METALLURGY

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CONDITIONS OF NITRIC ACID TREATMENT OF PHOSPHORUS SLAG FOR REMs RECOVERY AND PRODUCTION OF PRECIPITATED SILICON DIOXIDE

Abstract. Phosphorus slag is the most heavy-tonnage waste of yellow phosphorus production, which is stored in the dump fields for many years causing ecological problems in the regions. One of the relevant and priority directions is rare-earth metals (REMs) production, presence of which in the phosphorus slags allows considering the latter as an acceptable raw material source. Phosphorus slags contain about 30–40 wt % of silicon dioxide, therefore they can serve as a source of production of precipitated silicon dioxide highly required in different industries. The purpose of this work is studying the conditions for REMs recovery from phosphorus slag and further processing of silicon-containing cake to improve a quality of the obtained products. The work shows results of researches on the phosphorus slags' chemical and phase compositions identification, processes of leaching of phosphorus slag and the obtained silicon-containing cake by nitric acid. Instrumental and chemical methods of phosphorus slag content analysis give following data. It consists of 90–92 % of pseudowollastonite α-CaSiO$_3$, and also there are gyrolite Ca$_4$(H$_2$O)$_4$[Si$_6$O$_{15}$](OH)$_2$, small amounts of serpentine Mg$_6$[Si$_4$O$_{10}$](OH)$_8$, hydrated calcium aluminosilicate impurities CaO·2Al$_2$O$_3$·2SiO$_2$·H$_2$O, quartz α-SiO$_2$, calcite CaCO$_3$, hematite Fe$_2$O$_3$, iron phosphate FePO$_4$ and metallic iron with manganese impurity. As a result of kinetic studies of leaching process of phosphorus slag, the apparent activation energy for ΣREMs, calcium, aluminum and iron was determined which amounted to 4.31, 8.53, 7.43 and 12.31 kJ/mol, respectively. This, in combination with value of the Pilling-Bedward Criterion C$_{P-B}$ = 1.1 for orthosilicate acid H$_4$SiO$_4$, indicates that the process is characterized by an intradiffusion region. With a decrease in temperature of nitric acid treatment from 90 to 70 °C, purification degree of precipitated silicon dioxide from iron and aluminium impurities increases. Results of the experimental data will serve as a basis for development of the technology for complex processing of production waste of phosphorus industry and for improving quality of obtained products as REMs concentrate and precipitated silicon dioxide.

Introduction. Electrothermal melting of Karatau phosphorites (South Kazakhstan) while producing 1 ton of yellow phosphorus results in formation of 10 to 12 tons of slag [1]. Over the period of operation of the slag disposal area of New Dzhambyl Phosphorus Plant (Kazphosphate LLP, Zhambyl Branch) the waste volume exceeded 25 mln tons.

Current studies are aimed mainly at processing of phosphorus slag to manufacture construction materials and products [2-7]. However, they are not used properly and mostly stored complicating the environmental situation. One of the reasons of limited slag application is a low value of the products obtained.

One of the promising directions is slag processing to produce precipitated silicon dioxide. Depending on the grade the value of precipitated silicon dioxide in the international market varies from USD 650 to USD 1100 per ton.

In the work [8], in order to produce precipitated silicon dioxide the phosphorus slag was leached by phosphorus acid, calcium was produced in the form of monobasic calcium phosphate. Precipitated silicon dioxide produced was separated from iron by nitric acid [9], and also in the work [10] results of kinetic studies of purification process are shown.

In our previous studies [11] precipitated silicon dioxide was produced from phosphorus slag. The slag was leached by sodium carbonate solution. Silicon dioxide precipitated from the aluminum-free solution by the way of carbon dioxide carbonization.

However, phosphorus slag represents a potential source of raw materials to obtain not only precipitated silicon dioxide ("white soot"), but also rare-earth metals demanded in the industry.

Currently, in connection with intensive development of high – technology branches of

industry, REMs demand is growing. Rare earths are actively used in the nuclear power generation industry, radio electronics, aviation and rocket engineering, machine and instrument engineering. REMs are used to produce wind turbines, energy-saving lamps, electrical and hybrid vehicles.

According to the estimates of Industrial Mineral Company of Australia (IMCOA), the annual world demand for rare earths is expected to reach 200 to 240 thousand tons by 2020 [12], and prices for many rare-earth elements and oxides may increase 2 to 3 times in the coming 20 years.

In connection with increase of the demand and prices for the rare-earth products on the back of reduced by China REMs supplies to the global market, search for new sources of raw rare-earth metals is relevant.

Recently, interest has increased to such sources of raw materials as spent permanent magnets, wastes of nickel hydride batteries and fluorescent lamps [13, 14]. Along with this, technogenic wastes of chemical and metallurgical industries are promising.

In our pilot studies [15, 16] nitric acid was taken for complex processing of phosphorus slag with REMs extraction into the solution and production of siliceous cake as the slag breaker. However, conditions for carrying out of nitric acid leaching processes require of additional studies with aim of improving of quality of REMs-containing products and silicon-containing cake.

Experimental part. The experiments were conducted in a temperature-controlled airproof cell in accordance with the generally accepted methodology. The pulp was stirred using a variable-speed OST basic stirrer. The constant temperature kept using a thermostat TL-TS-01. The slags were first grinded in a grinding mill and then riddled to produce powder with grain size not exceeding 0.05 mm.

Pseudowollastonite contained in phosphorus slag interreacted with nitric acid with production of soluble calcium nitrate and siliceous cake. During the contacting of all acid at once, highly dispersed cake was generated. Silica sols originating at the adherence action may be made gel [17, 18]. While being formed the gel takes the most of the solution, since after the slag contact with HNO_3 almost no liquid phase was left.

