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POTENTIOMETRIC (ACIDIMETRIC) STUDY OF THE FLUOROAPATITE CONCENTRATE DECOMPOSITION REACTION WITH NITRIC ACID

The ionic equilibrium and kinetics of the fluoroapatite concentrate decomposition reaction with nitric acid were studied by the potentiometric (acidimetric) method. The joint solution of the material balance, electroneutrality and law of active mass equations determined the equilibrium in the reaction mixture for the quantitatively significant ionic and molecular forms. The algorithm of the calculations included the determination of the concentrations with the subsequent recalculation of the activity values of the dissolved forms. The kinetic parameters of decomposition process were determined according to the data of the glass electrode potential change dependence on time. As demonstrated by the results of the conducted measurements, the reaction order of the proton concentration in the interval of initial concentrations of HNO_3 0.05–0.2 $kmol/m^3$ is equal to 1. It was shown that the initial decomposition reaction rate is determined by the diffusion of the proton to the surface of fluoroapatite. This was confirmed by the linear dependence of the decomposition rate on the solid phase particle dispersity value. It was proved that the fluoroapatite decomposition reaction with nitric acid under experimental conditions is limited by H^+ ion transfer to the solid phase surface.

Recently there appears to be noticeable interest in the experimental analysis of the processing of both apatites and phosphorites and detection of the factors influencing the kinetics of the process of lead–acid decomposition. The influence of the nature of the phosphate substance on the rate of decomposition of apatite concentrates was studied by the calorimetric method [1].

In [2,3] it the established that the density change of the nitro–phosphoric filtered solution during process flow is proportional to the quantity of the components of the phosphate raw material. Thus, densimetric analysis of the reaction kinetics is possible.

By applying the conductometric method the authors [4] established the rate of process dependence on time, applying a 30–fold excess of hydrogen nitrate. The purpose of the present research was analysis of the fluoroapatite concentrate decomposition reaction with nitric acid, which included:

1) Determination of the stoichiometry of the reaction depending on the initial concentration of hydrogen nitrate and calculation of the most significant ionic forms in the equilibrium mixture, in terms of quantity;

2) Comparison of the results of the conducted calculations with experimentally measured values of the acidity in the reaction mixture after establishing ionic equilibrium;

3) Potentiometric (acidimetric) analysis of the kinetics of the proton (hydroxonium ion) concentration change during decomposition.

EXPERIMENTAL

The experimental part was performed using an apparatus consisting of a B7–29 voltmeter –

electrometer connected to a PC. The acidity was measured with a glass electrode relative to a saturated chlorine–silver electrode. The analogue electrical signal from the output of the voltmeter – electrometer was transfered as an input of the printed circuit board of an analog–to–digital converter of the PC.

The specifications of the experiments: an input resistance of $>> 1 \cdot 10^{12}$ Ohm, maximum input voltage $\pm$ 2.5V, average error of measurement $\pm$0.0005V, response time of the change of the input voltage – 0.5 seconds. The experimental data was recorded in real time with a controlled sampling step, the time from the beginning of experiment was registered in seconds with an accuracy of 0.01 sec.

The recording process was fully automated and did not require an operator. On expiration of the given time, the system is automatically disconnected with saving of the obtained information on the hard drive. Control of the device is implemented by a specially written program by interaction with the OS of the computer and the input/output ports of an analog–to–digital converter printed circuit board. The program allows the following functions: personal calibration, zero point drift compensation and sensitivity setting of the measuring channel, setting the time frames of the experiment. The experimental pathway is dynamically depicted in graphic form on the screen of the monitor.

Kola fluoroapatite was used which contained the following main components:

P_2O_5 – 39.4%, CaO – 52.0%, MgO – 0.15%,
R_2O_3 – 0.95%, F – 3 .17%

and "chemically pure" nitric acid were used in the experiments.

For analysis of the ionic equilibrium, the fluoroapatite concentrate was dissolved in nitric acid at 343K in excess solid phase for 60 minutes. Then the obtained mixture was cooled to 298K with continuous stirring, and the acidity of the liquid phase was

measured. The results of the conducted measurements at different initial concentrations of hydrogen nitrate are shown in Tab. 1 (experimental pH value).

