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Andriy Kontsevoy

DEVELOPMENT OF A KINETIC MODEL OF MAGNETITE LEACHING

The object of the research is the process of magnetite leaching with nitric acid solutions, and the subject of the research is the mathematical justification of the kinetic model and the calculation of kinetic parameters.

The article considers the case of leaching in the kinetic region, while magnetite is considered as a polydispersity material of spherical shape. It is proposed to use the distribution function of the number of particles N by their radius r in the form $N=a\cdot r^b$, where a and b are constants. This distribution was used to derive the equation for the rate of the process W, taking into account the change in the surface of the particles depending on the degree of leaching α: $W=d\alpha/d\tau=K^*\cdot(1-\alpha)^m\cdot((C_0(\gamma-\alpha)/\gamma))^n$, where K^* is the rate constant; m and n are the order of solid material and nitric acid, respectively; C_0 and γ are the initial concentration of nitric acid and its stoichiometric excess. The order m is defined as $m=(b+2)/(b+3)$, at $b\to\infty$ the order $m\to1$. When $b=0$, $m=2/3$ is the case of the equation for a shrinking sphere. An algorithm for calculating kinetic parameters in the Excel is proposed. Experimental dependences of the degree of transformation α on time τ are approximated by a third-order equation; by differentiating the obtained equation, the values of the velocity $W_{exp}=d\alpha/d\tau$ at individual points are calculated. After the logarithm of the above equation, there is the expression (γ=1): $\ln(W_{exp})=\ln(K^*)+m\cdot\ln(1-\alpha)+n\cdot\ln(C_0(1-\alpha))$.

With the help of the «LINEST» function in Excel, for a temperature of 373 K, the values of the order of $m=0.93$ and $n=1.29$ and the rate constant $K^*=0.08$ were obtained. Calculation of kinetic parameters for different temperatures takes into account the dependence of the rate constant on temperature: $\ln(W_{exp})=\ln k_0-E/R\times\times1/T+m\cdot\ln(1-\alpha)+n\cdot\ln(C_0(1-\alpha))$.

As a result of the calculations, the values $n=0.83$; $m=1.2$; $E/R=-10402$; $\ln k_0=25.09$ were obtained. The value of the multiplier $k_0=\exp(\ln k_0)=7.88\cdot10^{10}$, the activation energy $E=-8.31\cdot E/R=86440$ J/mol, the total reaction order $n+m=2.03$ was calculated. The obtained kinetic parameters were used to determine the calculated values of the rate W. The average relative error between the experimental and calculated values of the leaching rates is 10 %. The proposed method of processing experimental data using a mathematical leaching model can be used for any leaching process.

Keywords: *leaching, magnetite, distribution function of the number of particles by radius, kinetic equation, reaction order, activation energy.*

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1. Introduction

Leaching – extraction of one or more components from solid bodies (ores, concentrates, intermediate products, production waste) with an aqueous solution containing alkali, acid or other reagent. Usually, leaching is accompanied by a chemical reaction, as a result of which the extracted component changes from a water-insoluble form to a soluble one. At the end of leaching, in contrast to dissolution, a solid phase always remains, that is, the degree of leaching is less than 100 %. As a rule, crushed material of different granulometric composition is received for leaching. In the process of leaching, the surface of such material changes, which, together with a decrease in the concentration of reagents and the accumulation of products, leads to a decrease in the rate of leaching.

If the leaching reaction is irreversible and is not accompanied by the formation of a shell of a solid product, the leaching rate W can be expressed by the equation:

$$W=-dG/d\tau=K\cdot C^n\cdot S, \quad (1)$$

where G is the mass of the solid phase; τ is the reaction time; K is the rate constant; C is the reagent concentration; n is the order of the reagent; S is the surface of the solid phase.

The value of the surface depends on the shape of the particles (sphere, cube, plate and needle) of the monodisperse material. In practice, it is often necessary to deal with polydisperse materials with a wide range of particle sizes, while in the process of dissolution, not only the surface of the particles changes, but also their number, since small fractions first dissolve and disappear.