To prevent formation of highly dispersed silica and its gelling at nitric acid leaching of phosphorus slag, the conditions were created to reduce the rate of calcium silicate decomposition [19]. Prior to leaching slag was stirred with water with ratio S:L = 1:1. The pulp was heated to 10 ºC below the leaching temperature. Then, while stirring concentrated HNO_3 was being added to the pulp during 1 hour. Then, the pulp was heated up to the specified temperature and leaching was made.

The experimental data were processed by the method of initial rates using the formal kinetics equation (1) [20]:

$$w = \frac{d(1-\alpha)}{d\tau} = -K C^n , \qquad (1)$$

where K - reaction rate constant;
C - reagent concentration in the solution;
W - leaching rate;
n - the reaction order in reagent.

Solutions and cakes produced were analyzed for content of CaO, Al_2O_3, Fe_2O_3, and ∑REMs. Extraction of ∑REMs, CaO, Al_2O_3, and Fe_2O_3 was determined based on the solid product output. Quantitative content of basic components was determined by chemical analysis methods. Quantitative content of ∑REMs was determined using atomic emission spectrometer with inductively coupled plasma Optima 8300DV.

Results and Discussion. The raw material used for experimental purposes is long-storage phosphorus production slag from slag disposal areas of KazPhosphate LLP, Zhambyl Branch, (New Dzhambyl Phosphorus Plant, Kazakhstan), collected since 1990 till 1995. The slag composition is shown in Tables 1 and 2.

Table 1 – Chemical composition of phosphorus slag

Content of the slag (wt %)							
SiO₂	CaO	Al₂O₃	P₂O₅	Fe₂O₃	Na₂O	MgO	TiO₂
36.9	43.2	5.2	2.0	1.63	0.58	2.4	0.14

The following ten elements of rare-earth metals group have been identified in phosphorus slag: Sc, Y, La, Ce, Pr, Nd, Eu, Gd, Yb, Lu (Table 2).

Table 2 – Phosphorus slag content of rare-earth elements

Rare-earth element	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Yb	Lu
ppm	4.0	205.9	91.8	101.5	11.6	66.7	4.6	43.4	6.3	0.68

Among REMs Y has the highest content in phosphorus slag (~206 ppm) then follow Ce (~102 ppm), La (~92 ppm), Nd (~67 ppm), and Gd (~43 ppm). The content of other REMs is within the range of ~0.7 to ~12 ppm.

Based on results of earlier studies [16], phase composition of phosphorus slag was not determined

by X-ray diffraction method (XRD) because of its amorphous state. Therefore, it was analyzed by IR spectroscopy (IRS). According to the data of [16], granular phosphorus slag consists mainly of α-CaSiO$_3$ (90-92 wt % glass of pseudowollastonite composition), it was assumed that phosphorous slag contains the following compounds: gyrolite Ca$_4$(H$_2$O)$_4$[Si$_6$O$_{15}$](OH)$_2$, small amount of serpentine Mg$_6$[Si$_4$O$_{10}$](OH)$_8$, hydrated calcium aluminosilicate impurities CaO·2Al$_2$O$_3$·2SiO$_2$·H$_2$O, quartz SiO$_2$, and calcite CaCO$_3$.

For more information a sample of phosphorus slag was analyzed on SEM using the analyzer JEOL JXA-8230. SEM and EDS analyses of the slag are presented in Figure 1.

Metallic iron with manganese impurity is presented in phosphorus slag (Figure 1a). There are small amount of hematite (Figure 1a) and iron phosphate (Figure 1b). Among the non-metallic minerals basic is pseudowollastonite (Figure 1 a, b), the composition is closed to the natural wollastonite.

The presence of metallic iron in phosphorus slag can be explained by reduction to elemental state of a small part of its compounds, which are presented in phosphorite raw materials, under conditions of electrothermal melting in production of yellow phosphorus. On basis of results of physicochemical studies of phosphorus slag, it can be assumed that the main component is pseudowollastonite α-CaSiO$_3$, and also there are gyrolite Ca$_4$(H$_2$O)$_4$[Si$_6$O$_{15}$](OH)$_2$, small amounts of serpentine Mg$_6$[Si$_4$O$_{10}$](OH)$_8$, hydrated calcium aluminosilicate impurities CaO·2Al$_2$O$_3$·2SiO$_2$·H$_2$O, quartz α-SiO$_2$, calcite CaCO$_3$, hematite Fe$_2$O$_3$, iron phosphate FePO$_4$ and metallic iron. Rare earths are present in the slag in the form of carbonate apatite Ca$_{10}$[PO$_4$]$_6$CO$_3$ or rare-earth apatite impurities, in the crystal lattice of which REMs ions can isomorphically replace calcium ions close in radius. REMs are also present in the form of the compound La$_2$S$_3$ [16].

Taking into account the results of physical and chemical studies, when leaching of phosphorus slag with nitric acid, it was interest to study, in addition to REMs recovery, behavior of such accompanying impurities as calcium, aluminum, and also iron, which is present not only in the form of compounds but also in elemental state.

Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	49.55	67.48	2.37	225433	0.0936133	K
Mg	1.30	1.16	0.46	62762	0.0047656	K
Al	1.74	1.40	0.39	111385	0.0082514	K
Si	17.02	13.21	0.38	1262681	0.1000100	K
P*	1.22	0.86	0.45	70588	0.0092389	K
S*	0.20	0.13	0.39	12766	0.0013214	K
K*	0.53	0.30	0.46	39300	0.0050280	K
Ca	28.34	15.41	0.51	2003083	0.2480136	K
Ti*	0.11	0.05	0.71	5227	0.0007142	K
Total	100.00	100.00				

Elements	ms%	mol%	Sigma	Net	K ratio	Line
Si*	0.22	0.38	0.53	14901	0.0010400	K
P	21.91	33.43	0.48	1503541	0.1734173	K
Ti	0.87	0.85	0.63	60007	0.0072250	K
V*	0.31	0.29	0.71	20484	0.0027478	K
Cr*	0.42	0.38	0.77	26838	0.0039317	K
Mn	11.12	9.57	1.04	542420	0.0913809	K
Fe	64.58	54.65	1.05	2896477	0.5471434	K
Ni*	0.57	0.46	1.73	16873	0.0043340	K
Total	100.00	100.00				

a – part of sample without iron phosphate

b – part of sample without hematite and metallic iron with manganese

1 – metallic iron with manganese impurity;
2 – pseudowollastonite; 3 – hematite; 4 – iron phosphate

Figure 1 – SEM images and EDS analyzes of phosphorus slag

Conditions of Nitric Acid Leaching of Phosphorus Slag. In previous studies [16], influence of HNO₃ concentration, S:L ratio, temperature and process duration on leaching of phosphorus slag, and recovery of the studied metals in solution were studied. The experiments were carried out under the following constant conditions: S:L ratio = 1:2.6; temperature 90 °C; duration is 1 hour and agitator rotation speed is 500 rpm (revolutions per minute).

According to the results of research, the following parameters of leaching process were chosen: nitric acid concentration 7 – 7.5 mol/dm³; S:L ratio = 1: 2.6; temperature 60 ºC; process duration is 1 hour; stirring speed of pulp is 500 rpm.

As a result of the slag leaching process under the indicated conditions, extraction of ΣREMs was 85 %, Fe₂O₃ was recovered by ~ 12 %, Al₂O₃ and CaO by ~81 and 98 %, accordingly (Table 3). The concentration of ΣREMs was 0.203 g/dm³.

Table 3 – Slag leaching results under optimal conditions

Concentration in the solution (g/dm³)				Recovery into solution (%)			
CaO	Al₂O₃	Fe₂O₃	ΣREMs	CaO	Al₂O₃	Fe₂O₃	ΣREMs
229.7	18.6	0.1	0.203	98.0	80.7	11.8	85.0

Table 4 shows extraction of REMs present in phosphorus slag. REMs recovery to the solution was from ~92 to 99 %, except Sc (~39 %) and Lu (~28 %). Among the most demanded REMs slag contains Y, Nd, Eu, and Lu, their extraction rate is ~98, ~99, ~99 and ~28 %, accordingly.

Table 4 – Rare-earth elements extraction at leaching under optimal conditions

Rare-earth element	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Yb	Lu
Recovery, %	38.8	98.3	97.3	98.3	99.0	98.5	99.0	92.1	99.0	27.9

The possibility of concentrating the REMs from the resulting solution was shown in the work [16], where degree of concentration with respect to the initial slag of heavy REMs that are most in demand is ~ 2 times higher than of light. The resulting concentrate contained 17 wt % REMs oxides. Content of aluminum and iron oxides is 2.39 and 0.54 wt %, at the same time, content of calcium oxide reaches ~60 wt %. It is obvious that in order to improve quality of the concentrate in terms of REMs content, it is necessary to reduce concentration of calcium impurity in the product.

Another product is a cake after leaching of phosphorus slag, which is precipitated silicon dioxide "white soot" (WS). The silicon-containing cake obtained under optimal conditions has the following composition (wt %): 85 SiO₂; 0.54 CaO; 0.89 Al₂O₃; 2.7 Fe₂O₃. The cake also has a reduced content of silicon oxide and an increased content of aluminum and iron impurities.

In order to improve the process indicators aimed at improving quality of the obtained products, it was interest to study the kinetic regularities of nitric acid leaching of phosphorus slag.

Investigation of some kinetic regularities of phosphorus slag leaching with nitric acid. In process of studying the kinetics of phosphorus slag leaching with nitric acid, dependence of process speed on temperature, which is characterized by the apparent activation energy, was determined.

To determine the apparent activation energy, dependence of leaching degree on its duration at different temperatures was studied with observance of constancy of all other parameters (nitric acid concentration, amount of phosphorus slag, volume of nitric acid solution, etc.). Slag leaching was carried out at temperatures of 60, 70, 80 and 90 ºC, concentration of HNO₃ in solution of 7.5 mol/dm³ and S:L ratio = 1: 2.6. In previous studies [21], dependence of dissolution rate of ΣREMs on temperature was studied. However, to improve quality of such end products as REMs concentrate and precipitated silicon dioxide, it was of interest to study behavior during leaching of impurities such as calcium, aluminum and iron. In this connection, the kinetic characteristics for these metals were further studied.

Figure 2 shows the kinetic curves characterizing the effect of process temperature on degree of recovery of REMs (a) and iron (b) in solution. The character of the kinetic curves for calcium and aluminum is similar to the curves given for ΣREMs. With an increase in process temperature, there is an insignificant decrease in degree of recovery of REMs, calcium, and aluminum. While for iron this dependence is more pronounced (Figure 2 b). The maximum degree of extraction of these metals in the solution is achieved immediately at a temperature of 60 °C.

The temperature dependence of the initial section of the kinetic curve is subordinated to the process speeds equation (1) and Arrhenius [22]:

$$w = w_0 \cdot exp^{-Ea/RT}, \qquad (2)$$

where w and w_0 – process speed at two different temperatures;
E_a – activation energy;
R – universal gas constant 8.31 kJ/mol.

