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STUDY ON APPLICATION OF A NEW MODEL FOR THE KINETICS OF DIASPORE LEACHING PROCESS

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Abstract

The process of leaching diasporic bauxite in sodium aluminate solution is the most popular method to produce alumina in Chinese alumina industry. A new consistent kinetic model for gibbsite leaching process model has been developed in our previous work. This paper aims to study the application of the new model for the diaspore leaching in industrial alkali solution. The model equation was numerically integrated applying the fourth-order Runge-Kutta technique. Nonlinear regression analysis was carried out to estimate the unknown model parameters by comparing numerical solutions with available experimental data. The new model which considers the fractal geometry of the shrinking diaspore particles and the residual aluminium concentration in particles, is more consistent with the leaching process of the diaspore particles distributing in a narrow size range than the particles with the wide range of the size distribution.

Introduction

Alumina in Chinese is usually produced from bauxite which is a naturally occurring heterogeneous ore and primarily consists of diaspore, α-AlO(OH). The commercial production of alumina from bauxite is typically carried out according to the Bayer process which was invented and developed by Karl Josef Bayer in 1888[1, 2]. Digestion as one of the key steps of the Bayer process aims at dissolving the maximum aluminium available in the ore into caustic solution, which can be presented as

$$AlOOH + NaOH + H_2O = NaAl(OH)_4 \quad (1)$$

Chemical reaction between bauxite and caustic solution, as described by Eq.(1), is heterogeneous reactions involving the solid and liquid phases. The reaction is one of the main forms of metallurgical reactions[3], which can have many reaction pathways of the kinetics of the heterogeneous reaction described in the chemical engineering textbooks[4]. There have been lots of reports on the kinetic models of the bauxite leaching process. However, they were almost based on un-reacted core model which assumes that every particle involving in reaction is the ideal sphere shape [5-12]. Gu developed the diasporic bauxite leaching process[13, 14]. It was assumed that 1) the rate of surface reaction was of the first order, equal to the rate of each mass-transfer step which was defined as the difference between the rates of forward and backward reactions, 2) all the mass-transfer coefficients were not variable and 3) the activity and the activity coefficient of water were constant. The model can be expressed as

$$\frac{d(1-\alpha)}{dt} = k\left(C_{OH}^0 - \frac{C_{Al,1}^0}{K} - k^*\right)\alpha \quad (2)$$

where C_{OH}^0 is the initial concentration of OH , C_{Al}^0 is the initial Al concentration of the solution used in leaching, K is the equilibrium constant, k^* is another constant related to the initial mass and molecular weight of diaspore, the initial solution volume and the equilibrium constant.

Bi[1] developed anther model for diaspore leaching process by considering porous shrinking un-reacted cores for low, medium and high leaching temperatures. The models can be described by the following equations.

For the low temperature region:

$$\frac{dC_{Al}}{dt} = k_+\left(C_{OH} - \frac{C_{Al}}{K}\right) \quad (3)$$

For the medium temperature region:

$$\frac{dC_{Al}}{dt} = \sqrt{(k_+ + k_-)C_{OH}^2 - 2k_1 C_{OH}} \quad (4)$$

For the high temperature region:

$$\frac{dC_{Al}}{dt} = \sqrt{(k_+ + k_-)C_{OH}^2 - 2k_1 C_{OH}} + f(k_+ + k_-)C_{OH,s} - k_1 f \quad (5)$$

Where k_+ and k_- are the forward and backward reaction rate constants, respectively, f is the roughness factor of the particle surface and k_1 is a constant. C_{OH} and $C_{OH,s}$ describe the

concentrations of OH^- in the solution and on the particle surface, respectively. C_{Al} and $C_{Al,s}$ are the Al concentration in solution and on the surface, respectively.

The complexity and harsh condition of the diaspore leaching process restrict the further investigation and understanding of the leaching mechanism and kinetics. In this paper, a new kinetic model which was developed for gibbsite leaching process in our previous work[15], is analyzed and validated for the digestion of diaspore particles with particle size distributing in both a wide range and a narrow range.