Much and constant attention is paid to the leaching process in the scientific literature [1–3]. From the array of various information, it is possible to conditionally single out works devoted to the course of leaching in the diffusion region [4–7] with the provision of the corresponding kinetic equations. There are also works [8–10] in which the authors note the course of leaching in the kinetic region. The authors of [11] processed the data according to 18 kinetic equations that reflect various mechanisms on a solid material, but do not take into account the influence of the concentration of the solvent. The analysis of these and other literary sources indicates the absence of a universal approach to the kinetics of the leaching process, which takes place in the kinetic region.

Thus, the process of magnetite leaching with nitric acid solutions was chosen as *the research object*, and the mathematical substantiation of the kinetic model and the calculation of the kinetic parameters were *the subject of the research*. The work is given relevance by the use of the function of the distribution of the number of spherical particles of a solid material by their radius to determine the change in the surface of a solid material during the leaching process. Therefore, *the aim of research* is to substantiate the mathematical model of the leaching process and to develop an algorithm for determining the kinetic parameters of the leaching of polydisperse particles based on experimental data.

2. Materials and Methods

The analysis of equation (1) shows that it is enough to simply take into account the change in the concentration of C of the solvent, and the change in the process of leaching the surface of the solid material is proposed to be carried out as follows.

At the initial mass of the solid phase G_0 at the moment of reaching mass G, the degree of leaching α is equal to:

$$\alpha=(G_0-G)/G_0=1-G/G_0,$$

$$\text{whence } G=G_0(1-\alpha) \text{ and } dG=-G_0 d\alpha. \quad (2)$$

At the initial concentration of the liquid reagent C_0, the current concentration is determined as:

$$C=C_0\cdot(\gamma-\alpha)/\gamma, \quad (3)$$

where γ is the excess (shortage) of the reagent against stoichiometry; with the stoichiometric ratio $\gamma=1$.

Taking into account expressions (2) and (3), equation (1) takes the form:

$$W=d\alpha/d\tau=K\cdot S\cdot((C_0(\gamma-\alpha)/\gamma))^n/G_0. \quad (4)$$

To establish the functional dependence between the size of the surface S and the degree of leaching, let's assume the spherical shape of solid particles, the surface of which decreases due to the reduction of their radius r and the number of particles N.

In general, the distribution function can be expressed by the equation:

$$N=a\cdot r^b, \quad (5)$$

where a and b are constants.

If $b=0$, then $N=a=\text{const}$, the function is represented by a point and all particles have the same initial radius r_0. If $0<b<1$, then the function (5) is expressed by a convex curve, when $b>1$ – by a concave curve. If $b=1$, then the number of particles depends linearly on their radius.

Therefore, if the number of particles with a radius of r_0 and less is expressed by the function (5), then the number of particles with a radius from r to $r+dr$ is equal to:

$$dN=a\cdot b\cdot r^{b-1}\cdot dr. \quad (6)$$

The mass of particles with a radius in the interval from r to $r+dr$ is equal to:

$$dG=(4/3)\cdot\pi\cdot r^3\cdot\rho\cdot dN=(4/3)\cdot\pi\cdot r^{(b+2)}\cdot\rho\cdot a\cdot b\cdot dr, \quad (7)$$

where ρ is the density of the solid material. The total mass of particles in the limits of integration over r from 0 to r is equal to:

$$G=(4/3)\cdot\pi\cdot\rho\cdot a\cdot b\cdot\int r^{(b+2)}dr=(4/3)\cdot\pi\cdot\rho\cdot a\cdot b\cdot r^{(b+3)}/(b+3). \quad (8)$$

The initial mass of particles in the limits of integration over r from 0 to r_0 is equal to:

$$G_0=(4/3)\cdot\pi\cdot\rho\cdot a\cdot b\cdot\int r^{(b+2)}dr=$$

$$=(4/3)\cdot\pi\cdot\rho\cdot a\cdot b\cdot r_0^{(b+3)}/(b+3). \quad (9)$$

These formulas are valid for all values of b except $b=0$, since in this case the function (5) has a discontinuity and the total mass of the particles is equal to:

$$G=(4/3)\cdot\pi\cdot\rho\cdot a\cdot r^3.$$

Taking into account expressions (8) and (9), the degree of leaching can be expressed in terms of particle radius:

$$\alpha=(G_0-G)/G_0=(r_0^{b+3}-r^{b+3})/r_0^{b+3}=1-r^{b+3}/r_0^{b+3}. \quad (10)$$