From equation (2) it can be inferred that

$$E_a = -2.303 \cdot R \cdot tg\alpha, \qquad (3)$$

where 2.303 – transition factor from ln to lg;
α – angle of inclination of line lg *w* – 1/T to the axis of abscissa.

The apparent activation energy, found from angular coefficient of straight line in coordinates lgK - 1/T (Figure 3), for REMs, calcium, aluminum and iron was 4.31, 8.53, 7.43 and 12.31 kJ/mol, respectively. A low value of the apparent activation energy for REMs, calcium, aluminum and iron indicates a diffusion mode of the process.

Character of the kinetic curves shown in Figure 2 indicates that rate of decomposition of initial product in leaching irrespective of process temperature is most significant in initial period of time, during the first 0.5 h, where most of REMs, calcium, aluminum and iron dissolve.

Further increase in leaching time from 0.5 to 2.5 hours practically does not affect the degree of metals extraction in solution, which may be due to diffusion inhibition due to the formation of a solid reaction product on slag particles, which limits the access of nitric acid to reaction surface.

Process speed due to intra-diffusion inhibition decreases with time, and the kinetic curves have gentle appearance (Figure 2). An increase in temperature from 60 to 90 ºC practically has no effect on rate of recovery of REMs, calcium and aluminum in solution, while rate of iron extraction has a noticeable effect.

To determine the phase composition of cakes from nitric acid leaching of phosphorus slags, XRD analysis was carried out. It is established that substance of the investigated cake sample is in an amorphous state.

