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Fractal kinetic model for digesting alumina

Li Bao[1], Ting-an Zhang[2] , Anh V Nguyen[3],Weimin Long[1], Jia Ma[1], Zhihe Dou[2] , Guozhi Lv[2]
[1] State Key Laboratory of Advanced Brazing Filler Metals and Technology, Zhengzhou Research Institute of Mechanical Engineering, Zhengzhou, 450001, China
[2] School of Materials and Metallurgy, Northeastern University, Shenyang, 110819, China
[3] School of Chemical Engineering, The University of Queensland, Brisbane, Queensland, 4072, Australia

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Abstract

A new kinetic model for diaspore digestion process has been proposed in the view of fractals. Considering characteristics of the natural diaspore particles, this paper introduces two fractal parameters, reactive fractal dimension, D_R, and particle size distribution (PSD) fractal dimension, D_{PSD}, to describe the irregular shape and rough surface, and the ruleless particle size distribution, respectively. A piecewise volume cumulative distribution function with PSD fractal dimension has been developed to express the PSD of natural particles varying with digsting time. Combining the piecewise volume cumulative distribution function, the new model, PSD+RC+F model, could express the diaspore digestion process well, by carrying out numerical analysis.

Introduction

Bayer process is the popular method to produce alumina from Chinese diaspore which primarily consists of α-AlO(OH). 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

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

The reported models for digesting process of diaspore are almost based on the classic shrinking-core model[1-4], assuming that the diaspore particles involving in digestion process are uniform-size sphere, and the particles keep their geometric identity along with digesting time. However, there may be other unwanted minerals in natural diaspore, such as hematite, goethite, quartz, rutile or anatase, kaolinate and other impurities in minor or trace amounts. The changing rule of the natural ore particles in practice is hardly consistent with the assumption of the reported models.

Besides, most practical dissolution processes involve solids consisting of a wide range or distribution of particle sizes. Meanwhile, the particle size might be stochastic during the dissolution process where the rate which depends on the particle size is correspondingly random. This fact has been confirmed by the research of dissolving chemical reagent[5], minerals[6] and drugs. The investigation of Mihranyan[7] who studied the dissolution process of sparingly soluble calcium carbonate revealed that the particle size distribution altered during dissolution and the peaks of size distribution shifted gradually towards small-size side until it stabilized after 24 hours dissolution and remained unchanged. Taking into account the polydispersity of the solid dissolving, LeBlanc and Fogler[8] described the model of dissolution process using particle population balances, which was considered as an important influence factor on the dissolving kinetics in the latter research[6,9]. Hänchen[6] developed a general model for the dissolution of olivine, based on the population balance approach. Particle size distribution was combined with the shrinking core model by Gbor [10].

The concept of fractals was proposed by Mandelbrot in 1975 to describe the chaos system[11]. In this paper, the fractal concept is applied on the kinetics of digesting diaspore. In consideration of the practical situation of the particle size during the digestion process, the properties of diaspore particles (particle size distribution) of digesting in NaOH solution under various conditions will be examined to explore the essence of performance of the particles. In addition, the general model for describing the digesting of diaspore will be developed, on the base of the previous work[12]. The resulting model can be employed over a wide range of particle sizes as well as the irregular-shape particles. The model also will be estimated by comparing the experimental data and the modelling results.

Experimental

The diaspore was from Tiandong, Guanxi Province, China. The chemical analysis shows that the diaspore composed of Al_2O_3 45.80%，SiO_2 5.05% and Fe_2O_3 27.28%. The original material was crushed in rob mill and sieved under 630μm. The particle size distributed in the range of 0.3μm to 630μm, peaking at 52.48μm provided by Mastersizer 2000. Sodium hydroxide solution, the digesting solution, was prepared by the sodium hydroxide (AR).

The digesting experiment was carried out in a homogeneous ball milling reaction kettle. The digesting temperature was 240□. The initial concentrations of NaOH solution were 4mol/L and 6mol/L. The diaspore particles were digested in the solutions for 0 minute, 15 minutes, 30 minutes, 60minutes, 120 minutes and 300 minutes, respectively. The Al content in the digested solutions and the particle size distribution of the digested particles were obtained by analyzing the sodium aluminate solutions and the slurry samples using Prodigy XP ICP equipment and a Malvern Mastersizer 2000 equipment, respectively. The concentration of dissolved Al in solution varying with time is shown in Fig.1. Fig.2 displays the particle size distribution of diaspore particles varied with digestion time.

