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Effect of Temperature on Iron Leaching from Bauxite Residue by Sulfuric Acid

Zhi-Rong Liu · Kai Zeng · Wei Zhao ·
Ying Li

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Abstract Bauxite residue, as solid waste from alumina production, contains mainly hematite [Fe_2O_3]. Kinetic study of iron leaching of bauxite residue by diluted sulfuric acid at atmospheric pressure has been investigated. The results have been obtained as following: (i) Temperature play an important role in iron leaching from bauxite residue. Higher temperature is favor of Fe (III) leaching from bauxite residue. (ii) The leaching process is applicable to the intra-particle diffusion model and the apparent activation energy of model of leaching is found to be 17.32 kJ/mol.

Keywords Bauxite residue · Fe (III) · Leaching · Temperature

Polymeric iron compounds are becoming popular for water treatment due to their excellent application characteristics (Tang and Stumm 1987; Fan et al. 2002). The most important polymeric iron compounds for this purpose is polymeric ferric sulfate. Generally speaking, manufacturer uses ferric sulfate as the major raw materials to synthesize polymeric ferric sulfate. The main thing is to get cheaper ferric sulfate now.

Over 70 million tons of bauxite residues are generated annually in the world when aluminum is extracted from the principal ore, bauxite. The disposal of such a large quantity of this bauxite residue is expensive (up to 1–2% of the alumina price) due to its volume and alkalinity. Limited storage space for bauxite residue has heightened the need to develop sustainable alternatives for its use or disposal. (Leonardou et al. 2008; Fang and Wang 2004; Kasliwal and Sai 1999). Bauxite residue has been used in absorbents, building materials, catalysts, fillers, pigments and paints (Wang et al. 2008). However, it is noted that iron oxide is the major component of bauxite residue followed by alumina and silica. Its brick red color is due to the iron oxide. Bauxite residue most composed of iron oxide could be a good secondary raw material for ferric sulfate.

The composition of bauxite residue varies from source to source. The aim of this paper was to investigate the possibility of iron recovery from the bauxite residue by sulfuric acid leaching and develop the new application of the bauxite residue. The effect of temperature on the leaching process was studied.

Materials and Methods

Bauxite residue used in the current investigation was collected from Henan Changcheng Aluminum Co. Ltd. Prior to experiments bauxite residue was crashed and screened to <125 μm in order to keep samples even-grained, and then dried in 150°C for 24 h. Bauxite residue leaching procedure was carried out under atmospheric pressure. The experiments on iron leaching in sulfuric acid were conducted in a 500 mL three-necked flat-bottomed reactor, which was attached with a glass stirrer and a thermometer. In all the experiments a constant stirring speed was used to

Z.-R. Liu · K. Zeng · W. Zhao · Y. Li
Department of Applied Chemistry, East China University of Technology, Fuzhou City, Jiangxi 344000, China

Z.-R. Liu (✉)
Key Laboratory of Nuclear Resources and Environment, Ministry of Education, East China University of Technology, Nanchang City, Jiangxi 330013, China
e-mail: liu-zhi-rong-oyx@sohu.com

ensure suspension of the particle. A typical run was carried out as follows: specified amounts of sulfuric acid of known concentration and bauxite residue were loaded into the reactor. HDM-1000 Thermostat electric heating cover from China controlled the temperature of liquid. At the end of the runs, ferric sulfate was prepared through filtration. Solution aliquot was withdrawn periodically during the leaching and separated by centrifuges for determination of leaching ratio through analyzing Fe (III) molar concentration. The resulting leached bauxite residue were washed with water by re-pulping and dried overnight at 150°C. Each analysis was performed in duplicate. Analytically pure sulfuric acid from Agents for Chemicals in Shanghai (China) was used in the whole work.

The initial bauxite residue, as well as the leached bauxite residues and leach liquors were analyzed chemically using a GGX-9 atomic absorption spectrometer made in China. The mineralogical analysis was carried out by X-ray diffraction, using a Philips PW 1710 diffractometer with nickel-filtered CuKα radiation (=1.5405 Å) at the scattering angle (2θ) ranging from 10° to 90° at 0.02°/min scanning speed.

Results and Discussion

The chemical analyses indicated that the bauxite residue contains (by wt.): Fe_2O_3: 64.33, Al_2O_3: 12.19, SiO_2: 14.33, TiO_2: 2.13, CaO: 1.65, Na_2O: 0.66, MgO: 0.41. X-ray analyses confirmed that the initial bauxite residue includes much hematite and the leached bauxite residue contains diaspore mainly. The aluminum in bauxite residue mainly as diasporite and k-feldspar forms is too inert to be leached out in touch with sulfuric acid solution. High ferric sulfate content in the leaching solution could be used to synthesize superior polymeric ferric sulfate.

