

Dephosphorization of Nitric Acid Solutions from the Leaching of Monazite Ferrous Ores under Hydrothermal Conditions

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Abstract

The precipitation of phosphoric acid from nitric acid solutions in the presence of iron(3+) oxides and hydroxyoxides under hydrothermal conditions was studied. It was shown that the dephosphorization process proceeds with the formation of iron(3+) hydroxyphosphate (giniite) $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$. The most efficient and fast process is implemented at temperatures of 180-200 °C and above. It was found that the content of phosphoric acid in the solution as a result can be reduced to 10^{-3} mol/l and below. Lanthanide, uranium, and thorium nitrates are stable under conditions of hydrothermal dephosphorization of solutions, in contrast to iron(3+) nitrates decomposing to hematite and nitric acid. The features of the studied hydrothermal process were used to increase the efficiency of direct nitric acid leaching of monazite iron-bearing ores of the Chuktukon rare metal deposit.

Keywords: monazite, leaching, cleaning, phosphoric acid, giniite, iron oxide

1. Introduction

Previously, the authors of this article studied in detail the hydrothermal nitric acid leaching of monazite iron oxide ores from the Chuktukon deposit (Russia) (Kuzmin et al., 2012; Serdyuk et al., 2017). It has been established that at temperatures above 180 °C, a significant decrease in the concentrations of phosphorus and iron in solutions is observed. Simultaneously with an increase in temperature, the extraction of lanthanides into the solution increases, which reaches 97-98%. This creates great prospects for the practical use of the process (Kuzmin et al., 2015), both for processing rare earth ores of this type and monazite concentrates.

The hydrothermal precipitation of iron from acidic solutions is well known and is due to the hydrolysis of salts, in particular, for nitrate salts (Shang and Weert, 1993) with the formation of hematite at temperatures above 140 °C.

Dephosphorization of solutions under these conditions has not been studied. A study of the composition of ore leaching cakes showed that phosphorus is present in the solid phase in the form of the mineral giniite, a complex iron(3+) hydroxyphosphate $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ (Kuzmin et al., 2012; Serdyuk et al., 2017).

The discovered fact of acidic dissolution of lanthanide phosphates with simultaneous precipitation of iron phosphates cannot be called trivial. Under normal conditions the solubility product of ordinary iron(3+) phosphate (FePO_4) is $1.3 \cdot 10^{-22}$ and value of this parameter higher than the analogous for lanthanide phosphates (for lanthanum $K_{\text{SP}}[\text{LaPO}_4] = 4 \cdot 10^{-23}$). In other words, in the presence of comparable amounts of iron phosphates and lanthanides, an increase in the acidity of solutions should primarily promote the dissolution of iron(3+) phosphate. This is confirmed, in particular, by the data of acid leaching of fluorapatites containing iron and REM (Bandara and Senanayake, 2015) at temperatures below 100 °C. According to the authors of the work, in this process the extraction of Fe(3+) into the solution significantly exceeds the extraction of rare-earth metals for hydrochloric, nitric, perchloric, and phosphoric acids. The increase in solubility differs for different acids and is mainly related to the degree of their dissociation in aqueous solutions (acid activity) and complexing ability with respect to a particular cation. It was shown that the differences in the extraction of iron compared with lanthanides are especially large for phosphoric acid due to the higher strength of the phosphate complexes of these metals. It is obvious that the determining factor that changes the direction of the processes of leaching and reprecipitation of metal phosphates in the case of hydrothermal exposure of the Chuktukon ores is the leaching temperature. An increase in temperature to 180-200 °C leads to the formation of iron hydroxyphosphate – giniite, which is more stable than lanthanide phosphates.

Under normal conditions, at low temperatures, both in neutral and slightly acidic media, iron phosphates are formed. It is widely used to purify various solutions from phosphate ions by precipitation. The composition of the resulting products depends on the pH of the solutions and the Fe:P ratio (Cruz et al., 1980; Twidwell et al., 1986). So, at a solution pH of 4.5 and an equal Fe:P molar ratio, the formation of iron(3+) orthophosphate is observed, and with an increase in the proportion of iron, more complex phosphates $\text{Fe}_{2.5}\text{PO}_4(\text{OH})_{4.5}$ are formed.

Giniite, which was discovered as the main solid phase during the hydrothermal decomposition of Chuktukon ores, is a promising material (precursor) for obtaining electrode materials for lithium batteries. To obtain it, hydrothermal methods of synthesis are widely used (Chen et al., 2014; Liu et al., 2017; Song et al., 2015). The process is carried out under various conditions: by heating mixtures of iron nitrates with Na_3PO_4 in water at a temperature of 220 °C

for 8 hours (Chen et al., 2014); treatment of a mixture of FeCl_3 with $\text{NH}_4\text{H}_2\text{PO}_4$ in water also at 220 °C. In report Song et al. (2015) to obtain microspheres of a complex nature the decomposition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with $\text{NaNH}_4\text{HPO}_4$ in aqueous solutions at a lower temperature 180 °C and a processing time of 12 hours was used. It was also established (Yang et al., 2014) that giniite of the desired morphology can be obtained by the reaction of $\beta\text{-FeOOH}$ nanoparticles with $\text{NH}_4\text{H}_2\text{PO}_4$ and citric acid in water at 180 °C for 24 hours.