IRS Analysis of Cake (Figure 4) showed that spectrum has absorption bands characterizing vibrations ν_{as} SiOSi – 1200 shoulder, 1077 cm^{-1}, ν SiO$^-$ - 948 cm^{-1}, ν_s SiOSi - 797, 556 cm^{-1}, δ SiO - 461 cm^{-1} [23]. The band with a maximum at the wave number 948 cm^{-1} may be attributed to vibrations of non-bridging links Si–O$^-$, formed if the glass structure contains depolymerizing cathions breaking Si–O–Si links [24].
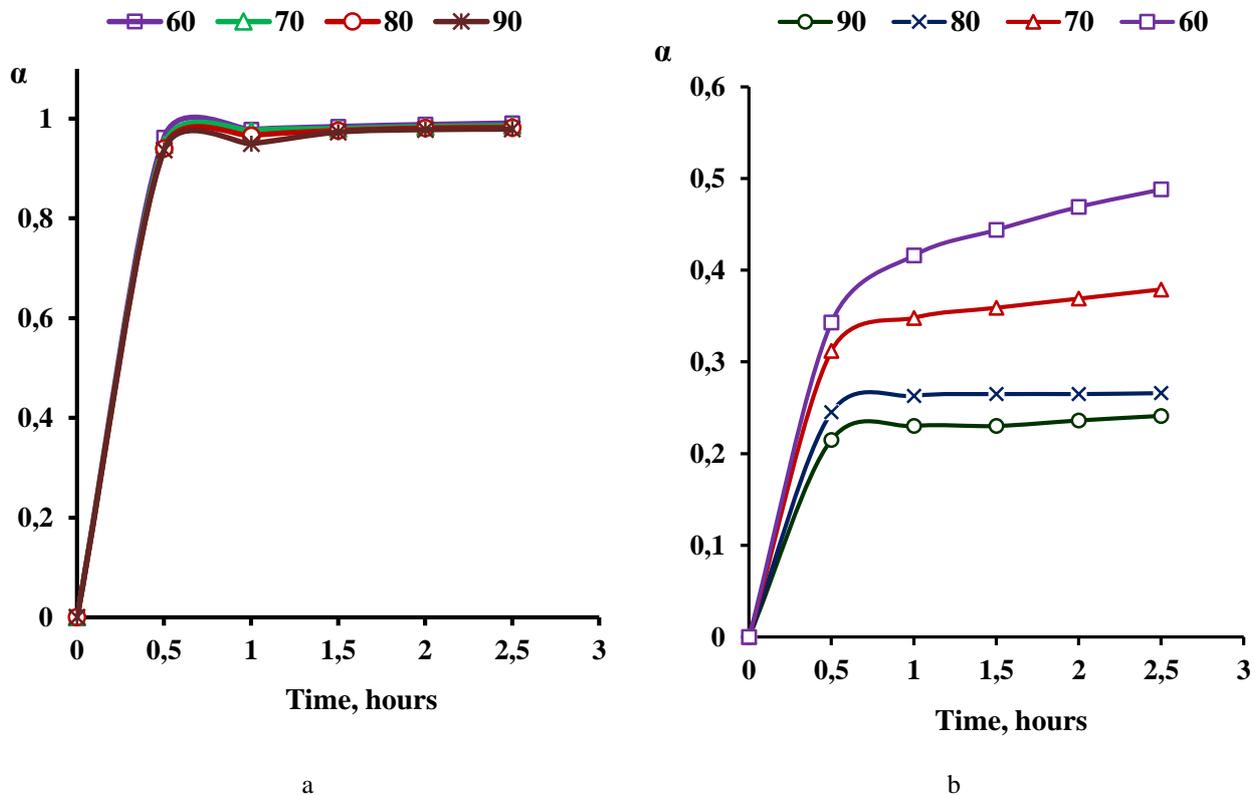
Figure 2 – Kinetic curves of slag leaching process with nitric acid solution for ΣREMs (a) and iron (b) at various temperatures
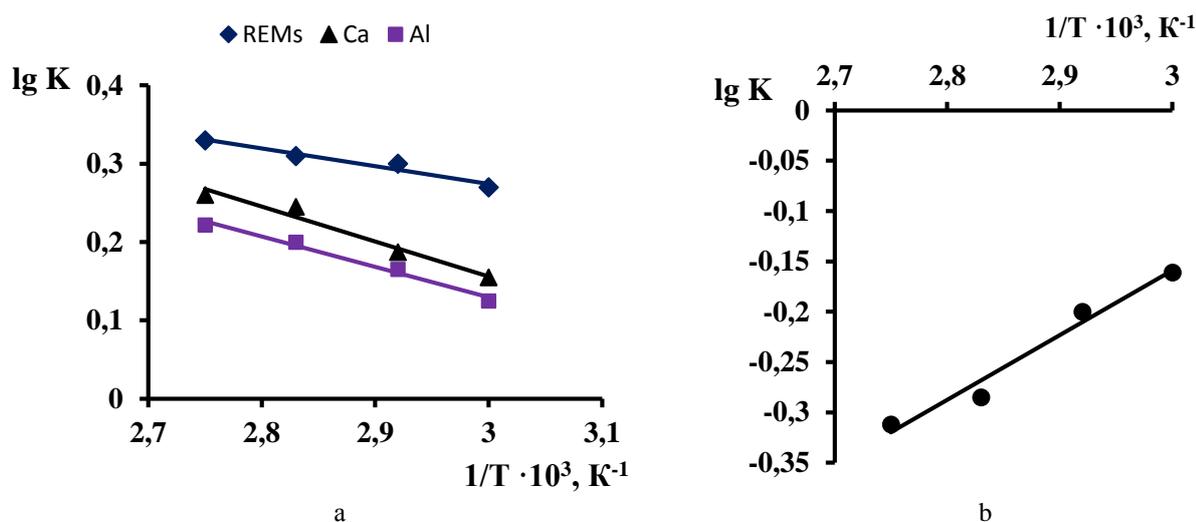
Figure 3 – Logarithmic dependences of the rate constant of leaching process for REMs, calcium and aluminum (a) and iron (b) on temperature
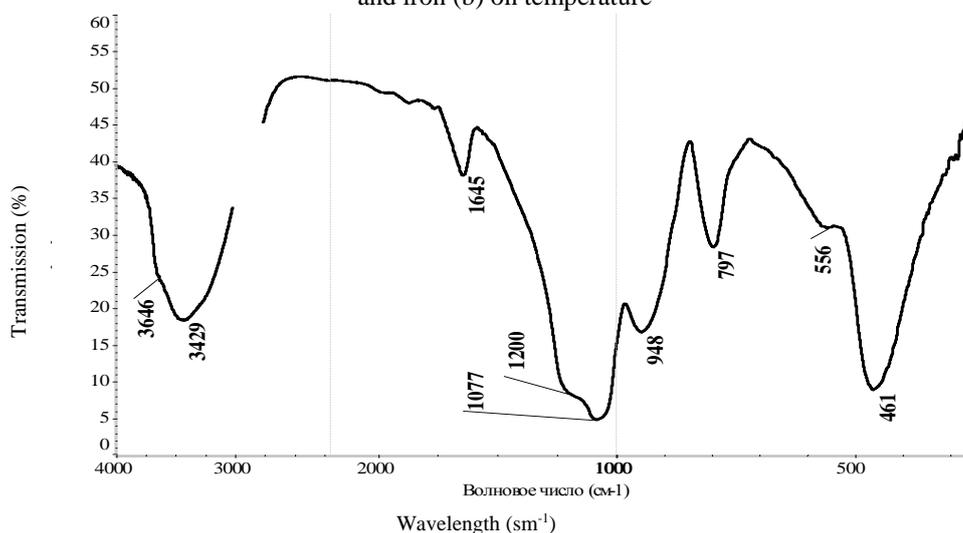
Figure 4 – IR spectrum of cake produced after slag leaching with HNO_3

Presence of SiOH groups in quartz and silicic acid appears close to 940-950 cm^{-1} [23]. Presence of the complex anion with SiOSi angles close to 180° is evidenced by absorption close to the wave number 1200 cm^{-1}. Valence vOH – 3646 shoulder, 3429 cm^{-1} and deformation vibrations δ HOH - 1645 cm^{-1} are observed in the spectrum.

It was established that cake has an irregular structure with formations with a high silica content, it may also contain metasilicate chains $[(SiO_3)]_\infty$ [25].

On basis of the obtained data, it can be assumed that during phosphorus slag leaching with solution of nitric acid the formation of silicic acid gel $nSiO_2 \cdot mH_2O$ takes place.

Silica gel represents a sum of silica acids, such as meta- (H_2SiO_3) and orthosilicate (H_4SiO_4). Therefore, using the reference data [26], the Pilling-

Bedward Criterion C_{P-B} for each of them was calculated using the formula:

$$C_{P-B} = v \cdot \frac{V_{prod.}}{V_{start.}} = v \cdot \frac{\dfrac{M_{prod.}}{d_{prod.}}}{\dfrac{M_{start.}}{d_{start.}}} \quad (4)$$

here v is number of moles of solid product formed from 1 mole of starting material;

$V_{prod.}$, $V_{start.}$ are molar volumes;

$M_{prod.}$ and $M_{start.}$, $d_{prod.}$ and $d_{start.}$ are respectively, the molecular weights and densities of the product and the starting material.

