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Particle size distribution model for kinetics of digesting alumina

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Abstract

The kinetic model for leaching process of Chinese diaspore with particle size distribution has been studied. This paper takes into account 1) the irregular shape and rough surface of the natural particles, 2) the residual concentration of Al in particles due to the impurities in natural diaspore, and 3) the particle size distributing in a size range and varying with digesting time. A new kinetic model, PSD+RC+F model, has been developed by the real characteristics of natural bauxite particles in leaching process. The modified gamma distribution function was applied to describe the particle size distribution of diaspore particles. PSD+RC+F model combined with gamma-like distribution function, validated by numerical analysis, shows good agreement with the experimental data.

Introduction

Kinetics of dissolving process is to seek the relationship of main parameters in the process, to find out the mathematical expression, i.e. mathematical model, to determine the optimal reactor calculation and operating parameters by the mean of the computer to work out all the quantitative relation on the base of hypothesis and experiment, and then to achieve automatic control. Therefore, the kinetics is the significant scientific method that could strength the smelting process, shorten the smelting time, save energy, enhance productivity, reduce the cost, improve product quality, promote industrial automation and informationization, and explore and develop new technology and new process.

The kinetic model of caustic solution dissolving diaspore has begun to be research thoroughly since the 1960s when various forms of kinetic expressions were proposed. Марић and Фил Бове [1,2] who researched the leaching kinetics of CIS diaspore digesting in alkali solution, developed two chemical reaction-controlling digestion rate equations, based on unreacted core model and shrinking unreacted core model. Diaspore digestion was also modeled by Gu [3,4]. 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 coefficient were not variable and 3) the activity and the activity coefficient of water were constant. Considering the influence of solution, Марић presented the kinetic model with diffusion controlling the digestion process.

The kinetic equations mentioned above were all based on the classical theory of unreacted model [5-7]. However, Bi [8] researched in the digesting features of a Chinese diaspore, and found its digestion process should not have been using unreacted core model to describe. Another three models were deduced for low, medium and high digesting temperature by assuming the porous particles, which were obtained theoretically without further experimental support.

On the basis of previous work, this paper has put forward a new kinetic model on particles size distribution and carried out the verification, according to the characteristics of natural

diaspore digesting in caustic solution.

Experimental

The natural diaspore used in this work was from Tiandong, Guanxi Province, China. The original material was crushed in rob mill and sieved under 630μm. Sodium hydroxide solution, the digesting solution, was prepared by the sodium hydroxide with analytical reagent.

The digesting temperature was fixed at 240□. The initial concentrations of NaOH solution were 4mol/L and 6mol/L. The diaspore particles were digested in different solutions for 0 minute, 15 minutes, 30 minutes, 60minutes, 120 minutes and 300 minutes, respectively.

Dispore particles of 20 grams and NaOH solution of 100ml reacted in an autoclave. The liquid sample, sodium aluminate solution, of around 10ml was collected from the reactive suspension by a plastic syringe with nylon filter for the detection. Al content in the digested solution was analyzed by a Prodigy XP ICP equipment, produced by American Leeman Company.Around. The slurry sample, the mixture of digested bauxite and sodium aluminate solution, was withdrew with a plastic syringe from the whole slurry while being stirred on a magnetic stirring apparatus at 600 rpm. The particle size distribution of the digested particles was measured by a Malvern Mastersizer 2000 equipment.

Kinetic model

In our previous work, a kinetic model for digesting gibbsite with uniform particle size was developed. It considered that the digesting rate is proportional to the effective reactive surface area of the particles rather than the total surface area [6,9], because the irregular shape of the particles which changes rulelessly in the digesting process. As well, the aluminium contained in the particles was regarded to be not extracted into solution totally, due to the influence of the impurities in natural ore particles. The model was expressed as [10]:

$$\frac{dC_{Al}}{dt} = k' A_e C_{OH} \left(C_{Al}^{o} - C_{Al}^{\infty} - C_{Al} \right) \tag{1}$$

where C_{Al} is the concentration of Al in solution, t is the reaction time, k' is the reaction coefficient, A_e is the effective reactive surface area of particles, C_{OH} is the concentration of OH^- in solution, C_{Al}^{o} is the initial concentration of aluminium in particles relating to the solution volume, and C_{Al}^{∞} is the concentration of residual aluminium in particles after digestion lasting for t time.