Thus, the conditions for obtaining giniite in the known works differ significantly from the conditions for its formation during the hydrothermal leaching of the Chuktukon ore (nitric acid dissolution of phosphates in the presence of oxides (hydroxides) of iron(3+)). It can be assumed that giniite is formed due to the secondary reaction of phosphoric acid, which is released during leaching of ores, with oxides (iron(3+) hydroxides). In this work, this process was studied in order to assess its possibilities for improving the leaching characteristics of ferruginous monazite ores.

2. Materials and methods

We used inorganic salts, acids and bases of "pure" and "chemically pure" grades. Hematite (alpha) "high purity" was used as an adsorbent for phosphoric acid. The behavior of phosphorus was studied on the model systems " $\text{Fe}_2\text{O}_3\text{-H}_3\text{PO}_4\text{-HNO}_3\text{-water}$ ", as well as " $\text{Fe}(\text{NO}_3)_3\text{-Ln}(\text{NO}_3)_3\text{-H}_3\text{PO}_4\text{-water}$ ". During the hydrothermal decomposition of nitrate solutions, the distribution of radioactive elements, thorium and uranium, between the aqueous and solid phases was also studied. The indicators of the breaking down of the ore were evaluated on a representative sample of the Chuktukon ore ChTP-3. Its composition by main components is presented in Table 1.

Table 1

Chemical composition of the ChTP-3 technological sample by main components (data of X-ray fluorescence analysis method, determination error from 1 to 10% depending on the content of the element).

Oxide	MgO	Al_2O_3	SiO_2	P_2O_5	CaO	TiO_2
Content, %	0.27	0.16	0.96	7.4	8.1	0.44
Oxide	V_2O_5	MnO_2	Fe_2O_3	ZnO	SrO	Y_2O_3
Content, %	0.27	21.2	49.0	1.21	0.53	0.31
Oxide	Nb_2O_5	BaO	$\sum\text{Ln}_2\text{O}_3$	PbO	ThO_2	U
Content, %	0.29	3.8	5.6	0.36	0.058	0.008

Hydrothermal processes were carried out in laboratory fluoroplastic autoclaves with a volume of 25 ml, placed in stainless steel cases (autoclave inner diameter 20 mm, vessel height 80 mm). The phases were mixed by rotating the reactor in an air thermostat. When performing experiments, the required solution, usually 10 ml, was placed in the reactor, and separately – the solid phase (iron oxide, ore) in a special container (boat) with a volume of about 2.5 ml. Mixing of the solid and liquid phases was carried out after heating the reactor (about 50-60 min). After completion of the process, the reactor was placed in a vertical position, held for about 1 minute to separate the phases by precipitation, and cooled with cold water without stirring the reaction mixture at the highest possible speed to "freeze" the reaction (time about 5 minutes). Then, the aqueous solution for analysis was separated by decantation. The solid phase was filtered on a Schott filter and washed with water.

The chemical and phase composition of the solid product was determined using an X-ray fluorescence analyzer (PANalytical Axios Advanced) and a DRON-3 diffractometer (Russia). Solutions were analyzed by atomic absorption (Analyst 400 PerkinElmer spectrometer) and mass spectrometric methods (ICP-MS 7500C, Agilent). In a number of cases, phosphorus in solutions was determined by the photometric method with molybdate according to a well-known method. Previously, iron(3+) was removed from the solution at an acidity of about 0.1 mol/L by sorption on the KU-2 cation exchanger at a solid to liquid ratio of s:l=1:10. To eliminate the effect of organic impurities contained in the cation exchanger, it was preliminarily washed with acetone and water.

3. Results and discussions

3.1 Sorption of phosphoric acid on hematite from nitric acid solutions

As noted above, the process of leaching of lanthanides from Chuktukon ores with nitric acid with dephosphorization of solutions and the formation of giniite proceeds most efficiently at temperatures above 180 °C. Under these conditions, iron nitrates in solutions are unstable and decompose with the formation of hematite. The reaction is endothermic in nature, and in the specified temperature range, the equilibrium of the process is significantly shifted towards the formation of hematite. This allows you to significantly reduce the iron content in leaching solutions and reduce the consumption of nitric acid. It should be noted that the reaction proceeds efficiently and smoothly in nitrate (nitric acid) systems. For sulfuric acid solutions, the formation of fairly stable mixed precipitates of hydroxysulfates is observed at the first stage. For hydrochloric acid solutions, iron(3+) complexation with chloride ions in solutions is observed, which leads to a significant increase in the concentration of iron in the solution.