So, for H_2SiO_3, the C_{P-B} Criterion is 0.6; for H_4SiO_4 - C_{P-B} = 1.1. The molar volume of

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orthosilicate acid is greater than molar volume of pseudowollastonite. Consequently, gel-like shell of the formed silica gel can envelop the slag particles and prevent access to them of nitric acid solution. This can confirm the assumption that for leaching process of phosphorus slag with nitric acid, the limiting stage is diffusion of nitric acid through the shell of resulting silicic acid H_4SiO_4.

The carried out investigations of kinetic regularities of leaching process of phosphorus slag with nitric acid also confirmed that the increase in temperature has a significantly smaller effect, unlike iron, on lowering degree of extraction into solution of REMs, calcium, and aluminum. The temperature factor can be used to separate REMs from a significant portion of iron impurity and to purify precipitated silicon dioxide.

Purification of silicon containing cake. After nitric acid leaching of phosphorus slag, as a result of decomposition of its phase constituents, the main of which is pseudowollastonite α-$CaSiO_3$, the silicon-containing cake of the following composition is formed, wt %: 79-85 SiO_2; 0.10-1.5 CaO; 0.02-0.6 Al_2O_3; 2.0-4.5 Fe_2O_3. However, according to "GOST 18307-78: Soot white. Technical conditions", content of SiO_2 should be not less than 87.0 wt %, and impurities of iron, aluminum and the amount of calcium with magnesium in terms of their oxides should not exceed 0.17, 0.1 and 0.8 wt %, respectively. As can be seen from the above composition, the cakes have a reduced content of silicon oxide and an increased content of aluminum, iron and calcium impurities.

For the production of precipitated silicon dioxide, which meets the requirements of GOST 18307-78 for the content of impurities in it, cakes were treated with solutions of nitric acid. The norms for impurities content and losses on ignition (LOI) in accordance with GOST 18307-78 for "white soot" WS-120 are shown in Table 5.

Table 5 – Norms in accordance with GOST 18307-78 for WS-120

SiO_2	Fe_2O_3	Al_2O_3	Cl^-	SO_4^{2-}	$\sum$(CaO, MgO)	Na_2O	LOI
≥ 87	≤ 0.17	≤ 0.1	≤ 0.3	≤ 0.5	$\sum \leq 0.8$	≤ 1.1	3.5-7

First of all, it should be noted that in all samples of precipitated silicon dioxide the content of impurities Cl^-, SO_4^{2-}, $\sum$ (CaO, MgO) and Na_2O does not exceed the norms indicated in Table 5. It is within the limits, respectively, from 0 to ~0.01, from 0.002 to

0.01, from 0.044 to 0.79, and from 0.0018 to 0.03 wt %, so data on them are not given.

Due to the fact that the content of iron, aluminum and calcium impurities exceeds the established standards for WS-120 in cake obtained after phosphorus slag leaching by nitric acid with a concentration of 7.5 mol/dm^3, the treatment of cakes was carried out at S:L ratio = 1:2.5 with a concentration of HNO_3 equal to 9 mol/dm^3. At higher HNO_3 concentrations of 10-12 mol/dm^3, elemental iron, which is present in phosphorus slag, passes from the active state to the passive state. The processing temperature kept at 90 °C (Table 6). Composition of the washed and dried initial cake, wt %: 84.4 SiO_2; 0.28 Al_2O_3; 4.23 Fe_2O_3; 1.37 CaO. As can be seen from Table 6, silicon oxide content in the resulting "white soot" is almost at the required level, however, in the sample, iron and aluminum impurities remain high, 2.11 and 0.14 wt %, respectively. It was found that with the increase in temperature of nitric acid leaching of the slag, extraction of iron and aluminum into solution is reduced. At high temperatures, degree of hydrolysis of iron and aluminum nitrates increases [27]. With increasing temperature, degree of dissociation of water molecules increases. This is the cause of hydrolysis, which affects the results of nitric acid treatment. The specific surface of resulting "white soot", determined by BET method, has a sufficiently high value of 198 m^2/g.

Table 6 – Nitric acid treatment of precipitated silicon dioxide (T of treatment 90 ºC, of drying 105 ºC, [HNO_3] 9 mol/dm^3, S:L = 1: 2.5, time 2 hours)

Content in WS, wt %			*S, m^2/g
SiO_2	Fe_2O_3	Al_2O_3	
86.90	2.11	0.14	198
*S – specific surface area, m^2/g			

In work [8] in leaching of phosphorus slag with phosphoric acid, precipitated silicon dioxide was obtained in which iron content exceeds the established norms. To reduce iron impurity, precipitated silica is leached with nitric acid at concentration of 1.27 mol/dm^3 (8 %) at S:L ratio = 1:4, temperature of 70 °C and duration of 2 hours [9]. In the resulting product, iron content decreases to ~ 0.02 wt %. In order to ascertain possibility of obtaining precipitated silica meeting the established standards, processing at lower concentrations of nitric acid, experiments were conducted while maintaining the concentration of HNO_3 in range from 1.27 to 1.90 mol/dm^3. The experiments were carried

out with initial cake obtained under phosphorus slag leach conditions chosen above. The conditions and results of experiments are presented in Table 7.