In practice, the particle size of a bulk of particles is impossible to be the uniform, but exists as a distribution in a relatively large size range. Even more, the particle size distribution will change with dissolution time elapsing as a result of the difference of reactivity of particles with different sizes and shapes. Therefore, the total effective reactive surface area is the sum of effective reactive surface area of each single particle. If the particle size of a population of particles ranges from l_{min} and l_{max}, the total effective reactive surface area could be expressed as

$$A_e = \int_{l_{\min}}^{l_{\max}} \pi N l^{D_R - 3} \frac{f_V(l)}{\int_0^{\infty} \frac{f_V(l)}{l^3} dl} dl \tag{2}$$

where N is the total number of particles involving in reaction, l is the radius of any particle, D_r is the fractal dimension which describes the relationship between the effective reactive surface area and the radius of irregular-shape particle [9], and $f_V(l)$ is the frequency distribution function by volume [11].

Taking Eq.(2) into Eq.(1), substituting concentration of Al into concentration of OH^-, lumping the constant coefficients, the model could be recast as

$$\frac{dC_{Al}}{dt} = k \left(C_{NaOH}^{0} - C_{Al} \right) \left(C_{Al}^{0} - C_{Al}^{\infty} - C_{Al} \right) \int_{l_{\min}}^{l_{\max}} l^{D_R - 3} \frac{f_V(l)}{\int_0^{\infty} \frac{f_V(l)}{l^3} dl} dl \tag{3}$$

Model of Eq.(3) is named as PSD+RC+F, because it considered the particle size distribution, residual concentration of aluminum in solid and the irregular shape of natural diaspore particles.

It is noted that, in Eq.(3), the initial concentration of Al in

solid, C_{Al}^{0}, the initial concentration of OH^- in solution, C_{NaOH}^{0}, and the Al concentration in solution at any time, C_{Al}, could be obtained by experiment, and the digestion condition has a responding residual concentration of Al in solid, C_{Al}^{∞}, and reaction rate, k, however, only the expression of $f_V(l)$ is unknown. So it is necessary to set up a function to describe the particle size distribution of the multi-particulate system of diaspore at any time to solve Eq.(3).

The model equation described by Eq.(3) can be numerically integrated to gain the transient aluminium concentration, C_{Al}, using the fourth-order Runge-Kutta technique and the non-linear regression analysis to compare the numerical solution with the available experimental data.

The regression analysis best fits the model results with experimental data by minimization of the sum, Q, of residual squares which is calculated as

$$Q = \left\| X_l - X_{\exp} \right\|^2 = \sum_{l=0}^{N} \left(X_{l,l} - X_{\exp,l} \right)^2 \qquad (4)$$

where X_l, and X_{exp} are the calculated and experimental data, respectively. $\left\| X_l - X_{\exp} \right\|$ describes the norm of the column vector ($X_l - X_{\exp}$). The sum of residual squares was minimized by changing the model parameters. The numerical codes were written and run using the Matlab software. An indicator of the model goodness was assessed using the correlation coefficient, R^2, calculated for the two column vectors X_l, and X_{exp}. X in Eq.(4) represents the aluminium concentration in solution in the case of Eq.(3), or the frequency distribution of particles by volume, $f_V(r)$.

Results and Discussion

Diaspore characterization and digestion performance

The chemical analysis shows that the particles composed of Al_2O_3 45.80%, SiO_2 5.05% and Fe_2O_3 27.28%. The particle size of the fresh particles population distributed in the range of 0.3μm to 630μm, peaking at 52.48μm, as the black curve shown in Fig.1, provided by Mastersizer 2000.

The performance of diaspore digesting in both 4mol/L and 6mol/L NaOH solution at 240□, has been investigated. The concentration of Al in particle relating to the solution volume was calculated as 1.796mol/L, when Al in 20 grams particles dissolved into solution totally. The concentration of dissolved Al in solution varying with time is shown in Fig.2. It reveals that the OH^- concentration impacted the digestion performance, that is, the denser OH^- solution contained, for the identical digesting time, the more aluminium extracted.

