 98.5 and 99.14 g, respectively. A gradual increase in the concentration of H_2SO_4 to 4 g/l resulted in the equalization of the mass to 100.98 g. However, at the H_2SO_4 concentration of 5 g/l and higher, there is a steady increase in the sediment mass from 103.30 g to 124.68 g (at the H_2SO_4 concentration of 40 g/l), which indicates the beginning of the stage of formation and an increase in the amount of gypsum and phosphogypsum (Table 5).

However, uranium compounds (59 g/ton in the initial slime) begin to dissolve even at low concentrations of sulfuric acid; and 49 g/ton and 59 g/ton was released into the solution at the concentration of 6 and 8 g/l H_2SO_4 , respectively, i.e. all uranium completely went into solution. It is known that weak concentrations of sulfuric acid dissolve hexavalent uranium when uranium is mined by the borehole method. This means that the phosphorite slimes contained mainly hexavalent uranium. Oxidation of tetravalent uranium to its hexavalent state in phosphorites is apparently due to the presence of phosphorite layers in the near-surface

Table 5
Contents of basic elements in phosphate rock after sulfuric acid treatment

Concentration of H_2SO_4 (g/l)	pH	Sediment weight (g)	P_2O_5 in solution H_2SO_4 (%)	P_2O_5 in sediment H_2SO_4 (%)	U in solution H_2SO_4 (g/t)
Ph S	8.17	100	0.096	15.10	59.0
2	8.1	98.05	0.096	15.00	13.0
4	7.77	99.14	0.096	17.10	24.0
6	7.86	100.98	0.093	19.10	49.0
8	7.71	103.30	0.096	19.10	59.0
10	7.56	103.88	0.091	14.80	11.0
15	7.46	107.00	0.143	10.80	7.3
20	7.23	111.06	0.16	9.38	6.3
30	7.01	117.3	0.121	10.80	3.3
40	6.61	124.68	0.227	10.70	7.0

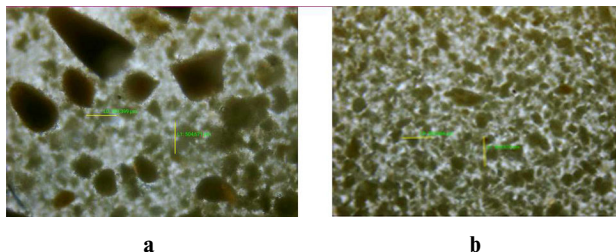


Fig. 1. Images of phosphorite slime: a – initial; b – after treatment with sulfuric acid (8 g/l)

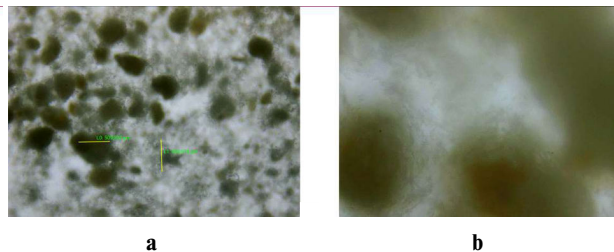


Fig. 2. Images of phosphorite slime after treatment with sulfuric acid (40 g/l) at the magnification: a – $\times 100$, b – $\times 400$

layers at a depth of 15–25 m, into which oxygen easily penetrates. Thus, an important fact of the separation of uranium from phosphorite slimes during sulfuric acid treatment has been noted.

Microscopic analysis of the initial sample at 100-fold magnification showed the presence of a large number of small, shapeless, angular, brown francolite grains, bordered on all sides by light gray, translucent calcite crystals (Fig. 1,a). Francolite grains have well-formed edges. Their size varies from 500 to 1200–1500 μm . The size of calcite grains was significantly smaller and ranged from 20 to 60 μm .

The most effective variant after sulfuric acid treatment with a concentration of 8 g/l was selected where a significant decrease in the size of francolite grains was noted on microscopic images at 100-fold magnification (Fig. 1,b). Images (Fig. 1,b) demonstrate dissolution of small francolite grains, and large francolite grains became loose, swollen and acquired a light brown tint. The size of the francolite grains is in the range from 40 to 160 μm . The number of semitransparent calcite crystals increased significantly and they acquired an irregular shape, covering the francolite grains with a light gray bloom.