Studies performed on a model system with hematite "Fe₂O₃-H₃PO₄-HNO₃-water" confirmed that under hydrothermal conditions, a fairly rapiddephosphorization of solutions is observed. Thus, at a temperature of 200 °C, the concentration of phosphoric acid in a nitric acid solution decreases from 0.5 mol/L to <0.001 mol/L (precipitation 99.8%) (Fig. 1, dependence 1) in 1 hour. The diffraction pattern of the precipitation product indicates the formation under these conditions of the predominantly giniite phase, Fe₅(PO₄)₃(OH)₃ (Fig. 2).

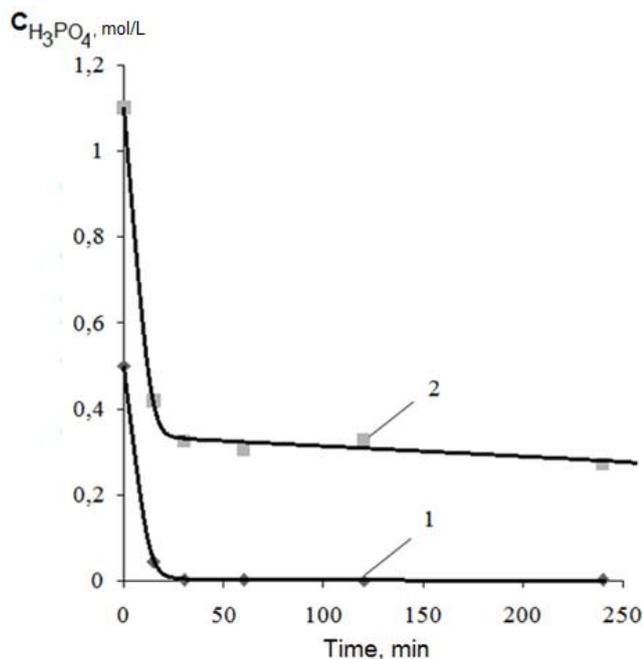


Fig. 1. Dependence of the phosphorus content in the solution on time during the sorption of phosphoric acid on hematite from a nitric acid solution. Initial solution: 1 - C_{H₃PO₄} = 0.5 mol/L (15.5 g/L for phosphorus), C_{HNO₃} = 1 mol/L; 2 - C_{H₃PO₄} = 1.1 mol/L (34.1 g/L for phosphorus), C_{HNO₃} = 1 mol/L, s:l=1:10 (g/ml); T= 200 °C.

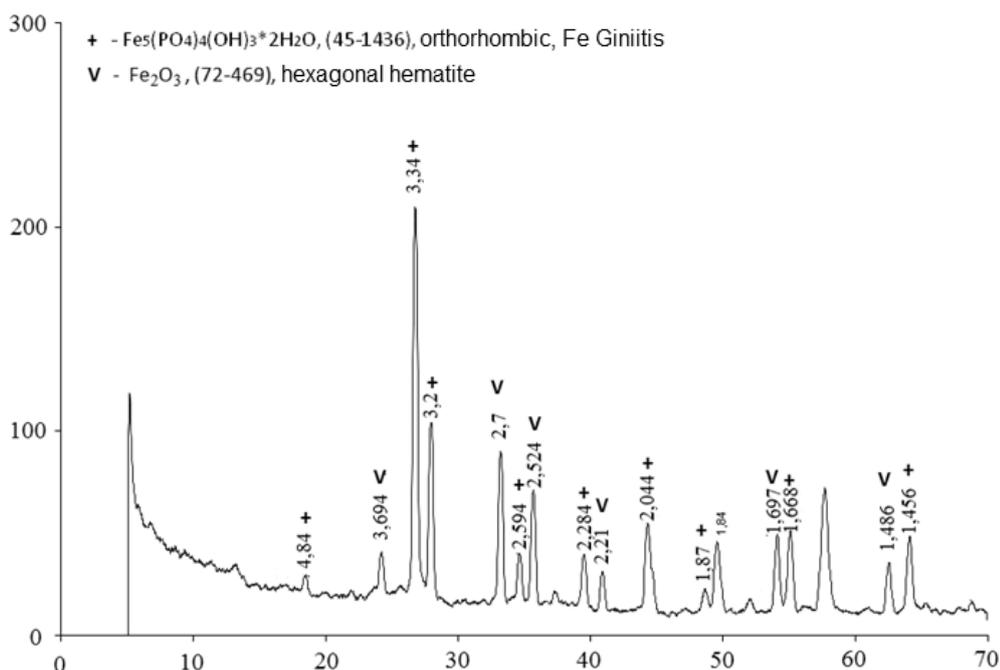


Fig. 2. X-ray diffraction pattern of the solid phase after sorption of phosphoric acid on hematite from a nitric acid solution. Initial solution: $C_{\text{H}_3\text{PO}_4} = 0.5 \text{ mol/L}$ (15.5 g/L for phosphorus), $C_{\text{HNO}_3} = 1 \text{ mol/L}$, $s:l=1:10$ (g/ml), temperature $200 \text{ }^\circ\text{C}$.