The PSD of diaspore particles varied with digestion time elapsing. As shown in Fig.1, the percentage of volume of the large particles, saying the particles with size distributing from 26μm to 631μm, accounting for the whole particle volume declined. It might be explained that the particles shrank with

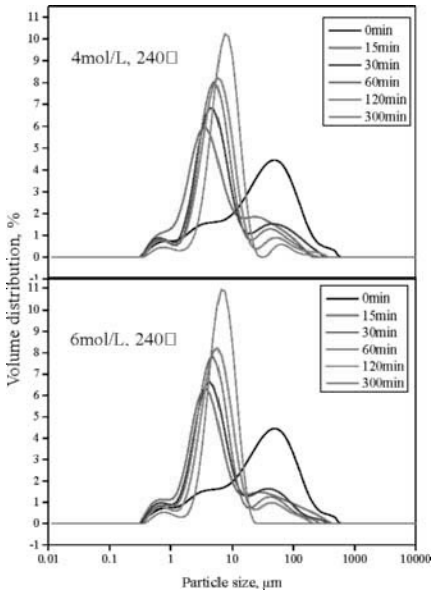

Fig.1 Particle size distribution of feed diaspore (black curve) and particles dissolved under various conditions (color curvers)

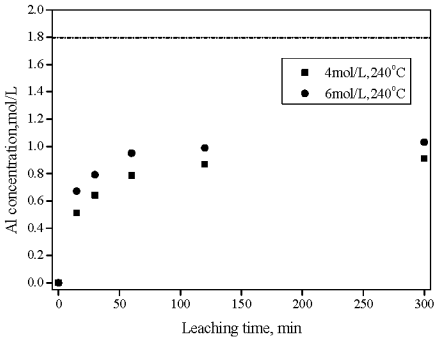

Fig.2 Results of diaspore digesting in caustic solution

reaction proceeding, or caustic erosion broke a particle into several pieces. After digesting for 300 minutes, the larger particles almost disappeared and the particle size dominated in the range of 0.36μm to 26μm.

Particle Size Distribution Function

The Gamma function is one of the widely-used density distribution function in probability theory [12], which could be expressed as

$$f(x)=\frac{1}{\beta^{\alpha}\Gamma(\alpha)}x^{\alpha-1}e^{-x/\beta} \tag{5}$$

where α is the shape parameter, and β is the scale parameter. The whole distribution could be regarded as the sum of each index distribution when α is the positive integer, while it is close to the normal distribution if the value of α is large.

The PSD of diaspore particles was too random to be described by the gamma distribution function. The modified gamma function might be workable. $1/\beta^{\alpha}\Gamma(\alpha)$ and $(\alpha-1)$ in Eq.(5) were simplified into τ and α, respectively. Instituting x in Eq.(5) into particle radius, l, the PSD function by volume might be described by gamma-like distribution function.

$$f_V(l)=\tau_1 l^{\alpha_1}e^{-l/\beta_1}+\tau_2 l^{\alpha_2}e^{-l/\beta_2}+\tau_3 l^{\alpha_3}e^{-l/\beta_3}+\tau_4 l^{\alpha_4}e^{-l/\beta_4} \tag{6}$$

where are α_1、α_2、α_3 and α_4 the parameters relating to shape, β_1、β_2、β_3 and β_4 are the parameters related with scale, and τ_1、τ_2、τ_3 and τ_4 are the related parameters of both shape and scale.

The gamma-like distribution function was evaluated by nonlinear regression analysis using PSD results obtained with different initial sodium hydroxide concentrations. The comparison between the model prediction and the experimental data is revealed in Figs. 3 and 4, showing that the model correlated with the experimental data well in this case. All of the numerical values obtained for correlation coefficient are higher than 0.99. Therefore, the modified model, gamma-like function was adoptable to describe the randomly changing PSD of diaspore particles during the digesting process.