The kinetics of the lead–acid decomposition of apatite were investigated in the following way. The reactor was filled up with 200 ml of nitric acid solution of given concentration and this solution was maintained at 298K for 15 minutes. After that the program was booted, in which the following parameters were set: time of experiment; time period between measurements 2 sec; range of the input signal and filename. The program was started, and in 8–10 seconds the reactor was filled up with an apatite concentrate sample. The ratio of the nitric acid, taken for decomposition, and the apatite sample corresponded to a stoichiometric relation of the reactants of 20:1. For comparison of the experimental data, identical hydrodynamic conditions were observed: speed of stirring, shape of the reactor and stirrer, volume of the reaction mixture, solid phase sample and particle size. The speed of stirring was chosen so that the particles of the solid phase were in suspension.

For determining the H^+ ion concentration by means of the potentiometric (acidimetric) method, it is necessary that the ionic strength of a reaction mixture be kept constant. In this case only the analytical concentration of the protons is directly proportional to the measured value of its activity [5]. Calculations of the ionic strength (I) of the reaction mixture and the mean ionic activity coefficients ($\gamma\pm$) by the Debye – Huckel equation [6] within the limits of one experiment demonstrate that the g$\pm$ difference at the end of the reaction (I = 0.104 mol/kg, $\gamma\pm$ = 0.773) regarding the initial value (I = 0.092 mol/kg, $\gamma\pm$ = 0.785) is no more than 1.5%. The results of the potentiometric (acidimetric) measurements were reduced to values of the analytical concentrations according to calibration relations. The change of the proton concentration depending on decomposition time at different initial concentrations of nitric acid is shown in Fig. 1. The initial rate of proton concentration change during decomposition as a function of the initial concentrations of nitric acid and the dispersity of fluoroapatite particles is shown in Fig. 2.
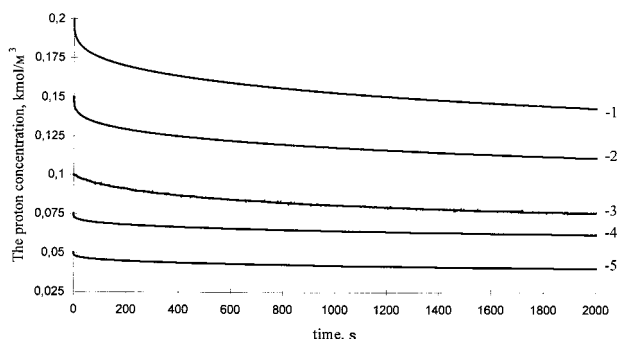

Figure 1. The proton concentration change depending on de-composition time of fluoroapatite concentrate with nitric acid (T = 298 K)
Nitric acid initial concentration: 1 – 0,20 kmol/m³; 2 – 0,15 kmol/m³; 3 – 0,10 kmol/m³; 4 – 0,075 kmol/m³; 5 – 0,05 kmol/m³.
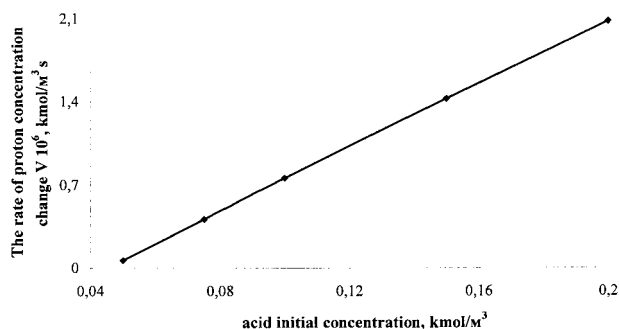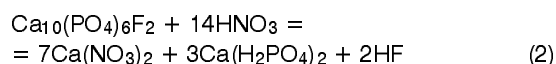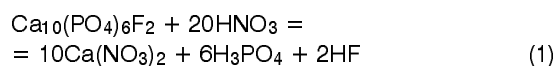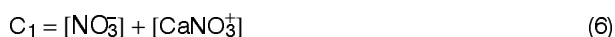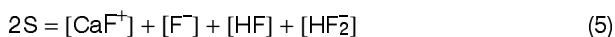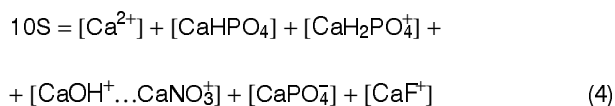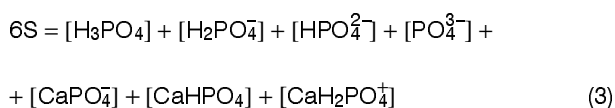

Figure 2. The initial rate of profon concentration change as a function of the initial concentration of nitric acid (T = 298 K)