The leaching ratio of Fe (III) from bauxite residue D is calculated as follows:

$$D = \frac{n_o - n_t}{n_o} \times 100\% \qquad (1)$$

In which D is leaching ratio of Fe (III) from bauxite residue at time t, n_o is initial molar concentration of Fe (III) before the leaching, n_t is remaining molar concentration of Fe (III) after leaching.

The relation between leaching time and leaching ratios of Fe (III) from bauxite residue with H_2SO_4 at different temperature are shown in Fig. 1. As “S-shaped” kinetic curves can be seen in Fig. 1, leaching ratio of Fe (III) increases with the increment of leaching time. At low temperature below 70°C, the increase of leaching rate of Fe (III) are slow and Fe (III) could not be leached out completely compared to higher temperature above 90°C. Enhancement of leaching out of Fe (III) at higher temperature may be attributed to the swelling effect within the internal structure of bauxite residue enabling Fe (III) ions to leach out further and/or activation of the surface of bauxite residue. The iron leaching from bauxite residue is carried out at higher temperatures to increase the overall efficiency of a process as well as to avoid the side reactions.

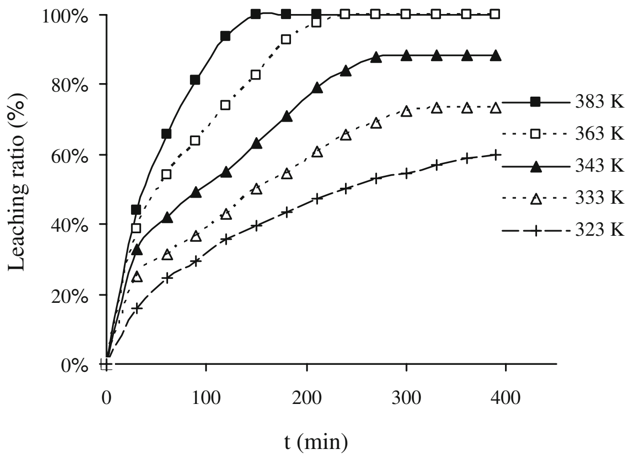

Fig. 1 Effect of leaching time and temperatures on leaching ratio of Fe (III) from bauxite residue $m = 20$ g of bauxite residue; $V = 300$ mL (20%, v/v) of sulfuric acid

As bauxite residue is reacted with H_2SO_4, full neutralization of caustic bauxite residue is achieved. Fe_2O_3 is converted to their respective sulfate according to the following reactions possibly:

$$Fe_2O_3(S) + 6H^+(1) \rightarrow 2Fe^{3+}(1) + 3H_2O(1) \qquad (2)$$

In which s represents solid phase, l represents solution phase.

Under standard condition, equilibrium relationship for leaching reaction can be expressed as:

$$\lg\frac{[Fe^{3+}]^2}{[Fe_2O_3]} = -\frac{\sum v_i \mu_i^0}{RT} + 6\lg[H^+] \qquad (3)$$

In which $[Fe^{3+}]$ is the molar concentration of Fe (III) ion in solution phase; $[Fe_2O_3]$ is the molar concentration of Fe_2O_3 in solid phase; $[H^+]$ is the molar concentration of H^+ ion in solution phase; v_i is stoichiometric number for i component; μ_i^0 is chemical potential for i component under standard condition; R is the gas constant; T is the leaching temperature.

From Eq. 3, it is evident that the amount of Fe (III) leaching increases with increasing temperature, which is in good agreement with the leaching results shown in Fig. 1.

The leaching species are most likely transported from the solid phase to the bulk of the solution phase through an intra-particle diffusion process. The possibility of intra-particle was explored by using the diffusion model (Shubha

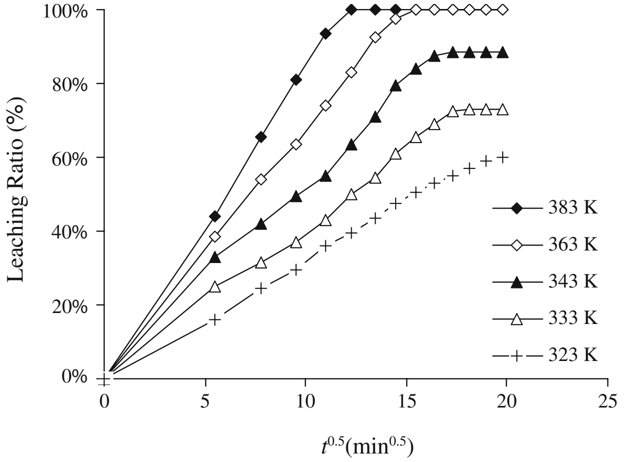

Fig. 2 Intra-particle diffusion plots of Fe (III) from bauxite residue at various temperatures $m = 20$ g of bauxite residue; $V = 300$ mL (20%, v/v) of sulfuric acid