Kinetic Model

In our previous work a new consistent kinetic model for gibbsite leaching kinetics was developed, which is based on the assumption that the leaching process is an irreversible first-order reaction with respect to OH^- concentration. In the establishment of the model, the reaction rate was considered to be proportional to the aluminium residual concentration in solid, C_{ore}^{*}, as well as the effective surface area of particles, A, as follows:

$$\frac{dC_{Al}}{dt} = kAC_{OH}\left(C_{ore}^{0} - C_{ore}^{*} - C_{Al}\right) \qquad (6)$$

where C_{ore}^{0} is the initial concentration of aluminium in the bauxite particle relating to the volume of caustic solution. Practically, the shapes of bauxite particles are irregular and change with the reaction time and pores and cracks might exist on the particle surface. It should be noted that the effective surface area where reaction between solid and solution occurs is no longer proportional to the square of the particle radius, r^2. According to the fractal theory[16], the reactive fractal dimension, D_R, is used to describe the effective surface area, that is, $A \propto r^{D_R}$. Besides, the concentration of OH^- in solution could be expressed by the difference between C_{OH}^{0} and C_{Al}.

Thus, Eq.(6) can be rewritten as

$$\frac{dC_{Al}}{dt} = kr^{D_R}\left(C_{OH}^{0} - C_{Al}\right)\left(C_{ore}^{0} - C_{ore}^{\infty} - C_{Al}\right) \qquad (7)$$

The model equation describe by Eq.(7) can be numerically integrated to obtain the transient aluminium concentration in solution using the fourth-order Runge-Kutta technique. The aluminium concentration is able to be measured as a function of leaching time, but the reaction rate constant ant the other model parameters are difficult to be determined experimentally. The non-linear regression analysis has been employed to compare the numerical solution with the available experimental data. The regression analysis best fits the model results with the experimental data by minimization of the sum, Q, of residual squares which is calculated as

$$Q = \left\|C_{Al} - C_{\exp}\right\|^2 = \sum_{i=0}^{N}\left(C_{Al,i} - C_{\exp,i}\right)^2 \qquad (8)$$

where $C_{\exp}$ is the experimental aluminium concentration measured at different reaction time, t_0, t_1, t_2, …, t_i, …, t_N, and $\left\|C_{Al} - C_{\exp}\right\|$ describes the norm of the column vector $\left(C_{Al} - C_{\exp}\right)$.

The sum of residual squares was minimized by changing the model parameters (k, K, and n) using the Levenberg-Marquardt method[17]. The numerical codes were written and run using the Matlab program. An indication of the model goodness was assessed using the correlation coefficient, R^2, calculated for the two column vectors C_{Al}, and C_{exp}.

Results

Application for the diaspore particles in a wide size range

The experimental data used in this section were obtained by Ke[18] who investigated the leaching performance of the diaspore from Henan Province, China. The chemical compositions of the diaspore sample are Al_2O_3 60.82%, SiO_2 11.07%, Fe_2O_3 9.10, TiO_2 2.91, CaO 0.55% and MgO 0.86%. The sizes of the initial diaspore particles distribute from 0.2μm to 250μm which is considered as a relative wide size range. The diaspore was leached in the caustic solution with the OH^- concentration of 7.5mol/L at 230℃ and 240℃ for various times.

The nonlinear regression analysis was carried out using the two sets of experimental data obtained with two different temperatures. The results of the analysis together with the experimental conditions are shown in Table 1. The comparison between the model prediction and the data is shown in Fig.1. It can be seen that the agreement between the model and the experimental data is not good. Eq.(8) for the leaching kinetic model is not suitable for the leaching process of diaspore with the particles in a wide size range.

