

**THE EFFECT OF STOICHIOMETRY OF IRON (II) AND (III)
AND MAGNETITE OXIDES ON THE KINETIC REGULARITIES
OF THEIR DISSOLUTION IN ORTHOPHOSPHORIC ACID
CONTAINING Fe (II) AND Fe (III) IONS**

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Abstract

The kinetics of dissolution of iron oxides FeO, α -Fe₂O₃ and Fe₃O₄ in orthophosphoric acid, including those containing additions of Fe (II) and Fe (III) ions (in the form of perchlorates), has been studied. The values of the stationary potential in the magnetite electrode system–solutions of orthophosphoric acid, including those containing additions of Fe (II) and Fe (III) ions are determined. The dissolution of Fe₃O₄ in orthophosphoric acid has been studied and described. Based on the experimental results, it was established that the stimulating and inhibitory effect of Fe (II) and Fe (III) ions is related to their effect on the value of the potential at the boundary of the iron oxide phases/electrolyte solution. The orders of reactions for ions Fe (II), Fe (III) and H₃PO₄ are determined

Keywords

Iron oxides (FeO, α -Fe₂O₃, Fe₃O₄), orthophosphoric acid, kinetics of dissolution, potential at the interface of the oxide/solution phases

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Introduction. The study of the kinetics of dissolution of iron oxides in acidic media, stimulation and inhibition of these processes is of some interest in theoretical terms primarily due to the need of creation models of physical and chemical processes of oxide phase's dissolution. In practical terms, these processes are interesting in relation to the need of removing sediments from heat and power equipment, improving the technology of leaching and beneficiation of ores, etc.

Numerous studies have been carried out and many reviews are devoted to research of the effect of various factors on the dissolution kinetics of iron oxide

phases in acidic electrolyte solutions [1–6], but the question of the stationary potential influence on the dissolution rate remains controversial even at present.

The purpose of the work is the research and explanation of the effect of ions Fe (II) and Fe (III) on the dissolution of iron oxides (FeO, α -Fe₂O₃, Fe₃O₄) in orthophosphoric acid H₃PO₄.

Materials and methods. Iron oxides were used during studying the kinetic processes: iron (II) oxide (wustite) FeO (*p.a.*); iron oxide (III) α -Fe₂O₃ (*p.a.*); magnetite Fe₃O₄ (*puriss.*). The phase of powdered oxides FeO, Fe₂O₃ and Fe₃O₄ with a particle size of 80–100 μ m was chosen in the kinetic studies. The working electrolyte was a solution of orthophosphoric acid (*puriss.*). Samples were identified by X-ray phase analysis.

Iron oxide weighing 0.100 g was placed in a thermostatic cell (heating block TC-16), in which there was a solution of phosphoric acid with a volume of 0.500 ± 0.005 L. In a few experiments, a solution of orthophosphoric acid, H₃PO₄, also contained Fe (II) and Fe (III) ions (in the form of perchlorates). Perchlorate ions have no significant effect on the kinetics of iron oxides dissolution [4, 6].

Experimental kinetic dissolution curves were obtained at a temperature of 313 K. The dissolution of the oxide phases was carried out in the mode of mechanical mixing of a water-dispersed mixture with a magnetic stirrer with a rotation frequency of 600–700 min^{-1} , since this dissolution mode eliminated diffusion difficulties. A portion of the solution was periodically taken from the reaction vessel and the total concentration of Fe (II) ions (Fe (III) ions were preliminarily reduced with hydroxylamine) [7] was determined by a photocolometric method (on a KFK-3-01 photometer) using *o*-phenanthroline reagent. The primary analysis of the kinetic data was performed in the coordinates “the proportion of the dissolved oxide α –time t ”. The fraction of dissolved oxide α was calculated using the equation $\alpha = A/A_{\infty}$, where A and A_{∞} were the optical densities of the filtrate solution at time t and with complete dissolution of the iron oxide phase, respectively.

The magnetite electrode, manufactured according to the method described in Ref. [8], was used for the study of the electrochemical features. A saturated KCl-AgCl electrode served as a reference electrode (the potential relative to a normal hydrogen electrode at a temperature of 20 °C was $0,201 \pm 3$ V). The potential was measured in a standard electrochemical cell at a temperature of $22 \pm 0,5$ °C in solutions of orthophosphoric acid, including containing additives of Fe (II) and Fe (III) ions (in the form of perchlorates).