et al. 2001). The rate constant for intra-particle diffusion (K_d) is analogous with Weber Morris equation:

$$D = K_\mathrm{d}\sqrt{t} \tag{4}$$

where a is leaching ratio of Fe (III) from bauxite residue at time t; K_d is the leaching rate constant for intra-particle diffusion of Fe (III) from bauxite residue at certain temperature.

Plots of D versus $t^{1/2}$ are shown in Fig. 2 under various leaching temperatures. All the plots have the same general features that a plateau follows the linear portion. The linear portion is attributed to the intra-particle diffusion and the plateau to the equilibrium.

K_d is obtained from the slope of linear portion of a versus $t^{1/2}$ at certain temperature and parameters of leaching kinetics are shown in Table 1.

K_d value (Table 1) increases with increased temperature indicating that the leaching process is endothermic. The higher temperature is, the shorter is $t_{1/2}$ (the time required for 50% leaching ratio of Fe (III)) value. K_d and temperature can be used to derive a mathematical relationship from Table 1. The relationship with correlation coefficient as high as 0.9921 is:

Table 1 Parameters of leaching kinetics of Fe (III) from bauxite residue at various temperatures

Temperature (K)	$t_{1/2}$ (min)	K_d	r^2
383	31	0.0904	0.9995
363	57	0.0664	0.9979
343	92	0.0521	0.9877
333	141	0.0421	0.9909
323	255	0.0313	0.9927

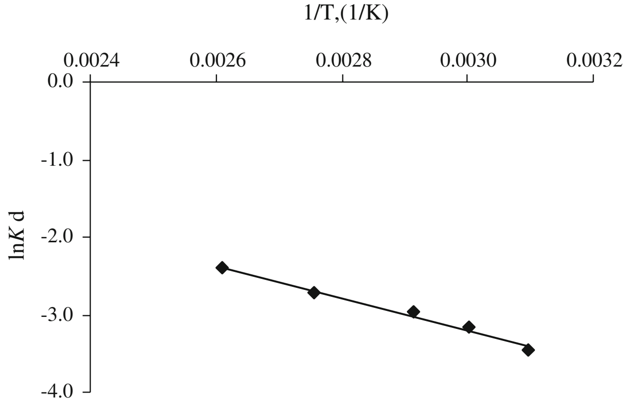

Fig. 3 Plot of Arrhenius curve

$$K_d = 0.00095\,T - 0.2750 \tag{5}$$

Substituting Eq. 5 into Eq. 6 yields:

$$D = (0.00095T - 0.02750)\sqrt{t} \tag{6}$$

D can be expressed as a function of temperature and time successfully according to Eq. 6.

The activation energy (E_a) of the intra-particle diffusion is calculated from the linear plot of lnK_d versus $1/T$ following Arrhenius equation:

$$\ln K_d = \ln A - \frac{E_\mathrm{a}}{RT} \tag{7}$$

where K_d is the leaching rate constant (m^2/min), A is the frequency factor (min^{-1}), E_a is the activation energy (J/mol), R is the universal gas constant (8.314 J/K mol), and T is the leaching temperature (K).

The goodness of the experimental data fit is indicated by the high regression coefficient ($r^2 = 0.9833$) value of the Arrhenius plot (Fig. 3). The apparent activation energy E_a value is found to be 17.32 kJ/mol and the frequency factor A 21.16 min^{-1}. Because E_a in the region of 0 to 20 kJ/mol would generally indicate intra-particle diffusion, E_a of 17.321 kJ/mol in this case may indicate the rate-determining step is intra-particle diffusion. In another similar work, Patermarakis and Paspaliaris (1989) claimed that the leaching of bauxite specimens was controlled by diffusion of the acid through the pores formed by dissolution of hematite along with the estimated activation energy of 19.6 kJ/mol.

Sulfuric acid was used to investigate the iron leaching from bauxite residue. It was found that the iron leaching increased with an increase of temperature and the leaching of bauxite residue was controlled by intra-particle diffusion. The apparent activation energy of model of leaching is found to be 17.32 kJ/mol and the frequency factor 21.16 min^{-1} obtained from the Arrhenius plot. The results obtained, therefore, shows that iron leaching from bauxite residue could be utilized to synthesize polymeric ferric sulfate.

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