Application for the diaspore particles in a narrow size range

Another type of diaspore, from Pingguo, Guangxi Province,

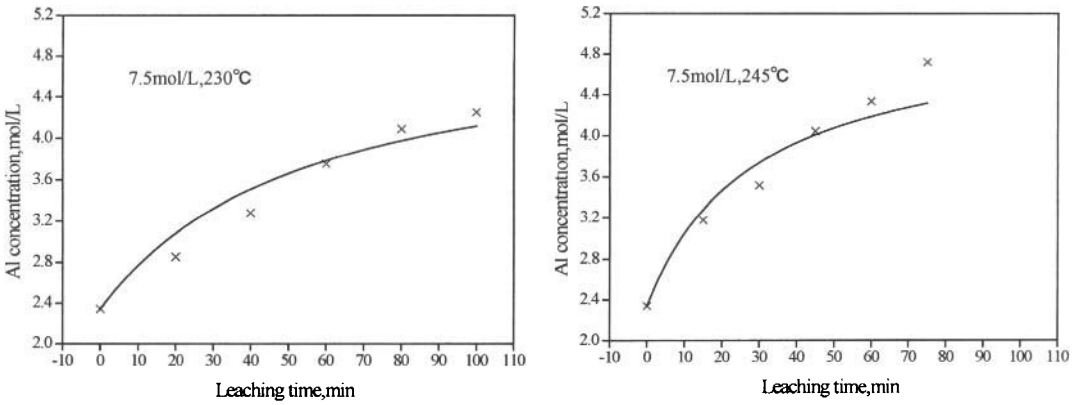

Fig.1 Comparison of the available kinetic model (curves) and the experimental data (symbols) for leaching diaspore from Henan.

Table 1 Parameters obtained by non-linear regression analysis of the availabe model using the Henan diaspore leaching data[18].

Leaching temperature, ℃	Rate constant k, $(mol/L)^{-1}min^{-1}$	Reactive fractal dimension D_R	Al residual concentration, mol/L	Correlation coefficient R^2
230	0.002775	1.5088	0.38355	0.9618
245	0.004998	2.0676	0.21141	0.9509

leaching in caustic solution was studied by Gu[14]. The chemical compositions are Al_2O_3 54.90%, SiO_2 7.50%, Fe_2O_3 20.32%, TiO_2 3.24%. The mineralogical phase of diaspore accounts for 56.23% of the natural ore. The size range of the diaspore particles involving in leaching process was from 0.2μm to 44μm. The initial concentration of OH^- ion in leaching solution was 4.75mol/L. The diaspore was digested at 224℃, 234℃, 239℃ and 248℃ for various times.

The kinetic model for the diaspore particles with small size range was validated using the fore sets of experimental data and the numerical code implemented into the Matlab program. The results of the analysis together with the experimental conditions are shown in Table 1. Comparison between the available model and the data is shown in Fig.2. Evidently, the available model correlates with the experimental data well. With the leaching temperature goes up, the rate constant and the reactive fractal dimension increase, while the residual concentration of aluminium in solid decreases. Taking account into the leaching performance of the diaspore, the obtained parameters are reasonable, since the raising temperature is benefit to extract aluminium from bauxite. The reactive fractal dimension reflects the irregularity of the leaching process. The higher value of fractal dimension with the temperature indicates the temperature drives the leaching system more chaos. Therefore, it could be concluded that, when the sizes of diaspore particles involving in the leaching process distribute in a small size range, the available kinetic model of Eq.(7) is consistent with the diaspore leaching process.

Table 2 Parameters obtained by non-linear regression analysis of the available model using the Pingguo diaspore leaching data[14].