Table 7 – Influence of nitric acid concentration on the cake treatment at T 70 ºC, drying at 300 ºC; S:L = 1:4; time 2 hours. (Composition of the washed and the dried initial cake, %: 84.4 SiO_2; 0.28 Al_2O_3; 4.23 Fe_2O_3; 1.37 CaO)

Concentration of HNO_3, mol/dm³	Content in WS, wt %				S, m²/g
	SiO_2	Fe_2O_3	Al_2O_3	LOI	
1.27	87.70	0.19	0.06	8.62	-
1.59	88.20	0.14	0.08	8.44	193
1.90	90.95	0.18	0.23	8.50	-

As can be seen from Table 7, "white soot" is characterized by a higher concentration of silicon dioxide, the content of which increases from 87.70 to 90.95 wt % with increasing concentration of HNO_3 in the processing from 1.27 to 1.90 mol/dm³. The content of aluminum impurities in samples increases with increasing concentration of HNO_3, while the values obtained at concentrations of HNO_3 of 1.27 and 1.59 mol/dm³ are in accordance with established standards. The admixture of iron has slightly higher values in samples obtained at concentrations of nitric acid treatment of 1.27 and 1.90 mol/dm³, however, the overall results are better. Despite the fact that the drying of samples was carried out at 300 °C, LOI has increased values.

The sample obtained after treatment with a solution of nitric acid with a concentration of 1.59 mol/dm³ corresponds to the standards of GOST 18307-78 for WS-120. The specific surface area in it was 193 m²/g.

In process of obtaining highly dispersed amorphous precipitates of silicon dioxide, it is important to study formation of silica gel, which has several stages. At the initial stage, the formation of silica gel can be represented by the reaction

$$\alpha\text{-}CaSiO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2SiO_3 \quad (5)$$

A monomer, truly dissolved SiO_2, forms. After that, polymerization process takes place with formation of polysilicic acids, which is accompanied by dehydration

$$nSi(OH)_4 = (SiO_2)_n + 2nH_2O \quad (6)$$
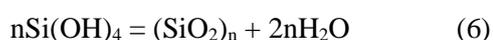
The gel formation process can be represented by the scheme [28]

$$Si(OH)_4 \rightarrow \text{polymerization} \rightarrow \text{colloidal particles (sol)} \rightarrow \text{aggregation} \rightarrow \text{gel}$$
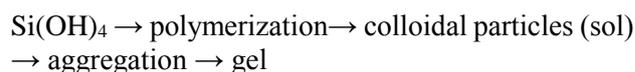
$Si(OH)_4$ molecules condense and form colloidal particles with formation of Si-O-Si bonds

$$2SiOH = SiOSi + H_2O \quad (7)$$

IR spectroscopic analysis of cakes after leaching slag with nitric acid indicated existence of such bonds. In the next step, condensation of colloidal particles leads to the formation of gel.

The iron impurities present in the phosphorus slag interact with the silicate formations according to the reaction [17]

$$(\text{-}SiOH)_m + Fe^{3+} = (\text{-}SiOH)_{m-n}(\text{-}SiO)_nFe^{3-n} + nH^+ \quad (8)$$

The reaction of silica $Si(OH)_4$ with aluminum ions proceeds with formation of halloysite

$$2Si(OH)_4 + 2Al^{3+} + H_2O = Al_2Si_2O_5(OH)_4 + 6H^+ \quad (9)$$

Presence of metal cations (especially multiply charged) causes the process of precipitation, rather than gelation, i.e. promotes destruction of polymer network of gel. Admixtures of iron and aluminum embedded in structure of the obtained precipitates, during re-treatment of the cake with nitric acid, being dissolved, can, apparently, lead to an additional rupture of the bonds and a decrease in the particle size.

Thus, the parameters of nitric acid treatment of cakes are largely influenced by temperature. Lowering of treatment temperature from 90 to 70 °C increases in most cases the degree of purification of precipitated silicon dioxide from impurities of iron and aluminum. An increase in concentration of HNO_3 during the cake treatment from 1.59 to 9 mol/dm³ is not advisable, since it does not lead to an increase in the content of silicon dioxide and degree of purification from impurities of aluminum and iron. Impurities Al and Fe, interacting with silicic acid, can contribute to the destruction of its colloidal structure.

Conclusions. While using IRS and SEM analyzes it was established that phosphorus slag contains pseudowollastonite $\alpha\text{-}CaSiO_3$, and also gyrolite $Ca_4(H_2O)_4[Si_6O_{15}](OH)_2$, small amounts of serpentine $Mg_6[Si_4O_{10}](OH)_8$, hydrated calcium aluminosilicate impurities $CaO \cdot 2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$, quartz $\alpha\text{-}SiO_2$, calcite $CaCO_3$, hematite Fe_2O_3, iron phosphate $FePO_4$ and metallic iron with manganese impurity.

The kinetics of phosphorus slag leaching with nitric acid was studied. The apparent activation energy for REMs, calcium, aluminum and iron was 4.31, 8.53, 7.43 and 12.31 kJ/mol, respectively, which, in

combination with the Pilling-Bedwards Criterion (C_{P-B}) for orthosilicate acid H_4SiO_4, equal to 1.1, indicates the intradiffusion nature of the process.

IR analysis of siliceous cake produced indicates that it has an irregular structure with formations with high silica content. The possibility of presence of metasilicate chains in cake can be indicative of the fact that silica gel is formed in the leaching process.

It was found that the parameters of the nitric acid treatment of silicon-containing cakes are largely influenced by temperature. Lowering the treatment temperature from 90 to 70 °C, raises degree of purification of precipitated silicon dioxide from iron and aluminum impurities.