RESULTS AND DISCUSSION

For quantitative data interpretation the authors [1–4] used equations (1), (2):

$$Ca_{10}(PO_4)_6F_2 + 20HNO_3 =$$
$$= 10Ca(NO_3)_2 + 6H_3PO_4 + 2HF \qquad (1)$$

$$Ca_{10}(PO_4)_6F_2 + 14HNO_3 =$$
$$= 7Ca(NO_3)_2 + 3Ca(H_2PO_4)_2 + 2HF \qquad (2)$$

It was assumed that the decomposition with excess nitric acid proceeds by equation (1) and with deficient acid by equation (2) [7]. However, in the literature there are reliable data on the conditions determining the change of stoichiometry. To answer this problem, a numerical calculation of the ionic and molecular forms present in an equilibrium reaction mixture was performed. According to the reference data [8], all the possible equilibria between the dissolved forms existing in solution were taken into account, as well as the solubility product of sparingly soluble substances. The material balance equations of the phosphate–ion (3), calcium–ion (4), fluorine – ion (5), nitrate – ion (6) and the equation of an electroneutrality (7) are as follows:

$$6S = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] +$$

$$+ [CaPO_4^-] + [CaHPO_4] + [CaH_2PO_4^+] \qquad (3)$$

$$10S = [Ca^{2+}] + [CaHPO_4] + [CaH_2PO_4^+] +$$

$$+ [CaOH^+...CaNO_3^+] + [CaPO_4^-] + [CaF^+] \qquad (4)$$

$$2S = [CaF^+] + [F^-] + [HF] + [HF_2^-] \qquad (5)$$

$$C_1 = [NO_3^-] + [CaNO_3^+] \qquad (6)$$

$$[H^+]+2[Ca^{2+}]+[CaH_2PO_4^+]+[CaOH^+]+[CaF^+]+[CaNO_3^+] =$$

$$= [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [CaPO_4^-] +$$

$$+ [F^-] + [HF_2^-] + [OH^-] + [NO_3^-] \qquad (7)$$
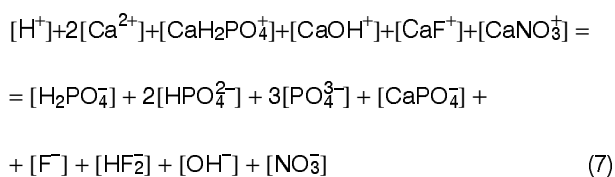
The joint solution of the material balance, electroneutrality and active mass law equations was obtained by numerical methods. The algorithm of the calculations included the definition of the concentrations with the subsequent recalculation of the activities of the dissolved forms for the given initial concentration of nitric acid (C_1) and reacted apatite (S). The average ionic activity coefficients were determined by the Debye – Huckel equation [6]. The criterium of the calculation termination was the achievement of the value of the solubility product of the first of the sparingly soluble substances (least soluble under the given conditions). The results of the calculations are shown in Tab. 1 and 2, data on PO_4^{3-} and $CaOH^+$ ions are absent, as their contents are less than $1 \cdot 10^{-9}$ kmol/m^3 and further decrease with increase of the acidity. As obvious from the obtained data (Tab. 1, 2), with increase of the nitric acid initial concentration, the solubility of fluoroapatite (S) increases and is a linear function of the reaction mixture acidity change. The results of the conducted proton concentration calculations are in good agrement with the experimental data of pH–values of the equilibrium mixtures (Tab. 1). The correlation of the quantity of bound protons (the difference between the initial HNO_3 concentration and the equilibrium proton

concentration) to the quantity of reacted fluoroapatite increases from 10.2 for 0.001 kmol/m^3 of HNO_3 up to 19.8 for 1 kmol/m^3 of HNO_3 (Tab. 1). Thus the value of the stoichiometric relationship of the reactants is a function of the initial concentration of nitric acid. As is obvious from Tab. 1, the decomposition reaction proceeded by equation (1) at acid concentrations greater than 0.5 kmol/m^3 and by equation (2) in the concentration interval 0.005 – 0.01 kmol/m^3 of HNO_3.