A PSD model is developed by combining Eq.(3) with gamma-like distribution function, Eq.(6).

$$\frac{dC_{Al}}{dt}=k\left(C^{0}_{NaOH^-}-C_{Al}\right)\left(C^{0}_{Al}-C^{\infty}_{Al}-C_{Al}\right)\cdot \int_{l_{\min}}^{l_{\max}} l^{D_R-3}\frac{\left(\tau_1 l^{\alpha_1}e^{-l/\beta_1}+\tau_2 l^{\alpha_2}e^{-l/\beta_2}+\tau_3 l^{\alpha_3}e^{-l/\beta_3}+\tau_4 l^{\alpha_4}e^{-l/\beta_4}\right)}{\int_0^{\infty}\frac{\left(\tau_1 l^{\alpha_1}e^{-l/\beta_1}+\tau_2 l^{\alpha_2}e^{-l/\beta_2}+\tau_3 l^{\alpha_3}e^{-l/\beta_3}+\tau_4 l^{\alpha_4}e^{-l/\beta_4}\right)}{l^3}dl}dl \tag{7}$$

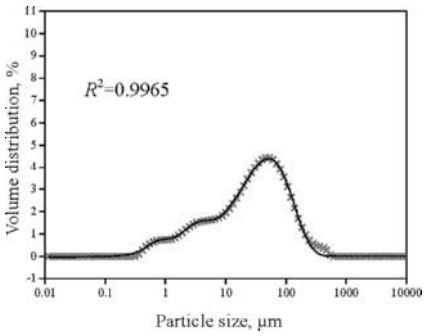

Fig.3 Comparison of the gamma-like distribution function (curve) and the experimental size data (symbols) of the feed diaspore from Tiandong

The new model could be calculated by nonlinear regression analysis using the obtained results of parameters in Table 1 together with the aluminium concentration in solution. The calculated results and the comparison between the experimental results and the modelling results are displayed in Table 1 and Fig.5, respectively. It indicated that the PSD model fits the experimental results well, since all the correlation coefficients are over 0.99. Besides, the denser concentration of OH^- in solution, the larger value of reaction rate is, and the larger D_R for the digestion condition, thus, the lower residual Al concentration in solid. The numerical values of fractal dimension, D_R, reflect the capability of dissolving aluminium of the responding condition, which is an indicator for the collection of all the sites on the digesting particles where dissolution of aluminium takes place. Even though the particle is enclosed by solution, there is no reaction occurring on the interface in the case of harsh leaching condition. The numerical parameters in Table 1 correlated with the practical digesting process. Therefore, it can be concluded that the kinetic model of Eq.(3) with gamma-like distribution function is consistent with the diaspore leaching process when the PSD