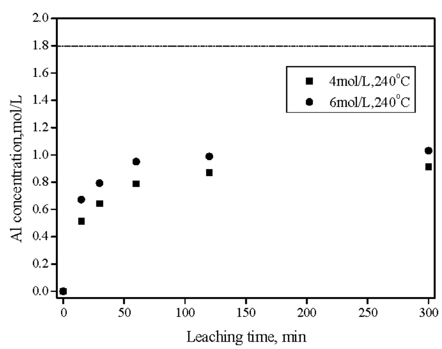

Fig.1 Results of diaspore digesting in caustic solution

Modelling

Kinetic model

A developed kinetic model that considered the fractal geometry of the shrinking diaspore particles and the residual aluminium concentration in particle, is suitable for the digestion process of diaspore with narrow particle size distribution rather than the wide particle size distribution in the previous work[13]. Considering the particle size distribution of natural ore particles, the kinetic model is modified as

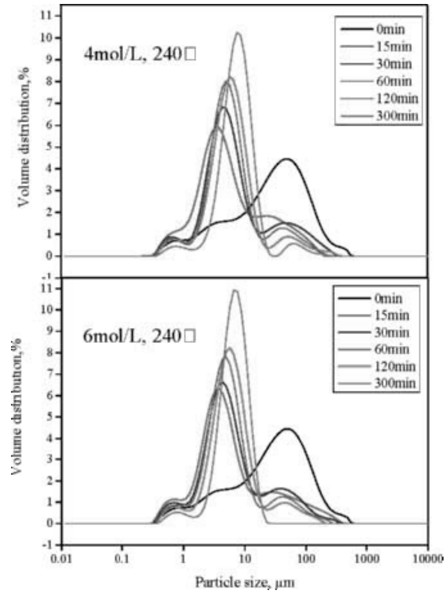

Fig.2 Particle size distribution of feed diaspore (black curve) and particles dissolved under various conditions (color curvers)

$$\frac{dC_{Al}}{dt} = k\left(C_{NaOH}^{0} - C_{Al}\right)\left(C_{Al}^{0} - C_{Al}^{\infty} - C_{Al}\right)\int_{l_{\min}}^{l_{\max}} l^{D_R-3}\frac{f_V(l)}{\int_0^{\infty}\frac{f_V(l)}{l^3}dl}dl \qquad (2)$$

where C_{Al} is the concentration of Al in solution, t is the reaction time, k is the reaction coefficient, C_{NaOH}^{0} is the initial concentration of OH^- in solution, C_{Al}^{0} is the initial concentration of Al in solid, C_{Al}^{∞} is the concentration of residual aluminium in particles after digestion lasting for t time, l is the particle size ranging from l_{min} and l_{max}, $f_V(l)$ is the frequency distribution function by volume, and D_R is the fractal dimension which describes the relationship between the effective reactive surface area and the radius of irregular-shape particle.

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 to the experimental data by minimization of the sum, Q, of residual squares which is calculated as

$$Q = \left\|X_l - X_{\exp}\right\|^2 = \sum_{i=0}^{N}\left(X_{l,i} - X_{\exp,i}\right)^2 \qquad (3)$$

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 scripts for calculation were written and run by Matlab software. An indication of the model fitness was assessed using the correlation coefficient, R^2, between the two column vectors X_{Al}, and X_{exp}.

Fractal function $f_V(l)$

All the parameters could be obtained via experimental measurement or calculation except for function $f_V(l)$ in Eq.(2). It is necessary to set up the expression of $f_V(l)$ for describing the particle size distribution during the digestion process to solve Eq.(2).

Tyler and Wheatcraft[14] suggested that the volume (of the particles whose sizes are larger than a certain size, L,) of cubes of size L needed to fill the gains of size Lor larger should be formulated by:

$$F_V(l>L)=c\left[1-\left(\frac{L}{\lambda}\right)^{3-D_{psd}}\right] \quad (4)$$

where F_V is the cumulative volume of the particles with the size l smaller than L, c and λ are constants relating to the shape factors and total size range of scale, D_{psd} is the particle size distribution fractal dimension. The higher fractal dimension was, the higher relative percentage of fine-grained material with the distribution[15], and the wider the range of particle size [16]. Eq.(4) represents a cumulative distribution by volume of a particle size distribution. However, in practice, a single D_{psd} value poorly describes a particle size distribution in a certain size range. It is assumed there exists one or several critical values l_c to partition the whole distribution into two or more intervals over which the fractal dimensions are different. Eq.(4) is modified as

$$\begin{aligned} F_V(l>L)&=c_1\left[1-\left(\frac{L}{\lambda_1}\right)^{3-D_{psd1}}\right](l_{\min}\le L\le l_{c1}) \\ &+c_2\left[1-\left(\frac{L}{\lambda_2}\right)^{3-D_{psd2}}\right](l_{c1}<L\le l_{c2}) \\ &+c_3\left[1-\left(\frac{L}{\lambda_3}\right)^{3-D_{psd3}}\right](l_{c2}<L\le l_{c3}) \\ &+c_4\left[1-\left(\frac{L}{\lambda_4}\right)^{3-D_{psd4}}\right](l_{c3}<L\le l_{\max}) \end{aligned} \quad (5)$$