At the H_2SO_4 concentration of 40 g/l, micrographs show the appearance of gypsum crystals, which resemble in their structure calcite crystals with a translucent, elongated and multifaceted shape (Fig. 2). Most of the francolite grains were light brown in color, sparse structure, and their size was from 20 to 50 μm . Large grains of francolite with the size more than 500 μm were only detected as a few pieces in the main field of view. It would appear that mineral calcite to have completely decomposed and turned into gypsum crystals. These crystals subsequently began to gather into conglomerates (lumps and clumps), and some turned into elongated, thin thread-like structures, which are clearly visible when the microscope objective is magnified by 400 times.

The mass spectrometry method was used to analyze the amount and mass of chemical elements

that could go into solution during the treatment with weak concentrations of sulfuric acid. Based on the obtained data, a material balance was compiled for the main dissolved elements (Table 6). In a quantitative ratio, the balance of the compounds that have passed into the solution is as follows: calcium compounds (62.10%), sodium compounds (17.63%) and magnesium compounds (9.74%). The amount of other compounds in the solution is insignificant, however this result will play an important role in the slime beneficiation. As expected, the interaction occurred with the most active alkaline and alkaline earth elements. The amount of other elements passed into the solution is insignificant.

The IR-spectra of the phosphate slime samples

Table 6
Material balance of basic compounds passed into solution

Components	Content (%)			
	Concentration of H_2SO_4 (g/l)			
	2	4	6	8
CaO	62.088	61.992	61.062	61.379
Na_2O	16.302	16.955	17.636	17.070
MgO	8.735	9.225	9.692	9.743
K_2O	0.947	0.849	0.818	0.822
B_2O_3	0.093	0.117	0.122	0.122
Fe_2O_3	0.007	0.006	0.005	0.006
Br_2O_7	0.147	0.12	0.115	0.116
SrO	0.548	0.47	0.458	0.432
BaO	0.001	0.00085	0.0017	0.003
UO_3	0.001	0.00085	0.0017	0.003
Li_2O	0.004	0.0054	0.006	0.006
Al_2O_3	0.004	0.0077	0.003	0.004
MnO_2	0.009	0.014	0.025	0.042
MoO_3	0.0035	0.0023	0.003	0.003
P_2O_5	0.020	0.0196	0.019	0.021
other impurities	11.087	10.215	10.032	10.230
total	100	100	100	100

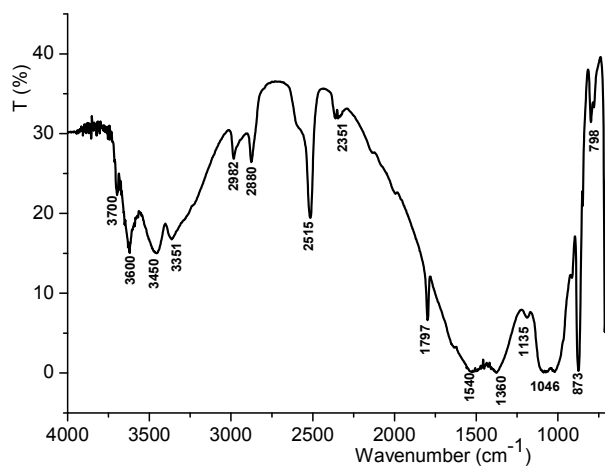


Fig. 3. IR spectrum of initial phosphorite slime

before (Fig. 3) and after acid treatment (Fig. 4) are the superposition of a large number of substantially overlapping bands. Figure 3 shows the characteristic bands corresponding to typical silicates. Asymmetric stretching vibrations at the wavelengths of 798 and 1046 cm^{-1} belong to Si–O–Si(Al)-bonds; deformation vibrations at 785 cm^{-1} correspond to O–Si(Al)–O. Calcite compounds yield three main absorption maxima at 713, 873, and 142 cm^{-1} (Fig. 3) due to the stretching vibrations of the carbonate ion CO_3^{2-} in the mineral structure; bands at 1797 and 2515 cm^{-1} and marked doublet at 2873–2983 cm^{-1} belong to composite frequency bands. P–O bonds in a complex phosphate ion PO_4^{3-} correspond to the stretching vibration bands (914 and 1046–1082 cm^{-1}). In addition, the absorption band of the PO_4^{3-} tetrahedron overlaps with the absorption band of silicates (1041–1068 cm^{-1}). The IR peaks appearing at 3300–3600 cm^{-1} are assigned to the stretching vibrations of adsorbed water molecules [8–10].

