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DISSOLUTION KINETICS OF SILICON FROM RED MUD IN PURE WATER

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Abstract

In this study, the dissolution kinetics of silicon from sintering red mud in pure water was investigated. Experimental factors such as particle size and stirring speeds were studied to test their effect on the extraction fraction of silicon from red mud. It was found that the silicon extraction increases with stirring speed and decreasing in the particle size of red mud. Based on the experimental results, the Noyes–Whitney equation was adopted to describe and explain the dissolution behavior of the red mud in pure water, and the experimental data fit the model quite well in the whole process of dissolution.

Introduction

Thousands of phytoplankton live under the surface water of the ocean and constitute the primary productivity of the ocean. The phytoplankton breeds rapidly under appropriate conditions, and the growth of phytoplankton would consume huge amounts of carbon dioxide through photosynthesis [1]. Of the global emissions of carbon dioxide, about 50% of those from human activities are captured the oceans [2]. Phytoplankton growth needs not only C, N, P nutrient sources, but also Fe, Si and other trace elements. Martin et al found that deficiency of iron can inhibit the growth of algae [3,4]. However, there are many oceans that lack trace elements such as Fe, Si. It is reported that about 20% of the ocean area has excessive N, P nutrients, but the phytoplankton biomass is very low, and this area is known as high nutrient-low chlorophyll (HNLC) [5]. The researchers found that the iron limits phytoplankton productivity in the HNLC, thus the deficiency of iron affected the carbon dioxide transportation from the upper sea water to the deeper [6,7]. If iron was added in the HNLC, the phytoplankton growth could be promoted, consuming excessive N, P nutrients and accelerating the carbon transporting from the ocean surface to depth and ultimately reducing the carbon dioxide level of atmosphere and so decreasing the greenhouse effect.

Haraguchi et al proposed that the utility of steelmaking slag as the nutritive elements to promote the growth of algae [8,9]. Now in this study, we have tried to check the feasibility of using red mud as a nutrient source. Our experiments indicated that it is also quite viable to use red mud for the significant promotion of the growth of algae and the results will be published later. In the process of the production of alumina, a huge amount of red mud is produced causing serious alkalization of the soil and polluting the underground water after long term storage, and the treatment and comprehensive utilization of red mud is a troublesome problem. Though a large number of studies have been conducted on the comprehensive utilization of red mud, the research progress is not significant. However, taking accountant of the fact that red muds are also rich in Fe and Si, we tried to investigate its dissolution behavior preceding its real application in promoting the growth of algae of the ocean.

Experimental

The red mud sample used in this study was donated by Shandong Aluminum Company. Samples were dried, crushed into smaller particles by ball milling and sieved to the different particle size fractions. Particles with the size range of 39~185μm were sent for analysis of chemical composition by X-ray fluorescence spectroscopy.

The dissolution experiments were carried out in the plastic containers. The suspension was agitated with a Teflon stirrer, driven by a magnetic stirring apparatus. A water-bath heater was employed to provide the stable heating conditions at the predetermined temperature. When the temperature reaches the required value, a certain amount of red mud particles was added and the dissolution reaction was started. After the different reaction time intervals, the solution was sampled, filtered and the clear supernatant solution was sent for analysis of the silicon content by UV visible spectrophotometer (UV2000). Taking into account the different factors to test the extraction efficiency of silicon from the red mud, dissolution time intervals from 0 to 120 min were examined.

In order to investigate the dissolution behavior of red mud, we have carried out long time dissolution trials up to 100 hours. An SEM instrument was also used to observe the morphology variation of the solid particles.

Results and discussion

Chemical composition

From the X-ray fluorescence spectrum, the composition of red mud can be determined as shown in Table 1. It was shown that the main metal elements include iron, silicon, aluminum and calcium etc, in which these elements mainly existed in the form of their oxide. According to our knowledge, all these oxides belong to the sparingly soluble phases, so it can be predicted that the concentration of the interesting elements such as silicon from dissolution in the leach liquor would be quite low.

Table 1.Chemical composition of the red mud sample (*wt.%*)

Cmp	CaO	Fe_2O_3	SiO_2	MgO	P_2O_5	MnO	TiO_2	Al_2O_3
Cont	36.01	29.61	21.44	6.49	1.71	1.7	1.31	1.73

Effect of stirring speed

Fig.1 shows the variation of extracted silicon concentration in the leach liquor from the red mud with different dissolution times, for the samples under different stirring speeds of 80rpm, and 160rpm. It can be seen that the silicon in the red mud could be extracted rapidly into water in the first 60 minutes, then the dissolution rate would gradually decrease, after 120 minutes it nearly reached an equilibrium state. It was found that increasing of the stirring speed could promote the extraction of silicon from the red mud.