Table 1

The basic equations of heterogeneous kinetics

Equation	Differential form	Integral form	The dependence of the proportion of α from the given time $t/t_{0,5}$
First order	$d\alpha/dt = W(1-\alpha)$	$-\ln(1-\alpha) = Wt$	$\alpha = 1 - e^{-0.693(t/t_{0,5})}$
Shrinking sphere	$d\alpha/dt = dW(1-\alpha)^{(d-1)/d}$	$\alpha = 1 - [1 - (Wt)^d]^d$	$\alpha = 1 - [1 - 0.206(t/t_{0,5})^3]^3$
Proutt — Tomkins	$d\alpha/dt = W(1-\alpha)\alpha$	$\ln(\alpha/(1-\alpha)) = Wt + B$	—
Yerofeyev — Avraami	$\frac{d\alpha}{dt} = W(1-\alpha) [-\ln(1-\alpha)]^{n-1/n} = W(1-\alpha)^b \alpha^a$	$-\ln(1-\alpha) = Wt^n$	$\alpha = 1 - e^{-0.693(t/t_{0,5})^n}$
Delmon — Hill	$\frac{d\alpha}{dt} = W(1-\alpha)\sqrt{A^2 + \ln(1-\alpha)} = W(1-\alpha)a^n$	$-\ln(1-\alpha) = AshWt$	$\alpha = 1 - e^{-Ash[t/t_{0,5} \operatorname{arsh}(0.693/A)]}$

Comment: $t_{0,5}$ is time of dissolution of half the amount of oxide phase.

The results and discussion. *The effect of orthophosphoric acid concentration on the dissolution rate of iron oxides FeO, α -Fe₂O₃ and Fe₃O₄.* The effect of orthophosphoric acid concentration on the dissolution of iron oxides was studied. Experimental data are presented in Fig. 1, 2 in α - t coordinates.

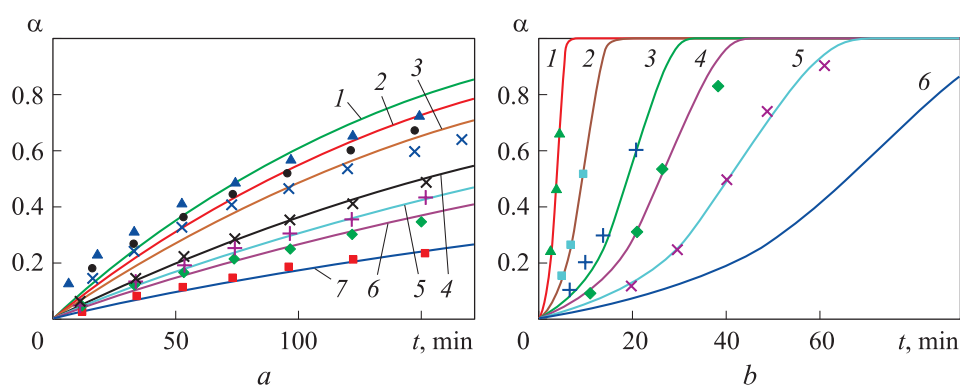


Fig. 1. The dependences of the proportion of dissolved oxide α on time t . *a* for hematite dissolved in orthophosphoric acid (curve 1 for concentration 6.67 mol/L; curve 2 for concentration 5.00 mol/L; curve 3 for concentration 4.00 mol/L; curve 4 for concentration 3.33 mol/L, curve 5 for concentration 2.83 mol/L; curve 6 for concentration 2.33 mol/L; curve 7 for concentration 1.67 mol/L). *b* for magnetite dissolved in orthophosphoric acid (curve 1 for concentration 6.67 mol/L; curve 2 for concentration 4.17 mol/L; curve 3 for concentration 2.83 mol/L; curve 4 for concentration 2.33 mol/L; curve 5 for concentration 2.00 mol/L; curve 6 for concentration 1.67 mol/L)

The intensities of the dissolution processes of the iron oxide phases increase with increasing concentration of orthophosphoric acid. A decrease in dissolution is observed in the series of oxides $\text{FeO} > \text{Fe}_3\text{O}_4 > \alpha\text{-Fe}_2\text{O}_3$. The points in the figures represent the experimental data, the lines represent the graphic representation of the Delmon — Hill equation given in the Table 1.