To carry on the estimation of the fractal function, Eq.(5), the experimental data of the cumulative volume distribution of diaspore leaching under different conditions at various times are applied by the nonlinear regression analysis performed on Matlab program. The comparison of experimental data and the calculated results are displayed by Figs.3-4. Seemingly, the fitness between the experimental and modelling data are perfect, reflected by the correlation coefficient all of which are over 0.999. Thus, the piecewise cumulative volume distribution fractal function is able to describe the irregular particle size distribution of diaspore ore during the digestion process.

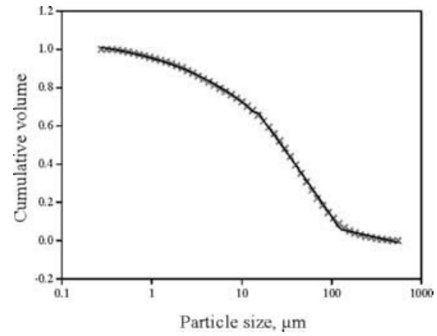

Fig.3 Comparison of the piecewise F_V of cumulative volume distribution (curve) and the experimental size data (symbols) of the feed diaspore

It is noted that the cumulative distribution is the integral of the frequency distribution, i.e. the frequency distribution, f, is equal to dF/dl. Therefore, the volume frequency distribution, $f_V(l)$, in Eq.(1) can be formulated from Eq.(5):

$$\begin{aligned} f_V&=-c_1\frac{3-D_{psd1}}{\lambda_1}\left(\frac{L}{\lambda_1}\right)^{2-D_{psd1}}(l_{\min}\le L\le l_{c1}) \\ &-c_2\frac{3-D_{psd2}}{\lambda_2}\left(\frac{L}{\lambda_2}\right)^{2-D_{psd2}}(l_{c1}<L\le l_{c2}) \\ &-c_3\frac{3-D_{psd3}}{\lambda_3}\left(\frac{L}{\lambda_3}\right)^{2-D_{psd3}}(l_{c2}<L\le l_{c3}) \\ &-c_4\frac{3-D_{psd4}}{\lambda_4}\left(\frac{L}{\lambda_4}\right)^{2-D_{psd4}}(l_{c3}<L\le l_{\max}) \end{aligned} \quad (6)$$

3.3 Estimation of fractal kinetic model

Taking Eq.(6) into Eq.(2), a new kinetic model with coupling fractal dimensions is obtained. Using the leaching results along with the analysis results in Figs.3-4, the fractal kinetic model is evaluated by nonlinear regression analysis. The outcomes are revealed in Table 1 and Fig.5. It is indicated that the results of reactive fractal dimension have the converse changing trend with the Al residual concentration in solid, implying the harsh degree of the dissolving condition, i.e., the harsher the condition is, the low reactive fractal dimension value. Both the comparison of experimental and modelling data in Fig.5 and the correlation coefficient values illustrate the good fitness of the kinetic model coupling reactive and particle size distribution fractal dimensions to the diaspore leaching process.