An increase in the concentration of phosphoric acid in the solution to 1.1 mol/L (ratio $s:l=1:10$) leads to a break in the kinetic dependence 30 minutes after the start of the process (Fig. 1, dependence 2), and the extraction of phosphoric acid at this is 70%. With further hydrothermal treatment under these conditions, the extraction of phosphorus into the precipitate gradually increases. This feature of the kinetic dependence for a high initial concentration of phosphoric acid in solution is due to the passivation of the hematite surface due to the formation on its surface of a fairly dense film of the reaction product, giniite.

Since only hematite and giniite phases are found in the solid phase after the precipitation reaction, the process of precipitation of phosphoric acid under these conditions can be written as a simple reaction (1).



The equilibrium constant for this process (K_1) is determined by equation (2). For dilute solutions of phosphoric acid and the constancy of the composition of the solid phases – crystalline hematite and giniite, equation (2) can be converted to a simple equation (3). From equation (3) it follows, that the equilibrium in such a system is characterized by a constant equilibrium concentration of phosphoric acid. Its change may be related to the complex formation of phosphoric acid with iron(3+) or other cations present in the aqueous solution.

$$K_1 = [(a_{\text{Fe}_5(\text{PO}_4)_4(\text{OH})_{3(s)}}^{0.4} \cdot a_{\text{H}_2\text{O}}^{1.1}) / a_{\text{Fe}_2\text{O}_{3(s)}}] \cdot 1 / C_{\text{H}_3\text{PO}_4}^{1.6} \quad (2)$$

$$K_{1(1)} = [K_1 \cdot a_{\text{Fe}_2\text{O}_{3(s)}}] / (a_{\text{Fe}_5(\text{PO}_4)_4(\text{OH})_{3(s)}}^{0.4} \cdot a_{\text{H}_2\text{O}}^{1.1})^{1/1.6} \approx 1 / C_{\text{H}_3\text{PO}_4} \quad (3)$$

where the symbol (s) indicates that the reaction component belongs to the solid phase; $a_{\text{Fe}_2\text{O}_{3(s)}}$, $a_{\text{Fe}_5(\text{PO}_4)_4(\text{OH})_{3(s)}}$ and $a_{\text{H}_2\text{O}}$ are the activities of hematite, giniite and water, respectively, close to constant values for crystalline solid products of constant composition and dilute solutions.

Fig. 3 shows the sorption isotherm of phosphoric acid as the ratio of the amount of sorbed phosphoric acid to the initial hematite (mol/mol) from the current concentration of phosphoric acid in solution. The extraction is accompanied by an increase in the mass of the precipitate, which reaches more than 60% of the initial mass of hematite at high initial contents of phosphoric acid in solutions. According to equation (1), the inflection on the isotherm should correspond to the ratio $n\text{H}_3\text{PO}_4 / n\text{Fe}_2\text{O}_3 = 1.6$, and the dependence should reach saturation. However, due to non-equilibrium in the system for the reason discussed above, a sharp increase in the content of phosphoric acid in the solution begins

after reaching the ratio $n_{\text{H}_3\text{PO}_4}/n_{\text{Fe}_2\text{O}_3} > 1.15$, which is 30% lower than the expected value. Further increase in the concentration of phosphoric acid leads to a gradual increase in the phosphorus content in the solid phase.