The effect of Fe (II) and Fe (III) ions (in the form of perchlorates) on the kinetic regularities of dissolution of iron oxides $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 in solutions of phosphoric acid. The influence of Fe (II) and Fe (III) on the dissolution kinetics of $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 was studied. The nature of the kinetic curves remains unchanged with the introduction of salts of Fe (II) and Fe (III), and the dissolution rate increases with an increase in their concentration in the solution, in the case of adding Fe (II) and decreases with the addition of Fe (III). These patterns are illustrated in Fig. 2, 3. The points on the figures represent the experimental data and the lines represent the graphical representation of the Delmont — Hill equation (see Table 1).

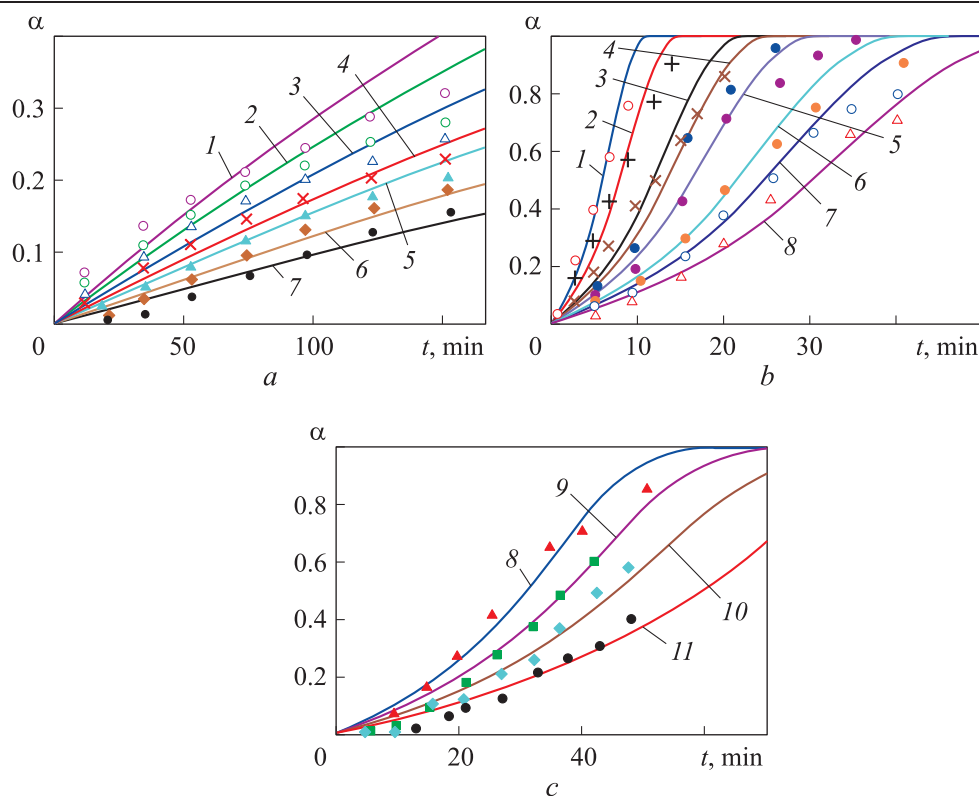
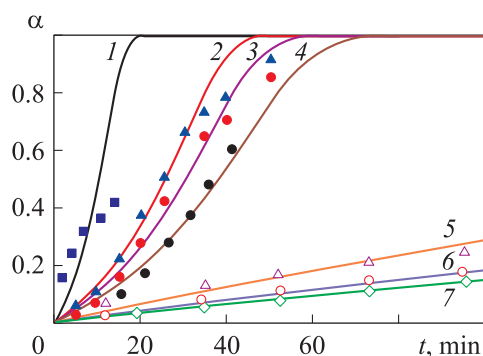