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ТҮЙІНДЕМЕ

Фосфорлы қож – ең көптонналы сары фосфор өндірісінің қалдығы, көп жылдар бойы үйінді қалдық алаңдарға жиналатын, аймақтардағы экологиялық мәселелерді туындатады. Сирек жер металдардың (СЖМ) өндірісі өзекті және басым бағыттардың бірі, олардың фосфорлы қождардағы ішінде болуы арқасында, соңғысы шикізат ретінде қарастыруға

болады. Фосфорлы қождардың құрамына, диоксидқа қайта есептеу істегенде, кремнийдің 30-40 (салм.) % кіреді, сондықтан оларды жоғарыдисперсті тұндырылған кремний диоксидін, әртүрлі салалық өнеркәсіптерде талап етілген, алудың көзі деп есептеуге болады. Алынатын өнімдердің сапасын жоғарылату үшін фосфорлы қождардан СЖМды алу шарттарын зерттеу және арықарай кремнийқұрамды кекті өңдеу осы жұмыстың негізгі мақсаты болады. Азотты қышқылмен кремнийқұрамды кекті алынған және фосфорлы қождарды сілтісіздендіру үрдістердің, фосфорлы қождардың химиялық және фазалық құрамдарды анықтау зерттеулердің нәтижелері осы жұмысында көрсетілген. Фосфор қожын талдауға арналған аспаптық және химиялық әдістердің деректеріне сүйеніп, ол құрамында 90-92 % псевдоволластонит α-CaSiO$_3$, гиролит Ca$_4$(H$_2$O)$_4$[Si$_6$O$_{15}$](OH)$_2$, аз мөлшерде серпентин Mg$_6$[Si$_4$O$_{10}$](OH)$_8$, кальций гидроалюмосиликатының CaO·2Al$_2$O$_3$·2SiO$_2$·H$_2$O қоспасы, кварц α-SiO$_2$, кальцит CaCO$_3$, гематит Fe$_2$O$_3$, темір фосфаты FePO$_4$ және марганец қоспасы бар металдық темірден тұратыны болып табылды. Фосфор қожының сілтілеу процесін кинетикалық зерттеу нәтижесінде СЖМ, кальций, алюминий және темір үшін көрінетін белсендіру энергиясы анықталған, бұл тиісінше 4,31, 8,53, 7,43 және 12,31 кДж/моль құрайды. Бұл Пиллинг-Бедвордс критерийінің шамамен бірге ортосикат қышқылы H$_4$SiO$_4$ үшін мәнімен К$_{P-B}$ = 1,1 процестің ішкі диффузиялық аймақпен сипатталатындығын дәлелдейді. Азот қышқылды өңдеу температурасы 90-нан 70 °C дейін төмендетуінде, темір және алюминий қоспаларынан тұндырылған кремний диоксидінің тазалау дәрежесі жоғарылады. Фосфор өнеркәсібіндегі техногенді қалдықтарды кешенді қайта өңдеу технология өңдеу үшін және алынған өнімдердің сапасын жоғарылату үшін: оның ішінде, тұндырылған кремний диоксиді мен СЖМ концентратын, экспериментті көрсеткіштер нәтижелері негізі ретінде бола алады.

Түйін сөздер: фосфорлы қож, сирек жер металдар, сілтілеу, кинетика, кремнийқұрамды кек, бөліп алу, тазалау.

РЕЗЮМЕ

Фосфорный шлак является самым многотоннажным отходом производства желтого фосфора, который много лет складируется на отвальных полях, создавая экологические проблемы в регионах. Одним из актуальных и приоритетных направлений является производство редкоземельных металлов (РЗМ), присутствие которых в фосфорных шлаках позволяет рассматривать последние как приемлемый сырьевой источник. Фосфорные шлаки содержат в своем составе порядка 30-40 мас. % кремния в пересчете на его диоксид, поэтому они могут служить источником получения высокодисперсного осажденного диоксида кремния, широко востребованного различными отраслями промышленности. Целью данной работы является изучение условий извлечения РЗМ из фосфорного шлака и дальнейшая переработка кремнийсодержащего кека для повышения качества получаемых продуктов. В работе представлены результаты исследований по установлению химического и фазового составов фосфорных шлаков, процессов выщелачивания фосфорного шлака и полученного кремнийсодержащего кека азотной кислотой. На основании данных инструментальных и химических методов анализа фосфорного шлака установлено, что он состоит на 90-92 % из псевдоволластонита α-CaSiO$_3$, присутствуют гиролит Ca$_4$(H$_2$O)$_4$[Si$_6$O$_{15}$](OH)$_2$, небольшие количества серпентина Mg$_6$[Si$_4$O$_{10}$](OH)$_8$, примесь гидроалюмосиликата кальция CaO·2Al$_2$O$_3$·2SiO$_2$·H$_2$O, кварца α-SiO$_2$, кальцита CaCO$_3$, гематита Fe$_2$O$_3$, фосфата железа FePO$_4$ и металлического железа с примесью марганца. В результате кинетических исследований процесса выщелачивания фосфорного шлака определена кажущаяся энергия активации для ΣРЗМ, кальция, алюминия и железа, которая составила 4,31, 8,53, 7,43 и 12,31 кДж/моль, соответственно. Это в сочетании с величиной критерия Пиллинга-Бедвордса К$_{П-Б}$ = 1,1 для ортосиликатной кислоты H$_4$SiO$_4$ свидетельствует, что процесс характеризуется внутридиффузионной областью. При понижении температуры азотно-кислотной обработки от 90 до 70 ºС степень очистки осажденного диоксида кремния от примесей железа и алюминия повышается. Результаты экспериментальных данных послужат основой для разработки технологии комплексной переработки техногенного отхода фосфорной промышленности и для повышения качества получаемых продуктов: концентрата РЗМ и осажденного диоксида кремния.

Ключевые слова: фосфорный шлак, редкоземельные металлы, выщелачивание, кинетика, кремнийсодержащий кек, извлечение, очистка