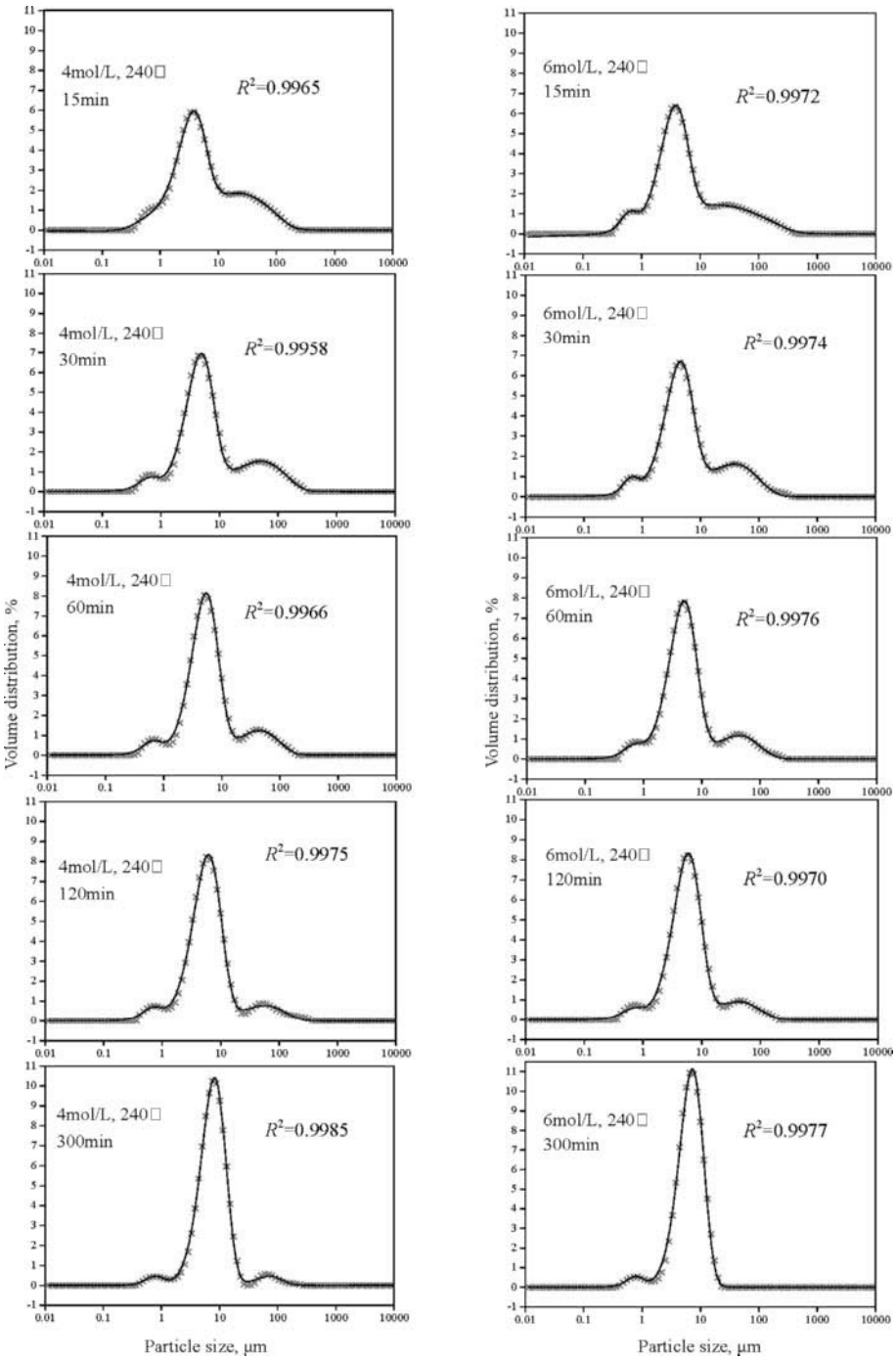

Fig.4 Comparison of the gamma-like distribution function (curves) and the experimental data (symbols) for diaspore from Tiandong digesting in 4mol/L and 6mol/L caustic solution at 240℃

Table 1 Parameters obtained by non-linear regression analysis of PSD+RC+F model combined with the gamma-like distribution function using the leaching data of diaspore from Tiandong

Digesting condition		Parameters			
C^0_{NaOH}, mol/L	Temperature, ℃	k, $(mol/L)^{-1}min^{-1}$	D_R	C^*_{gb}, mol/L	R^2
4	240	0.002724	2.3845	0.9191	0.9904
6	240	0.007354	2.6011	0.8028	0.9908

of diaspore involving in the digesting process is in a certain range.

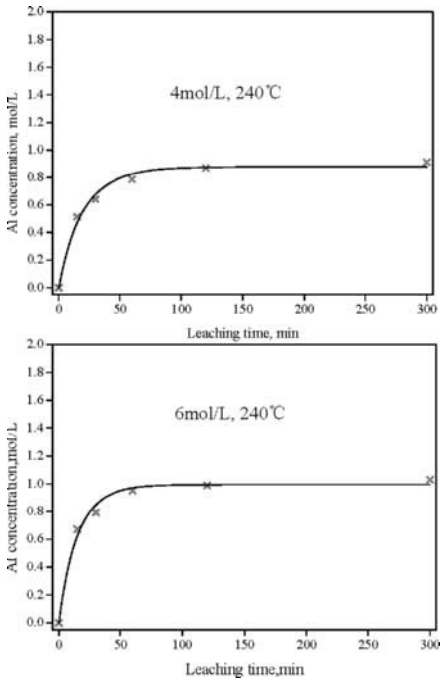

Fig.5 Comparison of the PSD+RC+F model combined with gamma-like distribution function (curves) and the experimental data (symbols) for leaching diaspore

Conclusion

This paper has investigated and developed the kinetic model for diaspore from Tiandong digesting in caustic solution, according to the digestion characteristics of natural ore particles. The results are concluded as following:

(1) On the basis of our previous work, a new kinetic model, PSD+RC+F model, was developed to describe the particles with sizes distributing in a size range.

(2) Validated by numerical analysis, a gamma-like distribution function was able to describe the random PSD of diaspore particles.

(3) The kinetic model obtained by combining PSD+RC+F model and gamma-like distribution function fit the experimental data well, indicating it could describe the kinetics of diaspore digesting in caustic solution.

Acknowledgements

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