Fig. 2. The dependences of the dissolved hematite (*a*, *b*) and magnetite (*c*) fractions α on time t in phosphoric acid. *a* concentrations 1,67 mol/L with Fe (II) ions addition (curve 1 for concentration $4.48 \cdot 10^{-5}$ mol/L; curve 2 for concentration $1.80 \cdot 10^{-5}$ mol/L; curve 3 for concentration $8.95 \cdot 10^{-6}$ mol/L; curve 4 for concentration 0) and Fe (III) ions (curve 5 for concentration $8.95 \cdot 10^{-6}$ mol/L; curve 6 for concentration $1.80 \cdot 10^{-5}$ mol/L; curve 7 for concentration $4.48 \cdot 10^{-5}$ mol/L). *b* concentration 2.33 mol/L with Fe (II) ions addition (curve 1 for concentration $2.24 \cdot 10^{-2}$ mol/L; curve 2 for concentration $4.48 \cdot 10^{-3}$ mol/L; curve 3 for concentration $4.48 \cdot 10^{-4}$ mol/L; curve 4 for concentration $1.43 \cdot 10^{-4}$ mol/L; curve 5 for concentration $7.16 \cdot 10^{-5}$ mol/L; curve 6 for concentration $1.43 \cdot 10^{-5}$ mol/L; curve 7 for concentration $1.43 \cdot 10^{-6}$ mol/L; curve 8 for concentration 0). *c* 2.33 mol/L with Fe (III) ions addition (curve 8 for concentration 0; curve 9 for concentration $8.95 \cdot 10^{-6}$ mol/L; curve 10 for concentration $1.79 \cdot 10^{-5}$ mol/L; curve 11 for concentration $4.48 \cdot 10^{-5}$ mol/L)

The experimental data shown in Fig. 3, detail the effect of Fe (II), Fe (III) ions and orthophosphoric acid H_3PO_4 on the dissolution rate of the oxide phases of iron FeO , $\alpha-Fe_2O_3$, Fe_3O_4 .

Analysis of kinetic curves using affine transformations and the choice of a mathematical model of their dissolution in orthophosphoric acid, including ones containing Fe (II) and Fe (III) ions (in the form of perchlorates). An analysis

Fig. 3. The dependence of the fraction of dissolved iron oxides (curve 1 for FeO; curve 3 for Fe₃O₄; curve 6 for α-Fe₂O₃) α from time *t* in phosphoric acid H₃PO₄ (curves 1, 6 for concentration 1.67 mol/L; curve 3 for concentration 2.33 mol/L); with the addition of Fe (II) (curve 2 for Fe₃O₄; curve 5 for α-Fe₂O₃) ions and Fe (III) ions (curve 4 for Fe₃O₄; curve 7 for α-Fe₂O₃)



of the kinetic data in the $\alpha-t/t_{0.5}$ coordinates showed that the dissolution mechanism FeO, Fe₃O₄ and α-Fe₂O₃ oxides in orthophosphoric acid H₃PO₄, also including one containing Fe (II) and Fe (III) ions [9–14], is the same. The results of the analysis on the magnetite example are shown at Fig. 4.

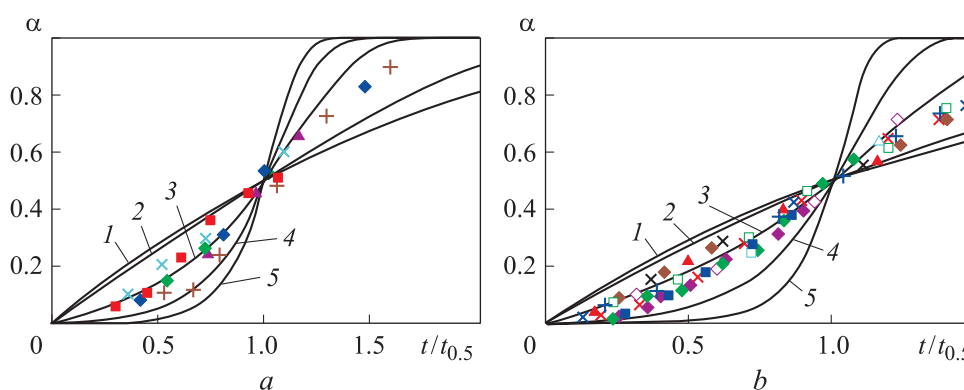


Fig. 4. The dependence of the fraction of dissolved oxide α on the reduced time $t/t_{0.5}$ for magnetite. *a* in phosphoric acid at different values of the constant *A* (curve 1 for *A* = 1; curve 2 for *A* = 0.5; curve 3 for *A* = 0.07; curve 4 for *A* = 0.01; curve 5 for *A* = 0.001). *b* in orthophosphoric acid 2.33 mol/L with the addition of ions of Fe (II) and Fe (III) and with different values of the constant *A* (curve 1 for *A* = 10; curve 2 for *A* = 1; curve 3 for *A* = 0.14; curve 4 for *A* = 0.01; curve 5 for *A* = 0.001)