IR spectra of phosphorite slime treated with weak concentrations of sulfuric acid (2–6 g/l) are identical to the initial slime spectrum. After treatment with sulfuric acid concentrations from 8 g/l to 15 g/l (Fig. 4), all IR spectra of phosphorite slime have the absorption bands at 1012–1155, 1622, 1683, 3412 and 3555 cm^{-1} . They belong to gypsum and phosphogypsum, which is formed during the phosphorite slime treatment with sulfuric acid and is a pure dihydrate of calcium sulfate with an admixture of anhydrite and $\beta\text{-SiO}_2$ traces. There is a shift of absorption bands of 1115, 1170 and 3450 cm^{-1} towards higher frequencies by 5–10 cm^{-1} , which is due to the formation of calcium hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). The bands observed in the spectra (Fig. 4) at 813 cm^{-1} indicate a silicate impurity. In

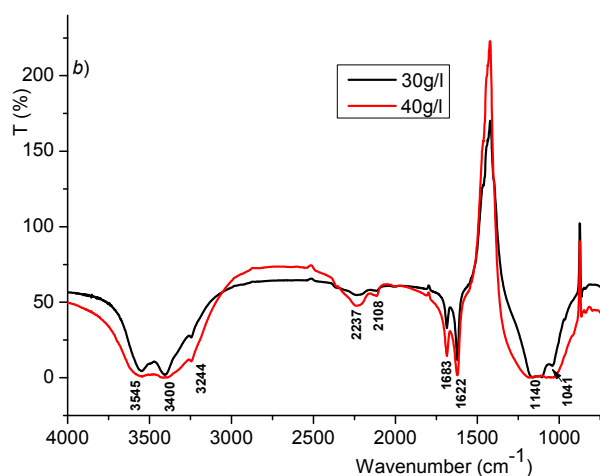
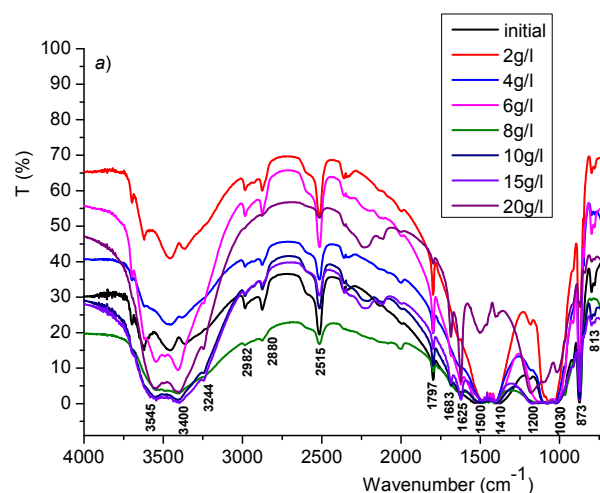


Fig. 4. IR spectra of phosphorite slime after sulfuric acid treatment: a – 0–20 g/l; b – 30–40 g/l

position and profile, this band is more consistent with amorphous SiO_2 . Intensity of bands at 873 and 1425 cm^{-1} (Fig. 4), caused by the stretching vibrations of the carbonate ion CO_3^{2-} in the mineral structure, decreases with an increase in the sulfuric acid concentration, and these bands completely disappear at the concentrations higher than 20 g/l (Fig. 4,a). These bands can also overlap stretching S–O vibrations in SO_4^{2-} (873 cm^{-1}).

After treatment with sulfuric acid having concentrations of 20, 30 and 40 g/l (Fig. 4,a,b), the IR spectrum of phosphorite slime changed significantly: no bands characteristic of CO_3^{2-} groups are observed. Thus, after the treatment with sulfuric acid, neither free carbonates nor carbonates remain, which are part of the crystal lattice of phosphorites.

There are also weak stretching vibration bands $\nu(\text{CH})$ at 2850 and 2990 cm^{-1} , indicating the presence of organic matter [10,11].

The manufacturing technology provides for the

burden preparation, which is formed by mixing ore from 1 and 2 layers with the addition of a mineralized mass (usually 10% P_2O_5 , less often 12% P_2O_5). Next, the burden washing is carried out in 3 stages on 3 hydrocyclones.