Calculations of the kinetic parameters of the process from data of the glass electrode potential change vs. time (Fig. 1) were conducted as follows. The expression for the rate of proton concentration change is:

$$V_{H^+} = -\frac{dC_{H^+}}{dt} \qquad (8)$$

$$V = kC_{H^+}^n \qquad (9)$$

The dependence of the glass electrode potential on the concentration of H^+ ions is expressed by the Nernst equation

$$E_{H^+} = E_{H^+}^0 - B\ln C_{H^+} \qquad (10)$$

When one differentiates equation (10) with time

Table 1. Results of the calculations of the equilibrium forms in the fluoroapatite–nitric acid system

Nitric acid initial concentration, C_0	kmol/m^3	Equilibrium concentrations of ionic and molecular forms, kmol/m^3											
HNO$_3$	Ca^{2+}	F$^-$	HPO$_4^{2-}$	NO$_3^-$	H$_3$PO$_4$	H$_2$PO$_4^-$	CaF$^+$	CaHPO$_4$	HF	CaH$_2$PO$_4^+$	CaNO$_3^+$	H$^+$
0.00	$3.58 \cdot 10^{-5}$	$7.54 \cdot 10^{-6}$	$2.05 \cdot 10^{-5}$	0	$1.00 \cdot 10^{-14}$	$1.53 \cdot 10^{-7}$	$2.90 \cdot 10^{-9}$	$4.16 \cdot 10^{-7}$	$4.75 \cdot 10^{-12}$	$1.38 \cdot 10^{-12}$	0	$4.71 \cdot 10^{-10}$
$1.00 \cdot 10^{-6}$	$3.70 \cdot 10^{-5}$	$7.8 \cdot 10^{-6}$	$2.13 \cdot 10^{-5}$	$1.00 \cdot 10^{-6}$	$1.01 \cdot 10^{-14}$	$1.55 \cdot 10^{-7}$	$2.83 \cdot 10^{-9}$	$4.18 \cdot 10^{-7}$	$4.88 \cdot 10^{-12}$	$1.40 \cdot 10^{-12}$	$6.70 \cdot 10^{-11}$	$4.76 \cdot 10^{-10}$
$1.00 \cdot 10^{-5}$	$4.22 \cdot 10^{-5}$	$8.83 \cdot 10^{-6}$	$2.43 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$	$1.70 \cdot 10^{-14}$	$2.42 \cdot 10^{-7}$	$3.86 \cdot 10^{-9}$	$5.39 \cdot 10^{-7}$	$7.58 \cdot 10^{-12}$	$2.48 \cdot 10^{-12}$	$7.59 \cdot 10^{-10}$	$6.54 \cdot 10^{-10}$
$1.00 \cdot 10^{-4}$	$1.44 \cdot 10^{-4}$	$2.99 \cdot 10^{-5}$	$7.24 \cdot 10^{-5}$	$1.00 \cdot 10^{-4}$	$1.74 \cdot 10^{-11}$	$1.17 \cdot 10^{-5}$	$4.26 \cdot 10^{-8}$	$5.00 \cdot 10^{-6}$	$4.27 \cdot 10^{-10}$	$3.91 \cdot 10^{-8}$	$2.47 \cdot 10^{-8}$	$1.11 \cdot 10^{-8}$
$1.00 \cdot 10^{-3}$	$9.25 \cdot 10^{-4}$	$1.94 \cdot 10^{-4}$	$4.04 \cdot 10^{-4}$	$9.98 \cdot 10^{-4}$	$1.23 \cdot 10^{-6}$	$9.04 \cdot 10^{-4}$	$2.56 \cdot 10^{-6}$	$4.45 \cdot 10^{-7}$	$5.64 \cdot 10^{-5}$	$9.58 \cdot 10^{-6}$	$5.39 \cdot 10^{-6}$	$1.02 \cdot 10^{-4}$
0.01	$1.03 \cdot 10^{-3}$	$2.05 \cdot 10^{-4}$	$1.12 \cdot 10^{-8}$	$9.96 \cdot 10^{-3}$	$6.86 \cdot 10^{-4}$	$1.57 \cdot 10^{-3}$	$3.75 \cdot 10^{-6}$	$3.27 \cdot 10^{-8}$	$6.28 \cdot 10^{-4}$	$9.20 \cdot 10^{-5}$	$4.32 \cdot 10^{-5}$	$3.99 \cdot 10^{-3}$
0.1	0.021	$9.94 \cdot 10^{-5}$	$7.43 \cdot 10^{-9}$	$9.87 \cdot 10^{-2}$	0.01	$2.29 \cdot 10^{-3}$	$7.63 \cdot 10^{-6}$	$1.02 \cdot 10^{-8}$	$4.44 \cdot 10^{-3}$	$4.12 \cdot 10^{-4}$	$1.32 \cdot 10^{-3}$	0.057
1	0.096	$5.76 \cdot 10^{-5}$	$5.46 \cdot 10^{-10}$	$9.56 \cdot 10^{-1}$	0.082	$1.59 \cdot 10^{-3}$	$1.52 \cdot 10^{-5}$	$1.92 \cdot 10^{-9}$	0.028	$9.79 \cdot 10^{-4}$	0.044	0.721