In this case, the dissolution rate of oxides can be represented as a function with separable variables: $d\alpha / dt = Wf(\alpha)$, where $f(\alpha)$ is a function characterizing the change in the oxide surface in time; W is the specific dissolution rate, depending on the studied parameters [9–14]. The equations of heterogeneous kinetics are used for calculation the W rate of iron oxides dissolution in acids (see Table 1).

A comparison of experimental data on the kinetics of iron oxides dissolution (see Fig. 1–4) with a graphical solution of the Delmon — Hill equation

(see Table 1) using the Fisher criterion shows good conformity. In addition, the model described by the Delmon — Hill equation suggests the presence of active dissolution centers on the surface of the solid phase, which is a confirmed fact [1–6].

The orders of the specific dissolution rate of the oxide phases of iron in the Fe (II), Fe (III) ions and in phosphoric acid H_3PO_4 . The dependence of $\lg W$ on the logarithm of the concentration of the ions of Fe (II), Fe (III) and orthophosphoric acid was used at determining the reaction order for these ions and H_3PO_4 . The effective order of W in orthophosphoric acid for $\alpha\text{-Fe}_2\text{O}_3$ и Fe_3O_4 is 1.6 ± 0.3 ; for Fe (II) ions 0.25 ± 0.1 and 0.25 ± 0.1 for Fe (III) ions.

The mechanism of magnetite dissolution in orthophosphoric acid. The data obtained by X-ray phase analysis (Fig. 5) in the study of the composition of the oxide phase of iron — magnetite in the process of dissolution in media containing acids, including phosphoric acid, allow for the conclusion that the composition of the oxide phase undergoes changes according to the scheme

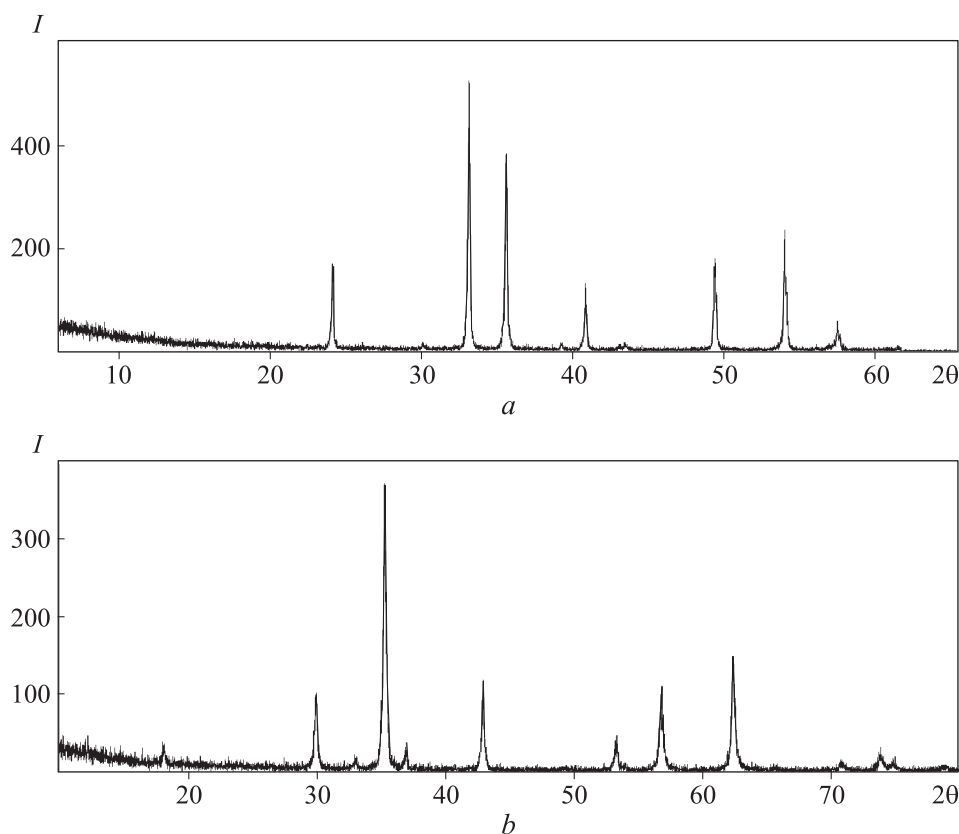


Fig. 5 (part 1). The results of X-ray phase analysis of hematite (a), magnetite (b)