Leaching temperature, ℃	Rate constant k, $(mol/L)^{-1}min^{-1}$	Reactive fractal dimension D_R	Al residual concentration, mol/L	Correlation coefficient R^2
224	0.010657	1.71.	0.32076	0.9845
234	0.015297	1.8013	0.094468	0.9983
239	0.032654	2.3283	5.64E-06	0.9944
248	0.033441	2.3742	1.2107E-013.	0.9981

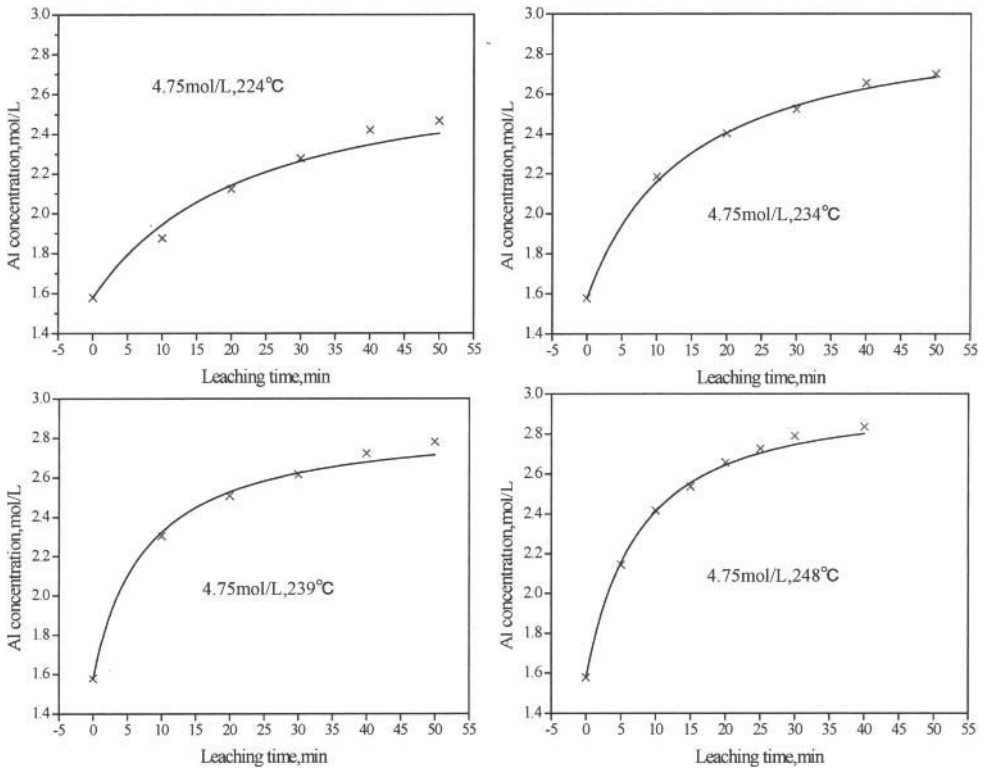

Fig.2 Comparison of the available kineti model (curves) and the experimental data (symbols) for leaching diaspore from Pingguo.

Discussion

The available kinetic model of Eq.(7) has considered the real characteristics of natural particles of diaspore. The first one is that the irregular shape of the particle and the coarse surface. As well, the whole content of aluminium contained in diaspore particle could not be dissolved totally, due to the impact of the impurities in the natural ore and the saturation of aluminate sodium solution under certain temperature. Therefore, it makes sense to apply the available model to describe the diaspore leaching process. However, the results of fitting model with experimental data show the good agreement is just observed in the case of the small range of particle size distribution. It might be explained that the total effective reactive surface area of particles was considered to be the reactive surface area of a single particle multiplying the number of the particles in the leaching process. In other words, it is assumed that the all the particles are self-similarity on the shape and have the uniform particle size. So, in the case of the particles distributing in a wide size range, the kinetic model seems to be not consistent with the bauxite leaching process. Further modification concerning with particle size distribution for the kinetic model should be needed.

Conclusion

This paper has studied the application of the available kinetic model which was developed in our previous work for leaching process of Chinese diaspore. The validation of the kinetic model on both the wide and narrow range of particle size distribution has been investigated. The available model could not describe the leaching process of diaspore particles which distribute in a wide size range consistently. In the case of the narrow range of size distribution, the model is consistent with the kinetics of diaspore leaching process.

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