Table 2. Dependence of the fluoroapatite decomposition reaction stoicheometry on the nitric acid initial concentration

Nitric acid initial concentration, C_0 kmol/m^3	$5.00 \cdot 10^{-3}$	$1.00 \cdot 10^{-2}$	$5.00 \cdot 10^{-2}$	$1.00 \cdot 10^{-1}$	$5.00 \cdot 10^{-1}$	1.00
Proton equilibrium concentration, C_{eq}, kmol/m^3	$1.58 \cdot 10^{-3}$	$3.99 \cdot 10^{-3}$	0.026	0.057	0.340	0.721
Quantity of fluoroapatite, S, kmol/m^3	$2.42 \cdot 10^{-4}$	$3.91 \cdot 10^{-4}$	$1.31 \cdot 10^{-3}$	$2.27 \cdot 10^{-3}$	$8.16 \cdot 10^{-3}$	$1.41 \cdot 10^{-2}$
Reaction stoicheometry, $(C_0–C_{eq})/S$, (kmol of HNO$_3$)/(kmol of apatite)	14.3	15.4	18.46	18.9	19.61	19.8
pH calculated value	2.84	2.45	1.68	1.36	0.63	0.29
pH experimental value	2.90	2.49	1.74	1.41	0.64	0.31

$$\frac{dE_{H+}}{dt} = -\frac{B}{C_{H+}}\frac{dC_{H+}}{dt}$$

from which

$$V_{H+} = -\frac{dC_{H+}}{dt} = \frac{C_{H+}}{B}\frac{dE_{H+}}{dt} \tag{11}$$

For the initial decomposition time (at t = 0) equation (11) will be

$$V^0 = C_{H+}^0 \cdot \frac{dE_{H+}}{dt} \tag{12}$$

The true rate of decomposition V^0 at t = 0 was calculated by equation (12) on the basis of measurements of the glass electrode potential vs. experiment time. The experimental data in the interval 0–100 seconds were approximated, and then differentiated by the Savitski–Golai method (program for mathematical data processing TableCurve).

The relation of V^0 to the initial concentration of H^+ ions is shown in Fig. 2. As visible from Fig. 2 the specific rate V^0 depends linearly on C_{H+}. This is possible, in case the order of the reaction of the proton concentration equals 1, and the concentration of the dissolved fluoroapatite near the solid surface remains constant during the reaction. Thus the decomposition reaction of apatite with nitric acid in the interval of initial concentrations 0.05–0.2 kmol/m^3 of HNO_3 obey a first order kinetic equation. If one assumes that the acid goes to the surface of the solid phase at the expense of diffusion, its concentration near the solid surface because of the fast chemical change, practically decreases to zero. In this case the rate of decomposition according to the law of active mass is determined by the strength of the acid in the phase volume

$$V = KC_{H+} \tag{13}$$

The constant K in equation (13) under steady state conditions equals

$$K = FC_{ap}\left(\frac{k\beta}{k+\beta}\right) \tag{14}$$

Such a mechanism will be realized in the case of fluoroapatite dissolution dissociation and subsequent interaction of the reactants in the ionic form. The rate of the ionic processes is rather high [9], then k>>b and it is possible to write equation (14) in the form

$$K = FC_{ap}\beta \tag{15}$$

Thus, the decomposition reaction rate is determined by the diffusion of the proton to the surface of the solid phase. This conclusion is confirmed by the results of the analysis of the solid phase average particle size on the process rate. The true process rate increases with increase of the dispersity of fluoroapatite. Therefore, the fluoroapatite concentrate decomposition reaction

with nitric acid under the conditions of experiment realization is limited by the diffusion of H^+ ions to the surface of the solid phase.

CONCLUSION

Similar experiments conducted at other temperatures, concentrations and nature of the decomposing agent, the specific surfaces of mineral raw materials have shown that the designed technique sufficiently precisely identifies the mechanism of the investigated process, executes the realization of the experiment under the given program, registers the occurrence of the reaction product ionic forms starting with concentrations of $5 \cdot 10^{-5}$ kmol/m^3.