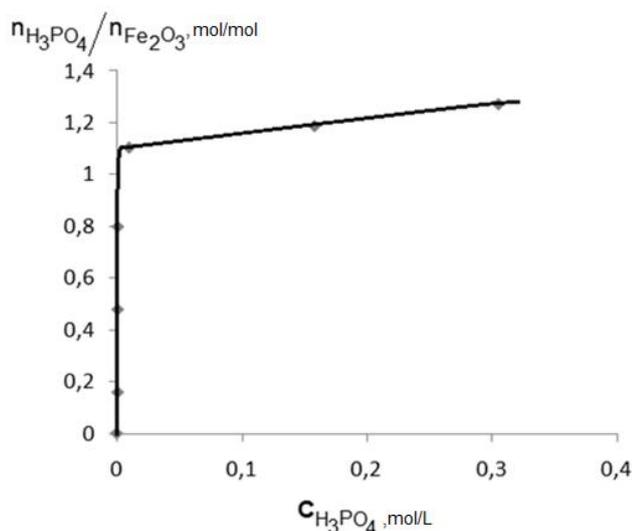


Fig. 3. Isotherm of sorption of phosphoric acid on hematite from a nitric acid solution. Initial solutions: $C_{\text{H}_3\text{PO}_4} = 0.1-1.5$ mol/L, $C_{\text{HNO}_3} = 1$ mol/L, $s:l = 1:10$ (g/ml), $T = 200$ °C, $t = 60$ min. $n_{\text{H}_3\text{PO}_4}/n_{\text{Fe}_2\text{O}_3}$ is the ratio of phosphorus and iron in the solid phase after sorption based on the molar ratio of sorbed phosphoric acid (H_3PO_4) to the initial hematite (Fe_2O_3).

In the area of low concentrations of phosphoric acid, its content reaches 20-25 mg/L for 1 hour of phase contact, but also gradually decreases. In the present work, the equilibrium level of the concentration of phosphoric acid was not reliably established due to low values that are beyond the detection limit of phosphorus according to the methods of analysis used. In particular, when evaluating the phosphorus content in a solution according to the reverse reaction - the dissolution of hematite in nitric acid (Table 2), a noticeable amount of phosphoric acid in the solution appears only in strongly acidic solutions at an HNO_3 concentration of 4 mol/L and reaches 18 mg/L ($\approx 6 \cdot 10^{-4}$ mol/L). Perhaps the appearance of phosphorus in solution is associated with an increase in the concentration of iron(3+), which increases under these conditions to 1.4 g/L due to the dissolution of hematite present in the system. A decrease in the temperature of hydrothermal treatment of such a product from 220 °C to 150 °C also leads to an increase in the content of phosphorus and iron in the solution. For a 1 mol/L nitric acid solution, there is an increase in the content of iron(3+) in the solution from 40 to 160 mg/L and phosphorus from <5 mg/L to 17 mg/L.

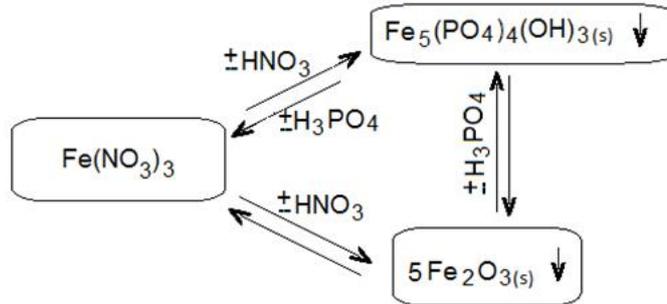
Table 2

Change in the content of phosphoric acid (phosphorus) and iron(3+) in solution upon interaction with nitric acid of the product of sorption of phosphoric acid on hematite: T= 200 °C, s:l=1:50, t= 120 min.

C_{HNO_3} , mol/L	0	0,5	1	1,5	2	4
Fe, mg/L	0	17	73	151	308	1400
P, mg/L	0	<5	<5	<5	<5	18

The data obtained from the study of direct and reverse reactions of sorption of phosphoric acid show the possibility of dephosphorization of nitric acid solutions to a level of less than 10⁻³ mol/L (<20 mg/L for phosphorus). The possibility of evaluating more accurate limit values under various process conditions requires further more detailed studies.

The above features of the process are also reflected in the behavior of iron(3+) in the system and the change in the metal content in the aqueous solution. Let's consider this question in more detail. Hydrothermal transformations of iron(3+) compounds in the studied system can be represented as a broader transformation scheme (4), which includes three main processes.



(4)

The first of these is the hydrolysis of salt (nitrate) to hematite and nitric acid. This process is well known and taking into account the ionic dissociation of the reaction components, can be written as reaction (5). For this process, the equilibrium constant (K_4) can be written as equation (6).



$$K_4 = (\text{C}_{\text{H}^+}^3 / \text{C}_{\text{Fe}^{3+}}) \cdot (\gamma_{\text{H}^+}^3 / \gamma_{\text{Fe}(\text{NO}_3)_3}) \cdot a_{\text{Fe}_2\text{O}_3(\text{s})}^{1/2} \quad (6)$$

where γ_{H^+} – ionic activity coefficients of H^+ and Fe^{3+} .

The second process – the sequential reaction of hematite formed during hydrolysis with phosphoric acid, was discussed above. This process leads to the formation of giniite (1), with an equilibrium constant (2).