On the first hydrocyclone, after washing, a fraction with a particle size of +5 mm comes out. It is considered out of balance ore and sent to special storage. On the second hydrocyclone, the phosphorite ore is continued to be washed, after that a fraction with a particle size of +0.5 mm comes out, which is called the mineralized mass. It has accumulated over 1.5 million tons. This mineralized mass is added during blending to the main initial material.

On the third hydrocyclone, after washing, a fine fraction of phosphorite slime comes out, which is pumped out to the tailing dump. Then the product is dried and called washed cake. There are two following types of cake: (1) washed concentrate after a belt filter with the P_2O_5 content of up to 19%; and (2) washed and dried cake, with the P_2O_5 content of up to 23%.

Based on the examples of phosphorite ore washing on hydrocyclones, as well as the obtained results on acid beneficiating, before ore washing it is proposed to use a technological scheme for processing phosphorite slime for practical use in industrial conditions. Figure 5 shows process flow diagram for the extraction of interfering and harmful impurities from phosphorite slime.

To perform the stages of the process flow diagram (Fig. 5), an aqueous solution of sulfuric acid with the concentration of 6 to 8 g/l is

preliminarily prepared, which is added to wash the phosphorite burden in hydrocyclones in the ratio S:L=1:10; then is mixed in them for 30 minutes, and after this a large fraction of out of balance ore is extracted from the mixture. The remaining mixture is moved for further washing on hydrocyclones 2 and 3, after that the solution is separated from the sediment, which is transferred for drying and roasting. Sediment with the P_2O_5 content of more than 19.1% is transferred for processing and obtaining a concentrate. It is proposed to supplement the main product with phosphorite slime and mineralized mass, without removing them from the process, since they also form a high content of P_2O_5 . Uranium is extracted from interfering and harmful impurities dissolved in water by selective ion-exchange resins. Thus, there is the possibility of introduction of waste-free technology. Process water with high hardness is proposed to be regenerated and reused.

Conclusions

Thus, based on the obtained data of mass spectrometry, neutron activation analysis and IR spectroscopy, the efficiency of phosphorite slime treatment with sulfuric acid as the beneficiation method was shown, that leads to an increase in the content of the useful component, P_2O_5 , in the sediment up to 19%. It was revealed that low concentrations of sulfuric acid (2–6 g/l) did not result in the formation of gypsum and phosphogypsum, that is very important in the production process. It was found that these compounds begin to form intensively at the concentrations of sulfuric acid from 20 g/l to 40 g/l.

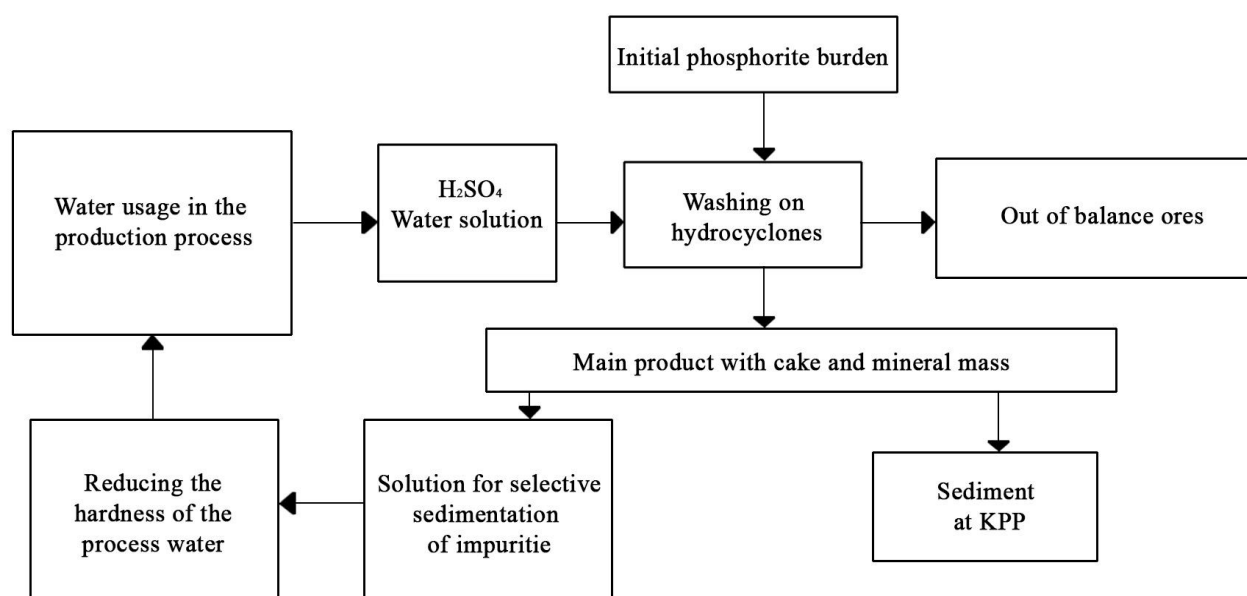


Fig. 5. Process flow diagram for the extraction of interfering and harmful impurities from phosphorite slime