List of symbols

B   – constant
C_{ap} – concentration of the dissolved fluoroapatite near the solid surface
C_{H+} – proton concentration
C_{H+}^0, H^+ – ion initial concentration (t = 0)
C_{eq} – equilibrium concentration of the H^+ ion
C_0 – nitric acid initial concentration
E_{H+}^0 – standard value of the glass electrode potential
F   – diffusive flow area
k   – chemical reaction rate constant
V_{H^+} – specific rate of proton concentration change
V^0 – H^+ ion concentration change rate at t = 0 (true rate)

Greek symbols

β   – diffusion rate constant (value of the diffusion coefficient relation to the diffusive layer thickness)
$\gamma\pm$ – mean ionic activity coefficient

Superscripts

+   – denotes proton
0   – denotes standard or initial value

Subscripts

ap   – related to apatite
eq   – related to equilibrium
H^+ – denotes value related to proton

REFERENCES

[1] Bovikin P.A., Tishkina N.S., Kostjanetc R.B., Savchuk S.N. Chem. Technology. Kiev. No 3 (1988) 43–47.

[2] Tishkina N.S., Parkhomenko V.D., Kostjanetc R.B., Mazupova L.G. Chem. Technology. Kiev, No 1 (1985) 43–47.

[3] Tishkina N.S., Kostjanetc R.B., Bondik I.G. Chem. Technology. Kiev, No 1 (1990) 71–73.

[4] Jambor Y., Beranek Y. Kinetika rozkladu Kola–apatitu kyselinou dusicnou // Chemicky pramysl., 34/59 (1984) No 6, 289–292.

[5] N. Lakshminarayanaiah, Membranes electrodes. Academic Press, New York – San Francisco – London, 1976, p. 358.

[6] Vasiljev V.P. Thermodynamic propeties of solutions of electrolytes: Manual. M., High Scool, 1982, p. 320

[7] Andreev M.V., Brodskij A.A. etc. Technology of phosphoric and complex fertilizers. M., Chemistry, 1987, p. 464

[8] D.Dobos, Electrochemical data, A handbook for electrochemists in industry and universities, Academiai Kiado, Budapest, 1978, p. 364.

[9] Karpov I.K., Shepot'ko M.L., Chernjak A.S. J. Phys. Chemistry, **53** (1979) 2476–2480.

[10] Koldin E.F., Fast reactions in solution. M, A., D.PHIL. Senior Lecturer in Physical Chemistry University of Leeds. 1964, p. 278.

IZVOD

POTENCIOMETRIJSKO (ACIDIMETRIJSKO) ISPITIVANJE REAKCIJE RAZLAGANJA FLUOROAPATITA SA AZOTNOM KISELINOM

(Naučni rad)

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Jonska ravnoteža i kinetika razlaganja koncentrata fluoroapatita sa azotnom kiselinom je proučavana potenciometrijski (acidimetrijski). Rešenje bilansa mase uz zadovoljenje zakona u pogledu postojanja elektroneutralnosti svih prisutnih jonskih vrsta definiše ravnotežni sastav reakcione smeše I koncentracije svih ključnih jona i molekula koji učestvuju u reakciji razlaganja fluoroapatita sa azotnom kiselinom. Postavljeni algoritam za izračunavanje koncentracija ovih komponenata zahteva prethodno, preliminarno izračunavanje uz kasniju korekciju i ponovno izračunavanje aktivnosti svih komponenata u rastvoru. Kinetički parametri procesa razlaganja su određeni prema eksperimentalno utvrđenim vrednostima promene potencijala staklene elektrode sa vremenom trajanja reakcije. Prema dobijenim rezultatima utvrđeno je da je reakcija prvog reda u odnosu na koncentraciju protona u rastvoru kada je koncentracija azotne kiseline od 0,05 do 0,2 kmol/m^3. Utvrđeno je da je početna brzina reakcije određena brzinom difuzije protona do površine fluoroapatita na osnovu linearne zavisnosti brzine od veličine čestica fluoroapatita. Takođe je potvrđeno da brzinu procesa razlaganja fluoroapatita određuje brzina difuzije protona do njegove površine.

Key words: Potentiometry • Acidimetry • Fluoroapatite • Decomposition • Kinetics •
Ključne reči: Potenciometrija • Acidimetrija • Fluoroapatit • Razlaganje • Kinetika •