The third process, the direct formation of giniite. It is possible during the decomposition of iron nitrate in the presence of phosphoric acid, in particular, when the process is implemented in an excess of phosphoric acid. This process can be written as reaction (7) with equilibrium constant (8).



$$K_6 = \left[\frac{C_{\text{H}^+}^3}{(C_{\text{Fe}^{3+}} \cdot C_{\text{H}_3\text{PO}_4}^{0,8})} \right] \cdot \left(\frac{\gamma_{\text{HNO}_3}^3}{\gamma_{\text{Fe}(\text{NO}_3)_3}} \right) \quad (8)$$

The last reaction (7) makes it possible to evaluate the behavior of iron(3+) in solutions both for systems in which both solid phases, hematite and giniite, and only one giniite phase are present under equilibrium conditions, which is realized in an excess of phosphoric acid.

Taking into account the relations obtained, we consider the behavior of iron under various conditions. If the solubility of giniite in nitric acid solutions at temperatures of 180-200 °C is low and does not exceed 10^{-3} mol/L in terms of phosphorus, then the solubility of hematite is significantly higher and the iron content in the presence of this iron(3+) oxide is determined precisely by the process of dissolution. Equilibrium in terms of iron in the system with hematite is achieved fairly quickly within 1 hour, as can be seen from Fig. 4 (dependence 1). The content of iron in solution for this mineral form is determined by the concentration of nitric acid and temperature: with an increase in the concentration of acid from 0.5 mol/L to 4 mol/L (Table 1) it increases by almost 2 orders of magnitude. A decrease in temperature also leads to an increase in the concentration iron in solution. At low concentrations of phosphoric acid in an excess of hematite, the kinetic dependence of the change in the content of iron(3+) in solution on time (Fig. 4, dependence 2) is close to the system without phosphoric acid (dependence 1). At high concentrations of phosphoric acid (dependence 3), during the first 30 minutes, there is a sharp increase in the iron content in the solution, which can be associated with the formation of phosphate complex compounds of the metal. Then there is a fairly rapid decrease in the concentration to a level significantly lower due to the solubility of hematite. In our opinion, the decrease in solubility is due to the formation of the giniite phase and the blocking of the surface of unreacted hematite, which was discussed in the analysis of the sorption of phosphoric acid in this experiment (Fig. 1, dependence 2).

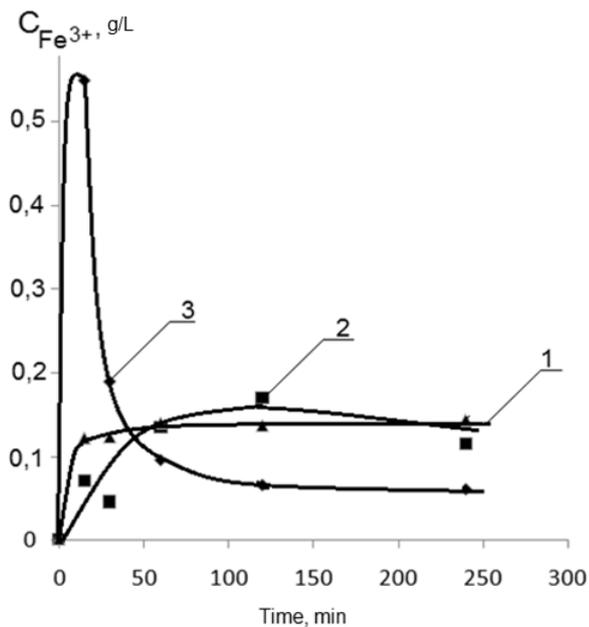


Fig. 4. The dependence of the iron content in the solution on time during the sorption of phosphoric acid on hematite from a nitric acid solution. Initial solution: 1- $C_{\text{H}_3\text{PO}_4} = 0 \text{ mol/L}$, $C_{\text{HNO}_3} = 1 \text{ mol/L}$; 2 - $C_{\text{H}_3\text{PO}_4} = 0.5 \text{ mol/L}$ (15.5 g/L for phosphorus), $C_{\text{HNO}_3} = 1 \text{ mol/L}$; 3 - $C_{\text{H}_3\text{PO}_4} = 1.1 \text{ mol/L}$ (34.1 g/L for phosphorus), $C_{\text{HNO}_3} = 1 \text{ mol/L}$; s:l= 1:10 (g/ml); $T = 200 \text{ }^\circ\text{C}$.

It should be noted that a change in the content of iron(3+) in solution with a maximum on the kinetic dependence is also observed when hydroxide – $\text{Fe}(\text{OH})_3$ and iron(3+) hydroxyoxide – FeOOH are used to precipitate phosphoric acid. Moreover, this also takes place in systems without phosphoric acid. The reason for the decrease in the iron content from the time of hydrothermal treatment in these cases is due to the transition of iron hydroxyoxides to a more stable phase of hematite, which was established by XRD.