From equation (10), let's obtain the dependence of the radius of the particles on the degree of leaching:

$$r=r_0(1-\alpha)^{1/(b+3)}. \quad (11)$$

The surface of particles with a radius in the interval from r to $r+dr$, taking into account expression (6), is equal to:

$$dS=4\cdot\pi\cdot r^2\cdot dN=4\cdot\pi\cdot r^{b+1}a\cdot b\cdot dr.$$

The total surface of all particles in the limits of integration over r from 0 to r:

$$S=4\cdot\pi\cdot a\cdot b\cdot\int r^{b+1}dr=4\cdot\pi\cdot a\cdot b\cdot r^{b+2}/(b+2). \quad (12)$$

This formula, like formula (9), is valid for all values of b, except $b=0$. For $b=0$, the outer surface of the spherical particles is equal to:

$$S=4\cdot\pi\cdot a\cdot r^2.$$

Taking into account expression (11), the total surface of all particles:

$$S=4\cdot\pi\cdot a\cdot b\cdot r_0^{b+2}(1-\alpha)^{(b+2)/b+3)}/(b+2). \quad (13)$$

After substituting the initial mass of particles according to equation (9) and the total surface of all particles according to equation (13) into equation (4), let's get the leaching rate equation:

$$W=d\alpha/d\tau=K^{*}((C_0(\gamma-\alpha)/\gamma))^{n}(1-\alpha)^{m}, \quad (14)$$

where $K^{*}=3\cdot K\cdot(b+3)/((\rho\cdot(b+2)\cdot r_0))$, $m=(b+2)/(b+3)$.

Let's note that when $b\to\infty$, the order in the solid material is $m\to1$. When $b=0$, $m=2/3$ is the case of the shrinking sphere equation. Therefore, the order of the solid material for polydisperse spherical particles can vary from 2/3 to 1.

With a stoichiometric ratio of liquid and solid $\gamma=1$, equation (14) is simplified:

$$W=d\alpha/d\tau=K^{*}((C_0(1-\alpha))^{n}(1-\alpha)^{m}). \quad (15)$$

3. Results and Discussion

The reaction of magnetite leaching, as a production waste (the main component of the spent CO steam conversion catalyst), is as follows:

$$3FeO\cdot Fe_2O_3+28HNO_3=9Fe(NO_3)_3+NO+14H_2O.$$

Table 1 shows the dependence of the degree of leaching α on time τ, temperature T and the initial concentration of nitric acid C_0, taken in a stoichiometric amount ($\gamma=1$). The data are obtained for the kinetic region of the process at 700 revolutions of the stirrer per minute, which corresponds to the turbulent regime, and the average particle size is 0.2 mm.

Table 1

Output and calculation data

T=373 K				T=363 K			
C_0, fraction	τ, min	α	W_{exp}	C_0, fraction	τ, min	α	W_{exp}
0.2	20	0.31	0.0076	0.2	20	0.14	0.0049
	30	0.38	0.0063		30	0.19	0.0048
	60	0.52	0.0035		60	0.32	0.0038
	80	0.58	0.0025		80	0.39	0.0026
	90	0.60	0.0023		90	0.41	0.0019
	120	0.67	–		120	0.43	–
0.3	20	0.36	0.0098	0.3	20	0.28	0.0054
	30	0.45	0.008		30	0.33	0.0049
	60	0.62	0.0038		60	0.46	0.0036
	80	0.68	0.0022		80	0.52	0.0029
	90	0.70	0.0017		90	0.55	0.0026
	120	0.75	–		120	0.61	–
0.4	20	0.45	0.0078	0.4	20	0.22	0.0066
	30	0.52	0.0065		30	0.28	0.0059
	60	0.67	0.0035		60	0.43	0.0041
	80	0.72	0.002		80	0.50	0.0031
	90	0.74	0.0014		90	0.53	0.0027
	120	0.76	–		120	0.6	–

Below is the algorithm for calculating kinetic parameters and its implementation in the Excel:

1. A diagram of the dependence of the degree of transformation α on time τ *was constructed for 6 curves (6 points for each curve) and each curve was* approximated by a third-order equation:

$$\alpha=z_1\cdot\tau^3+z_2\cdot\tau^2+z_3\cdot\tau+z_4,$$

where z_1, z_2, z_3, z_4 are coefficients of the approximation equation.