Effect of particle size

Fig.2 shows the variation of extracted silicon concentration in the leach liquor from the red mud with dissolution time for the samples with different particle sizes of 74~185μm and 39~46μm. It was found that the decrease of the particle size could enhance the extraction of silicon from the red mud, i.e., the smaller the particle size, the higher the extraction rate of silicon. With decrease of particle size, the corresponding particle surface area will increase, leading to a larger contact interface between the particles with the solution. It was shown that the decreasing of particle size can provide greater diffusion area, which made the extraction of silicon increase.

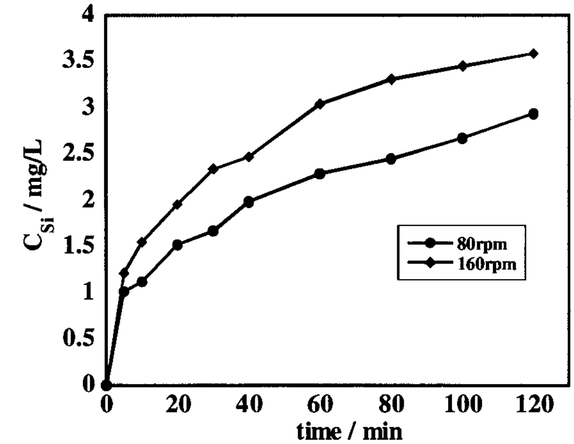

Fig.1. Effect of stirring speed and time on the silicon concentration in the leach liquor (particle size range: 46~74μm, 0.5 g/L, T=20°C)

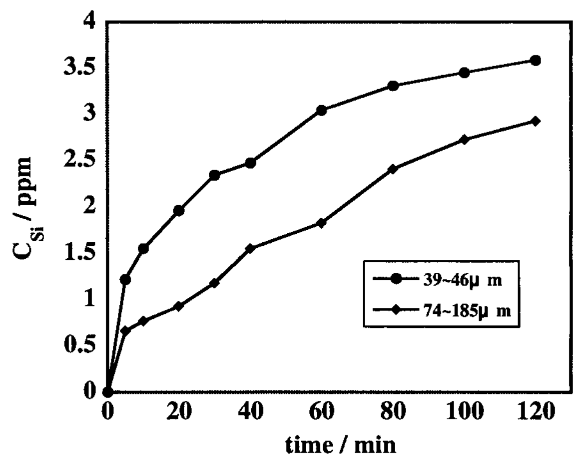

Fig.2. Effect of particle size and time on the silicon concentration in the leach liquor (T=20°C, 0.5 g/L, 300 r/min)

Kinetics analysis

In order to study the changes of surface morphology before and after long term dissolution, samples were observed by SEM after dissolution for 100h. As shown in the Fig.3, there seems almost no difference in the microstructure for the samples after long term dissolution in pure water. Considering that the extraction of silicon in pure water is quite low as shown in Fig.2, the maximum amount of silicon extraction from the red mud reached only 3.57ppm. It can be concluded that the dissolution of silicon from red mud in the pure water was a very slow and is a nearly homogeneous dissolution process.

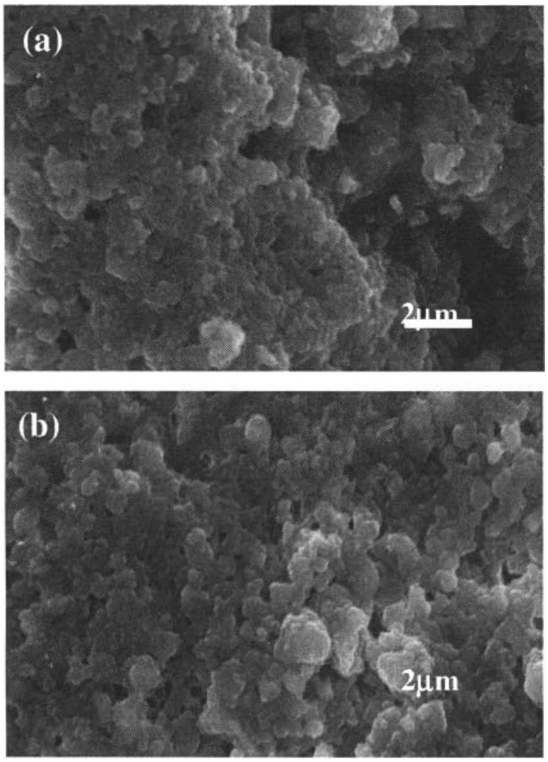

Fig.3. Scanning Electron micrograph photos of red mud sample before and after dissolution 100hours, (a) before, (b) after.