3.2 Hydrothermal decomposition of phosphorus-containing solutions of iron nitrates and lanthanides

During nitric acid leaching of Chuktukon ores containing >50% iron hydroxyoxide, at the initial time the iron content in solutions increases to 4-5 g/L, and phosphorus to 2-2.5 g/L (Serdyuk et al., 2017). Also, significant amounts of lanthanides, thorium and uranium are extracted into the solution. The further breaking down process is accompanied by hydrothermal decomposition of iron nitrates to hematite. Such a direction of the process with the reprecipitation of iron(3+) oxides can contribute to a deeper dephosphorization of solutions due to the renewal of the hematite surface and the prevention of passivation of its surface during the formation of a giniite film on the surface. In this case, it is also possible to implement the process of direct precipitation of hydroxyferrophosphate according to reaction (7) without the participation of iron(3+) oxides. In this

regard, the hydrothermal decomposition of iron(3+) nitrates with phosphoric acid in the presence of lanthanide, thorium, and uranium nitrates is considered.

At a temperature of 200 °C, the hydrolysis of iron(3+) nitrate with the formation of hematite proceeds quite rapidly (Fig. 5) and about 95% of all iron passes into the solid phase in 2 hours. This produces an equivalent amount of nitric acid, which in the above example was 1.5 mol/L. The hydrolysis of nitrate is also accompanied by the co-precipitation of phosphoric acid, the extraction of which into the precipitate reaches more than 99%. In the solid phase, hematite and giniite are detected by X-ray diffraction. During decomposition, lanthanum nitrate remains in solution and is not detected in the solid phase.

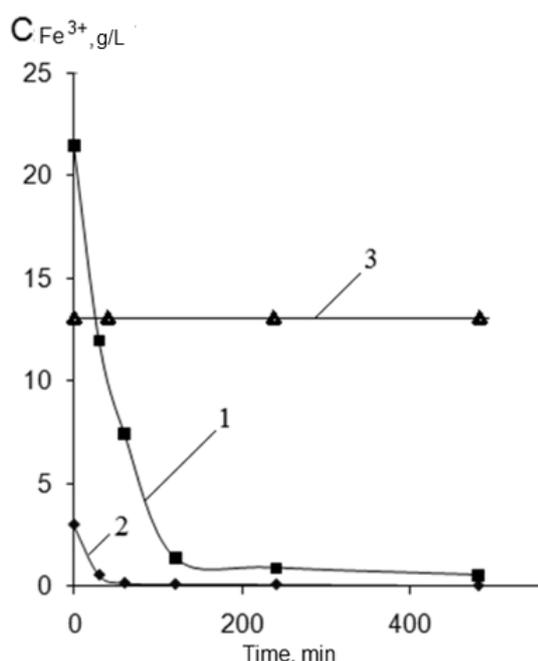


Fig. 5. Dependence of the content of iron (1), phosphorus (2) and lanthanum (3) in solution on the time of hydrothermal decomposition of nitrate solutions. Initial solution: $C_{\text{Fe}(\text{NO}_3)_3} = 0.5 \text{ mol/L}$, $C_{\text{La}(\text{NO}_3)_3} = 0.1 \text{ mol/L}$, $C_{\text{H}_3\text{PO}_4} = 0.1 \text{ mol/L}$; $T = 200 \text{ }^\circ\text{C}$.

The lanthanides of the medium and heavy groups also do not precipitate during the hydrothermal decomposition of iron nitrate in the presence of phosphoric acid. This was established by hydrothermal decomposition of a solution containing iron, lanthanum, dysprosium and ytterbium nitrates at temperatures of 150-210 °C ($\text{Fe}(\text{NO}_3)_3 - 0.05 \text{ mol/L}$; $\text{La}(\text{NO}_3)_3$, $\text{Dy}(\text{NO}_3)_3$ and $\text{Yb}(\text{NO}_3)_3 - 0.01 \text{ mol/L}$ each; $\text{H}_3\text{PO}_4 - 0.03 \text{ mol/L}$). It is shown that at 150 °C nitrate solutions are quite stable for 3 hours. At 180 °C iron nitrate decomposes with the formation of mainly X-ray amorphous products, and an increase in temperature to 210 °C leads to the formation of hematite and giniite phases. Under the conditions of iron hydrolysis and dephosphorization of the solution, all REM remain in solution and are not detected in the solid phase. A study of the decomposition of nitrate solutions of iron and phosphoric acid in the presence of additions of nitrates of

radioactive impurities of thorium and uranium shows that uranyl nitrate remains in solution in a wide range of nitric acid concentrations. Thorium nitrate, when the concentration of nitric acid decreases to 0.5 mol/L, loses its stability and precipitates together with hematite and giniite.

