Study of the interaction kinetics of apatite ore with nitric acid by independent analytical methods

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Abstract. With the help of ionometric and photometric methods of analysis, the kinetics of the interaction of a low-grade enrichment product of apatite ore with nitric acid was investigated. Presents the results of changes in the concentration of the ion H⁺ and P₂O₅ in the reaction mixture during the reaction. The influence of physicochemical factors on the decomposition rate is shown.

1. Introduction
Apatite and phosphate ores are a source of phosphorus, which is extracted from mineral raw materials by acid extraction methods. The speed of interaction of components in a heterogeneous system depends on many factors: the chemical composition of the ore, hydrodynamic regime, acid concentration, particle dispersion, process temperature, time etc. The kinetics of acid decomposition of phosphate ores of various classes, deposits and genesis [1–4] is also determined by different energy values destruction of their crystal lattices. Therefore, the study of the kinetic regularities of certain types of phosphate ores with mineral acids is of great importance in the development of the scientific basis of the process of extraction of phosphoric acid from mineral raw materials and its implementation in industry. Identifying the factors that have the maximum effect on the kinetics of acid ore breakdown allows you to find effective technologies for its processing.

The relevance of work aimed at studying the kinetics of decomposition of low-quality phosphate raw materials, due to the resulting shortage of high-quality raw materials. This is due to the long-term exploitation of deposits, which leads to their depletion.

Objective: to study the effect of mixing, the initial concentration of nitric acid and temperature on the rate of extraction of phosphorus from poor apatite.

2. Experimental part
The object of the study was a representative sample of poor siliceous apatite ore from the Laokai deposit, containing: 21.23% P₂O₅, 28.08% CaO, 6.03% MgO, 0.98% Fe₂O₃, 1.38% Al₂O₃, 13% SiO₂, 1.5% F. Based on the X-ray diffraction pattern of the Laokai apatite ore, three main phases were identified [5]: phosphate substance with the structure of hydroxyfluoroapatite Ca₅(PO₄)₃(OH)₀.₂F₀.₈, admixture of carbonates with the structure of dolomite CaMg(CO₃)₂ and silicates – α-quartz SiO₂ [6]. We used the ion meter “Econix-Expert-001” (RF) and the spectrophotometer “SPECOL 1500/1” (Germany). The decomposition of apatite was performed with nitric acid with an excess of 40% of stoichiometry.

The decomposition of the phosphate substance and impurities present in the apatite of the Laokai deposit with nitric acid is described by the equations:

\[ \text{Ca}_5(\text{PO}_4)_3\text{F} + 10\text{HNO}_3 = 3\text{H}_3\text{PO}_4 + 5\text{Ca(NO}_3)_2 + \text{HF} \]
\[
\text{CaMg(CO}_3\text{)}_2 + 2\text{HNO}_3 = (\text{Ca, Mg})(\text{NO}_3)_2 + 2\text{CO}_2 \uparrow + \text{H}_2\text{O} \\
\text{SiO}_2 + 4\text{HF} \uparrow = \text{SiF}_4 + 2\text{H}_2\text{O}
\]

Experimental data were obtained by two independent methods. The process of interaction of nitric acid with apatite by the ionometric method was studied directly in the reactor. The analytical concentration of hydrogen ions was determined in 3 s steps. It was previously shown [7] that in the process of nitric acid decomposition of apatite, the potential of the glass electrode depends linearly on the logarithm of the calculated values of the concentrations of hydrogen ions. Consequently, the obtained concentration dependences can be used for the quantitative determination of H⁺ ions in the studied range pH = 1–3. It should be noted that the decomposition process was carried out under conditions of constant ionic strength of the reaction mixture.

In parallel, in the same reactor using the traditional differential photocolorimetric method, the current concentration of extracted phosphorus (in terms of P₂O₅) was determined according to GOST [8] by sampling a volume of 1 ml. For braking the reaction, dilution of the sample with distilled water was used.

When studying the influence of physicochemical factors on the kinetics of decomposition of apatite, they varied: mixing speed in the range of 60–120 turn/min, HNO₃ concentration in the range of 0.05–1.0 M, and temperature in the range of 20–50°C.

Analysis of the kinetic dependences showed that the efficiency of decomposition of apatite increases with increasing mixing and reaches a maximum of 99.9% at a stirrer rotation speed of 120 turn/min (Figure 1).