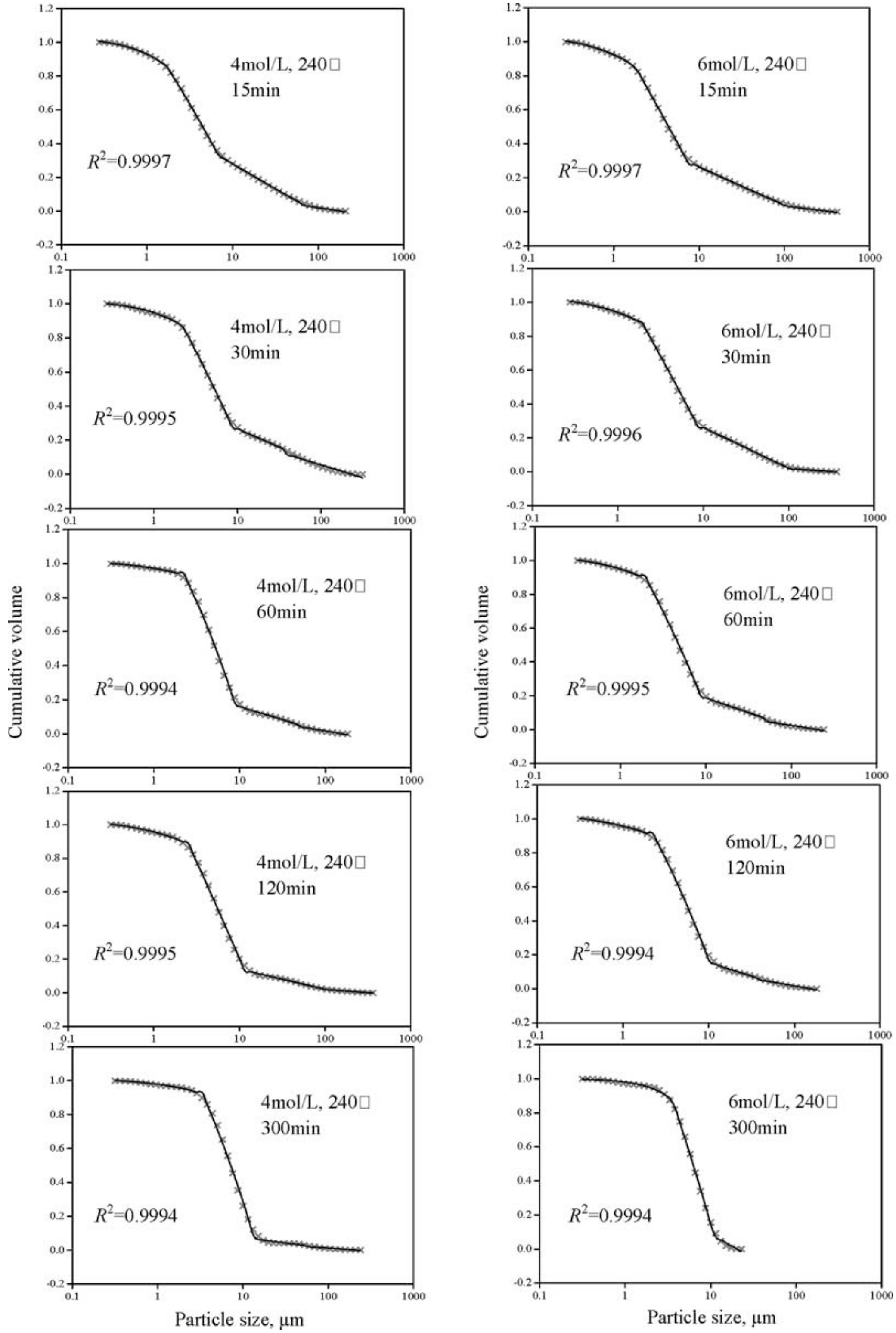

Fig.4 Comparison of the piecewise F_V of volume cumulative distribution (curves) and the experimental data (symbols) for diaspore digesting in 4mol/L and 6mol/L caustic solution at 240℃

Table 1 Parameters obtained by non-linear regression analysis of fractal kinetic model coupling reactive and particle size distribution fractal dimensions using the digestion data of diaspore

Digesting condition		Parameters			
C^0_{NaOH}, mol/L	Temperature, ℃	k, $(mol/L)^{-1}min^{-1}$	D_R	C^{∞}_{gbb}, mol/L	Correlation coefficient R^2
4	240	0.005595	2.3122	0.9194	0.9906
6	240	0.01156	2.5747	0.8074	0.9907

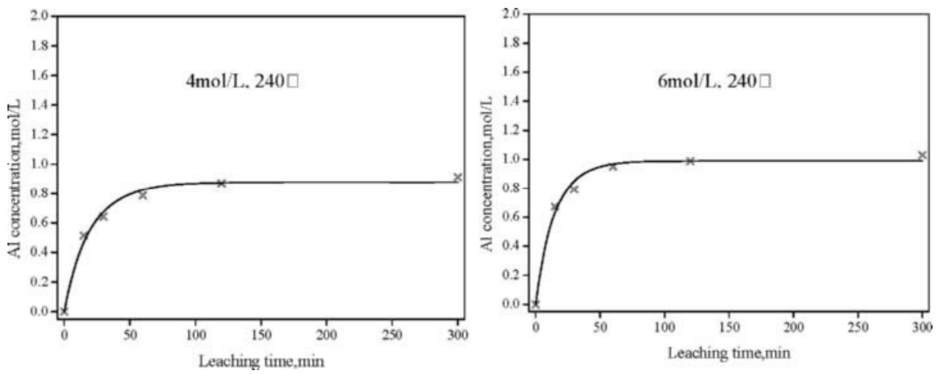

Fig.5 Comparison of the new fractal kinetic model (curves) and the experimental data (symbols) for digesting diaspore

Conclusion

This paper has developed a new kinetic model with coupling reactive and particle size distribution fractal dimensions for the digesting process of Chinese diaspore. A piecewise particle size distribution fractal function was applied to describe the irregular system of diaspore particle population during the digesting process. The fractal kinetic model has been estimated to be consistent with the kinetics of diaspore digesting process by non-linear regression analysis.

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