So, for the first curve (T=373 K, C_0=0.2), the equation was obtained:

$$\alpha=0.00000031\cdot\tau^3-0.00008919\cdot\tau^2+$$
$$+0.01080896\cdot\tau+0.12725881.$$

The coefficients of the equation must be issued with a digit of at least 8 (significant difference in time values and degree of conversion). To do this, mark the resulting equation on the diagram, press the right mouse button and select *Format cells – number – decimal places* – set to 8.

2. The reaction rate was calculated (the results are given in Table 1) for 6 points of each curve at the corresponding residence time t. For the first curve:

$$W_{exp}=d\alpha/d\tau=3\cdot z_1\cdot\tau^2+2\cdot z_2\cdot\tau+z_3=$$
$$=3\cdot0.00000031\cdot\tau^2-2\cdot0.00008919\cdot\tau+0.01080896.$$

The value of the speed at the last point increases compared to the previous one, and therefore, to increase the accuracy of the calculation, the last point was discarded and further calculations were carried out for the first 5 points.

3. Calculation of kinetic parameters for a specific temperature involves the logarithmization of equation (15):

$$\ln(W_{exp})=\ln(K^{*})+n\cdot\ln(C_0(1-\alpha))+m\cdot\ln(1-\alpha). \quad (16)$$

The spreadsheet is supplemented with appropriate cells in which the logarithm of the components of equation (16) is calculated, except for the unknown constant K^*. For further calculations, the «LINEST» function was used. Thus, for a temperature of 373 K, values of the order of m=0.93 and n=1.29 and the rate constant K^*=0.08 were obtained.

4. The calculation of kinetic parameters for different temperatures is carried out according to the following equation, which takes into account the effect of temperature on the rate constant:

$$\ln(W_{exp})=\ln k_0-E/R\cdot1/T+n\cdot\ln(C_0(1-\alpha))+$$
$$+m\cdot\ln(1-\alpha). \quad (17)$$

Thus, let's get an array of 30 horizontal cells and 4 vertical cells – three variable parameters $1/T$, $\ln(C_0(1-x))$, $\ln(1-x)$ and the function $\ln(W_{exp})$.

For further calculations, the «LINEST» function was used. As a result of the calculations, the values n=0.83 were obtained; m=1.2; E/R=–10402; $\ln k_0$=25.09. The value of the pre-exponential factor is calculated by software as: $k_0=exp(\ln k_0)$=7.88·1010, activation energy E=–8.31E/R=86440, total reaction order $n+m$=2.03. The obtained kinetic parameters were used to determine the calculated values of the W rate, after which the average relative error between the experimental W_{exp} and calculated W values of the leaching rates was determined, which is 10 %.

Therefore, the proposed algorithm for processing experimental data can be used to determine the kinetic parameters of any leaching processes occurring in the kinetic region.

4. Conclusions

It is proposed to take into account the function of the distribution of spherical particles of solid material according to their size, and the equation of the rate of the process in the kinetic region of the leaching course is mathematically substantiated. An algorithm for processing experimental data is proposed, which can be used for processing any leaching data. Close to the first order for magnetite and nitric acid and the total second order of the kinetic equation, as well as the activation energy, were determined. The relative deviation of the experimental and calculated data on the leaching rate is 10 % and indicates the complete possibility of using the proposed model and algorithm for calculating the kinetic parameters of the magnetite leaching process with nitric acid.

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Conflict of interest

The author declares that he has no conflict of interest in relation to this study, including financial, personal, authorship or other, which could affect the study and its results presented in this article.

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Data availability

The manuscript has no associated data.

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Andriy Kontsevoy, *PhD, Associate Professor, Department of Inorganic Technology, Water Purification and General Chemical Technology, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine, e-mail: kontsev@xtf.kpi.ua, ORCID: http://orcid.org/0000-0002-1753-416X*