![Figure 1](image_url)

**Figure 1.** The effect of mixing on the concentration of H⁺ in the resulting suspension (a) and the decomposition coefficient of Laokai apatite (b).
The completeness of decomposition of apatite was evaluated by the value of the decomposition coefficient \( K_p \). The \( K_p \) value of the photometric experiment was calculated as the ratio of the concentration of extracted phosphorus \((P_2O_5)\) to the nitric acid solution to its concentration in apatite (Figure 1a): \( K_p = C(P_2O_5)_{\text{water}}/C(P_2O_5)_{\text{total}} \), and the ionometric experiment – using the ratio of current ion consumption hydrogen to its full consumption for the decomposition of apatite (Figure 1b).

An increase in the initial concentration of nitric acid contributes to an increase in the rate of the process; the maximum value of 0.04 \((\text{mol}/\text{l} \cdot \text{s})\) is achieved when decomposition of apatite with nitric acid with a concentration of 1.0 M. In Figure 2, it can be seen that all the dependences presented have the same character.

![Figure 2](image2.png)

**Figure 2.** The change in the concentration of the \( H^+ \) ion with time at temperatures 20 (1), 30 (2), 40 (3), 45 (4) and 50°C (5); ([HNO₃] = 0.1M; \( \nu = 120 \) tur/min).

Using the graphical method, the order of reaction \((n)\) is determined. It is shown that the approximation of the dependence of concentration on time in the coordinates \(1/C - 1/C_0 = f(\tau)\) is expressed by a straight line, which corresponds to the second order of the reaction (Figure 3).

![Figure 3](image3.png)

**Figure 3.** Determination of the reaction order graphically.

According to the Arrhenius equation, the apparent activation energy is determined: \( E_a = 48.75 \) kJ/mol (Figure 4).
3. Results and discussion

As follows from the results of the kinetic experiment, with an increase in the concentration of nitric acid, there is a reduction in the half-transformation period calculated by the formula $\tau_{1/2} = (kC_0(CaCO_3))^{-1}$ and, as a result, the time to reach complete decomposition (Table 1).

| n | T(K) | lnK[(mol/l)^{-1}s^{-1}] | C_o(mol/l) [H^+] | $\tau_{1/2} = \frac{1}{K \times C_o}$ |
|---|---|---|---|---|
| 2 | 293 | 0.0139 | 0.1 | 719 |
|   | 303 | 0.0246 | 0.1 | 407 |
|   | 313 | 0.0449 | 0.1 | 223 |
|   | 318 | 0.0634 | 0.1 | 158 |
|   | 323 | 0.0912 | 0.1 | 110 |

Comparison of the results of ionometric and photometric analysis indicates their convergence. It is important to note that the half-transformation time obtained by intersecting the experimental kinetic dependences of the ionometric and photometric determinations – 150 s (Figure 5) is consistent with the calculated value $\tau_{1/2} = 158$ s, which indicates the correctness of the data.
Figure 5. Time dependence of the decomposition coefficient of apatite.

At the initial stage of decomposition of apatite, the interaction of carbonate impurities contained in the composition of the ore with nitric acid is intensive. Over time, acid diffusion to phosphate particles becomes the limiting factor. The transition to the diffusion region is due to the formation on the phosphorite particles of a dense shell of a precipitate of SiO$_2$, which in the first stage was destroyed by the liberated CO$_2$, and hardly soluble compounds of iron and aluminum phosphates, which crystallize from a saturated solution. The low temperature coefficient (Table 2) of the decomposition reaction also indicates diffusion inhibition.

Table 2. Temperature coefficient of Van't-Goff.

| T (K) | 293   | 303   | 303   | 313   | 313   | 323   |
|-------|-------|-------|-------|-------|-------|-------|
| lnK([mol/l]$^{1,1}$s$^{-1}$) | 0.0139 | 0.0246 | 0.0246 | 0.0449 | 0.0449 | 0.0912 |

$k_2/k_1 = \gamma^{3/10}$

|   | 1.77 | 1.83 | 2.03 |

4. Conclusion:
The optimal decomposition conditions in the temperature-concentration range studied are nitric acid concentrations of 1.0 M and a temperature of 50°C, with a decomposition coefficient of 99.7% achieved in 1800 s.

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