When red mud particles were put into the pure water, the particle surface reached saturation solubility rapidly and a liquid layer will be established around the particle in the dissolution process. Between the two sides of the liquid layer, a concentration gradient will appear between the solid particle surface and bulk solution, which makes the elements diffuse from the particle surface through the liquid layer into the bulk solution. The experimental results suggest that the dissolution is quite fast at the beginning, then the extraction of silicon will gradually decrease and after 120min it nearly reaches equilibrium. It was found that the extraction of silicon from the red mud is increased with faster stirring. Because in this case, the thickness of liquid layer will gradually become thinner and the extraction of silicon will consequently increase. So the observed dissolution seems follow a process of dissolution of silicon through a saturated solution layer to the bulk solution, and it can be defined as limited by liquid layer diffusion.

Under the different conditions of the dissolution of red mud particles, the variation of the silicon concentration extracted into the water may follow the liquid layer diffusion control model as shown in equation (1) which was derived from the classic Noyes-Whitney equation [10], and at $t=t_0$, $C=0$, $C_{surface}=Cs$, the corresponding initial conditions of equation (1) can be derived.

$$\ln(\frac{C_s}{C_s - C}) = \frac{DA}{\delta}\cdot t + C_{error} \qquad (1)$$

In which, D—diffusion efficiency of silicon through in the bulk liquid layer; C—silicon concentration in the leach liquor at the moment of t; Cs— water solubility of silicon compound under the experimental conditions; A—contact interface area between the red mud particles and water; δ—liquid layer thickness; C_{error}—the error of experimental data.

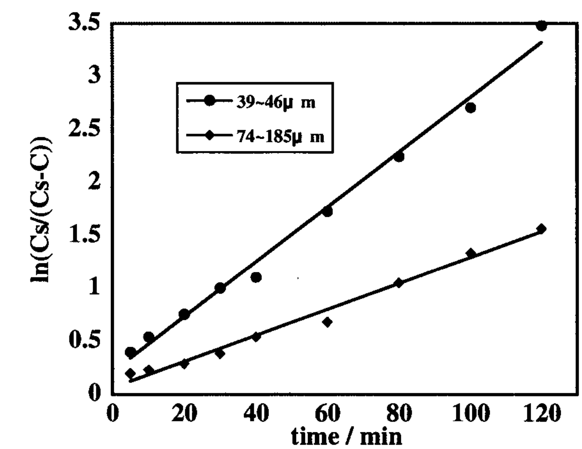

Fig.4. Fitting curves based on the liquid layer diffusion equation for different particle sizes of red mud

(T=20°C,300r/min,0.5g/L)

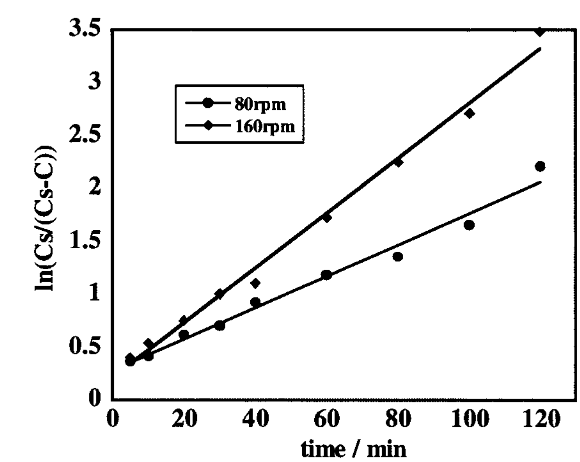

Fig.5. Fitting curves based on the liquid layer diffusion equation at different stirring speeds (particle size ranged in:46~74μm, T=20℃, 0.5 g/L)

Based on the dissolution experimental data of silicon from red mud in pure water at different stirring speed and particles sizes, the fitting results were calculated and depicted in Fig.4 and Fig.5, respectively. All the curves fitted quite well according to the equation (2). It was found that the whole process of dissolution was in agreement with the results of our proposed assumption, suggesting that the whole dissolution process of silicon was controlled by liquid layer diffusion step. Moreover, this simple diffusion model can be used to describe this kind of dissolution process where the extraction rate of substances are quite low, there is negligible change of the particle size, and the particle surface reaches saturation solubility in a very short period of time.

Conclusions

The dissolution process and kinetics of silicon dissolution from red mud in pure water was studied. It was found that the silicon extraction was a quite slow and is a nearly homogeneous dissolution process with the change of particle size negligible after the long dissolution times. In this kind of dissolution system, the concentration of silicon would reach a saturation equilibrium state around the particle surface in a very short time, that is, a saturation layer was quickly established close to the phase interface, and its thickness was affected by stirring speed and so on. Based on the dissolution experimental data for silicon from red mud in pure water, the models are fitted very well according to the equation, suggesting that the whole dissolution process of silicon follows the liquid layer diffusion model.

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