Based on the results obtained, a method has been developed for phosphorite slime beneficiation at the Kyzylkum Phosphate Plant by separating interfering and harmful impurities with aqueous solutions of sulfuric acid. The process is technologically feasible under production conditions, which will allow utilizing phosphorite waste from the tailing dump, and also makes it possible to introduce waste-free technology. This goal is achieved by adding phosphorite slimes to sulfuric acid solutions in the ratio S:L=1:10, by mixing and separating in three hydrocyclones and then separating sediments from solutions. It is recommended to extract uranium from solutions with selective ion-exchange resins. The proposed process flow diagram is designed for the separation of interfering and harmful impurities from the sediment into the solution while maintaining the useful component in the sediment.

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КИСЛОТНЕ ОБРОБЛЕННЯ ЯК СПОСІБ ЗБАГАЧЕННЯ ФОСФОРИТОВИХ ВІДХОДІВ КИЗИЛКУМСЬКОГО ФОСФОРИТНОГО КОМБІНАТУ

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У статті розглянуті проблеми утилізації відходів Кизилкумського фосфоритного комбінату у вигляді фосфоритових шламів, маса яких на даний час перевищує 3 млн т. Оброблення шламів сульфатною кислотою з концентрацією від 2 г/л до 40 г/л дозволила визначити найбільш оптимальні концентрації (до 10 г/л), при яких відбувається відділення солей лужних та лужноземельних металів, урану та інших елементів. Даний метод дає можливість одержати більш багату фракцію корисного компоненту – оксиду фосфору(V) до 19,1%. При цьому рН середовища зберігається в нейтральному діапазоні. Методом мас-спектроскопії показано, що таке оброблення сульфатною кислотою з концентрацією до 10 г/л дозволяє селективно розчиняти карбонати, не розкладаючи при цьому фосфати. ІЧ-спектри фосфоритового шламу після кислотного оброблення не містять смуг поглинання, характерних для груп CO_3^{2-} . На підставі отриманих результатів запропонована мало витратна технологічна схема утилізації фосфоритових шламів з подальшим впровадженням її в виробничий процес без порушення основного технологічного регламенту. Збагачена шламова фракція за своєю якістю відповідає шихтованій фосфоритній руді і може бути використана як додаткова продукція.

Ключові слова: фосфоритовий шлам, відходи виробництва, кислотне оброблення, сульфатна кислота, технологічна схема.

ACID TREATMENT AS A BENEFICIATION METHOD FOR PHOSPHORITE WASTE OF KYZYLKUM PHOSPHORITE PLANT

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This article addresses matters relating to the recycling of waste from the Kyzylkum phosphorite plant in the form of phosphorite slimes, the mass of which exceeds 3 million tons at present. The treatment of slime with sulfuric acid having the concentrations from 2 g/l to 40 g/l made it possible to determine the most optimal concentrations (up to 10 g/l), at which the salts of alkali and alkaline earth metals, uranium and other elements are separated. This method permits obtaining a richer fraction of the useful component, phosphorus(V) oxide (up to 19.1%). At the same time, the pH value of the medium remains in the neutral range. Mass spectroscopy showed that such treatment with sulfuric acid having the concentrations up to 10 g/l allows selectively dissolving carbonates without decomposing phosphates. IR spectra of phosphorite slime after acid treatment do not contain absorption bands characteristic of CO₃²⁻ groups. In accordance with the obtained results, a low-cost technological scheme for the phosphorite slime utilization was developed, followed by its introduction into the production process without violating the main technological regulations. The enriched slime fraction corresponds in quality to the burdened phosphorite ore and can be used as an additional product.

Keywords: phosphorite slime; production waste; acid treatment; sulfuric acid; manufacturing scheme.

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