3.3 Nitric acid hydrothermal leaching of the Chuktukon ore with solution dephosphorization

The performed studies have shown that efficient precipitation of phosphoric acid on oxides (hydroxides) of iron(3+) with the formation of giniite can be achieved in a wide range of nitric acid concentrations at temperatures above 180-200 °C. Under these conditions, the process proceeds quite quickly and deeply. An increase in temperature also contributes to the decomposition of monazite and the leaching of REM. When the temperature drops to 150 °C and below, reverse processes are possible, leading not only to an increase in the concentration in the solution of phosphoric acid, but also of iron(3+) due to the dissolution of hematite in nitric acid. This is an undesirable phenomenon for the breaking down of monazite ores and to reduce its negative impact on the technological parameters of the process, it is possible to recommend rapid cooling of the pulp after leaching of REM to freeze heterogeneous reactions.

It was also found that the rate of dephosphorization of solutions can be significantly reduced due to the passivation of the surface of iron oxides due to the formation of giniite films on the surface. On the other hand, the opposite effect of hematite surface renewal is observed during direct hydrothermal decomposition of iron(3+) nitrate with an increase in temperature. This can be used to improve process performance. To do this, a stage of pre-treatment of the pulp at a low temperature (150 °C) is introduced to accumulate iron(3+) in solution, followed by leaching in the operating mode (180-200 °C). The process can also be carried out in a slightly different way, increasing the time for heating the pulp to the operating temperature.

The leaching of the Chuktukon ore with nitric acid in these modes was tested. The breaking down of the ore was carried out with a solution of nitric acid 6 mol/L at a ratio of s:l=1:2. At the first stage, the pulp was heated for 1 hour to 200 °C, then the pulp was stirred for another 2 hours. At the final stage, the reactor was rapidly cooled with water, the pulp was filtered, and the cake was washed with water. The results of hydrothermal breaking down of the Chuktukon ore are given in Table 3.

Table 3

Extraction of REM, thorium and uranium into solution depending on the time of nitric acid leaching of Chuktukon ore (ChTP-3 sample): 6 M HNO₃, s:l=1:2, T= 200 °C, pulp heating time to operating temperature – 1 hour.

Leaching time at 200 °C, hour	0.5	1.0	2.0
Element	Extraction into solution, % (concentration in solution, g/L)		
REM	95.5 (22.7)	96.4 (22.9)	97.4 (23.1)
Th	83.5	81.3	88.9
U	94.0	89.1	87.3
Fe	1.7 (2.9)	1.2 (2.0)	0.9 (1.7)
P	4.8 (0.77)	0.56 (0.091)	0.17 (0.027)

As can be seen from the data obtained, hydrothermal leaching of iron – bearing Chuktukon ores with nitric acid under the selected conditions provides a large depth of extraction of REM and radioactive impurities into the solution, low rates of associated extraction of iron, and deep purification of solutions from phosphoric acid. The proportion of phosphorus to REM in the solution at the end of the leaching process is about 0.1% (weight).

4. Conclusion

Hydrothermal treatment of solutions containing phosphoric and nitric acids in the presence of iron(3+) oxides and hydroxyoxides leads to the sorption of phosphoric acid with the formation of iron(3+) hydroxyphosphate (giniite). The most efficient and fast process can be implemented at temperatures of 180-200 °C and above. The process proceeds according to a complex scheme and provides deep dephosphorization of solutions in a wide range of nitric acid concentrations (1-6 mol/L). By carrying out the direct reaction (precipitation of giniite) and the reverse reaction (its dissolution in nitric acid), it was found that the content of phosphoric acid in the solution as a result can be reduced to 10^{-3} mol/L and below. The process is accompanied by hydrothermal transformations of iron(3+) compounds: in the process, its hydroxide and hydroxyoxides are transformed into hematite, which is more stable in nitric acid, and nitrate salts in solution are also hydrolyzed to form hematite. The hydrolysis of nitrates proceeds by a reversible reaction, and the equilibrium shifts towards the formation of hematite with an increase in temperature. It is shown that the dephosphorization of solutions with the formation of the most stable phosphate compound in the system, giniite, is also achieved by direct hydrothermal decomposition of iron(3+) nitrates in water in the presence of REM, thorium, and uranium nitrates. Under these conditions, solutions are acidified, depending on the content of iron nitrate, while REM and uranium

remain completely in solution. Thorium precipitates when the concentration of nitric acid drops below 0.5 mol/L. Features of the formation of giniite under hydrothermal conditions and the behavior of iron(3+) compounds can be used to improve the efficiency of direct nitric acid stripping of ferruginous monazite ores in order to dephosphorize the obtained productive solutions and reduce the concentration of iron(3+) in them.

CRedit authorship contribution statement

Dmitry V. Kuzmin: Conceptualization, Methodology, Writing - Original Draft. **Natalia V. Gudkova:** Investigation, Writing - Review & Editing. **Marina N. Leskiv:** Methodology, Investigation. **Anna A. Kuzmina:** Investigation, Validation. **Vladimir I. Kuzmin:** Conceptualization, Writing - Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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