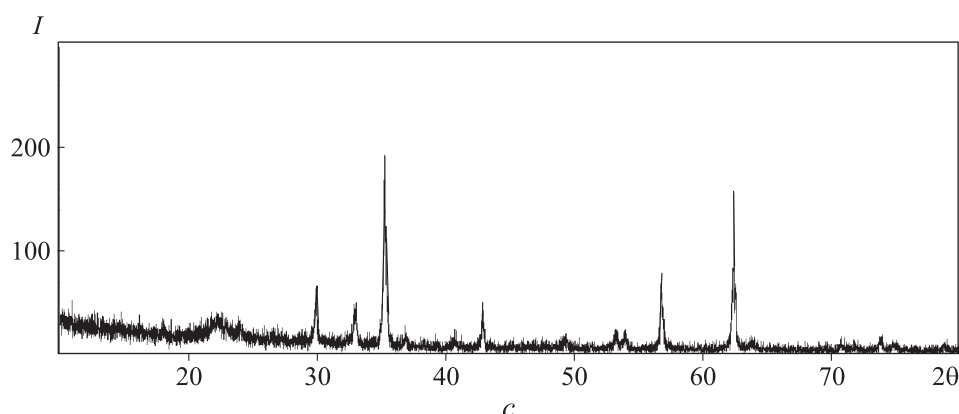


Fig. 5 (part 2). The results of X-ray phase analysis of hematite magnetite aged in orthophosphoric acid (~ 45 min) at a temperature of about 313 K (c)

Potential at the phase boundary of magnetite/orthophosphoric acid solution, also including ones containing Fe (II) and Fe (III) ions (in the form of perchlorates). The results describing the influence of the iron oxides character on the specific rates of their dissolution in orthophosphoric acid are explained by the presence (absence) of ions of Fe (II) and Fe (III) in oxide phases. The regularities are associated with the different effects of these types of ions on the value of the potential at the interface of iron oxide/electrolyte solution (Table 2) [15].

Table 2

The values of the potential (mV) depending on the concentration of orthophosphoric acid, including ones with the addition of Fe (II) and Fe (III) on the magnetite electrode relative to the KCl-AgCl electrode

Solution	Acid concentration, mol/L			
	0.5	2.5	3.5	5.0
Orthophosphoric acid	375	307	288	274
Orthophosphoric acid, add. Fe (II), 0.004 mol/L	291	280	276	266
Orthophosphoric acid, add. Fe (II), 0.002 mol/L	295	284	278	268
Orthophosphoric acid, add. Fe (III), 0.0017 mol/L	404	324	303	285
Orthophosphoric acid, add. Fe (III), 0.017 mol/L	426	363	326	295

Conclusion. Analysis of the kinetic data showed that the mechanism of iron oxides dissolution in orthophosphoric acid, including those containing the addition of Fe (II) and Fe (III) ions, is identical. The dissolution rate increases with an increase in the concentration of orthophosphoric acid H_3PO_4 , Fe (II) ions, and decreases in the case of Fe (III) addition.

It was established during the study of the iron oxides dissolution in solutions of orthophosphoric acid, including those containing additives of Fe (II) and Fe (III) ions, that the dissolution rate of iron oxide phases has been described by the equation

$$W = W_0[\text{Fe}^{2+}]^{0.25}[\text{Fe}^{3+}]^{-0.25}[\text{H}_3\text{PO}_4]^{1.6} \exp\left(-\frac{(1-\beta_+)z_+F}{RT}E\right),$$

where W_0 is the specific coefficient of dissolution rate; z_+ is the atomic number of the cation; $F = 96485.3$ C/mol is the Faraday constant; $R = 8.314$ J/(mol · K) is the ideal gas constant; T is temperature, K; E is activation energy.

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