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Dissolution kinetics of aluminum and iron from coal mining waste by hydrochloric acid ☆

Li Cui [1], Yanxia Guo [1], Xuming Wang [2], Zhiping Du [1], Fangqin Cheng [1],*

[1] *Institute of Resources and Environment Engineering, Shanxi University, State Environmental Protection Key Laboratory of Efficient Utilization Technology of Coal Waste Resources, Taiyuan 030006, China*
[2] *Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah, Salt Lake City 84112, UT, USA*

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ABSTRACT

The extraction of aluminum from coal mining waste (CMW) is an important industrial process. The two major problems in applications are low aluminum dissolution efficiency and high iron content in the raw material, which affect the quantity and quality of products. To improve the aluminum recovery process, the leaching kinetics of CMW with hydrochloric acid was studied. A shrinking core model was used to investigate aluminum and iron dissolution kinetics. Based on the kinetic characteristics, a process for recovering aluminum was proposed and tested experimentally. It is found that the aluminum leaching reaction is controlled by surface reaction at low temperatures (40–80 °C) and by diffusion process at higher temperatures (90–106 °C). The iron dissolution process is dominated by surface reaction at 40–100 °C. The results show that iron could be dissolved or separated by concentrated hydrochloric acid. Fine grinding will improve aluminum dissolution significantly.

1. Introduction

Coal mining waste (CMW) is the largest industrial solid waste generated from coal preparation plants. Its total discharge in China is estimated at 560 million tons annually. In most cases, CMW contains approximately 18%–32% aluminum oxide (Al_2O_3), 48%–52% silicon dioxide (SiO_2), 2%–8% iron oxide (Fe_2O_3), and about 2% other metal compounds. Most of the CMW is used to manufacture building materials or goes directly to landfill mine goafs [1,2]. It poses a significant threat to the environment because it contains many potentially hazardous substances [3]. One of the most serious environmental problems associated with the unsafe disposal of CMW is the oxidation of the inherent pyrite and consequent generation of acidity [4].

With the increasing demand for metals and decreasing grade of bauxite, extraction of aluminum from CMW is becoming more and more commercially attractive [5–8]. Furthermore, amorphous silica could be prepared from the aluminum leaching residue [9]. The extraction of aluminum and silicon would provide a new approach to utilize CMW.

The dissolution of Al_2O_3 from untreated CMW is low due to its inactive and stable structure and thus CMW activation is needed. The most common method for CMW activation is the thermal treatment at temperatures from 650 to 800 °C [10,11]. Al_2O_3 dissolution is improved by 70% using this method under optimum conditions. However, impurities in CMW are more easily introduced into the filtrate in Al_2O_3 dissolution process after thermal activation, particularly for iron [7]. The presence of iron in the filtrate is detrimental to the quality of aluminum products, such as aluminum chloride hexahydrate and polyaluminum chloride. In addition, the remaining aluminum and iron in leaching residues will limit the production of silica and increase alkaline consumption in the silicon extraction process [12,13]. Therefore, removing iron and promoting aluminum dissolution are greatly significant for fine and step utilization of CMW. It is desirable to understand the dissolution kinetics of aluminum and iron from CMW for further optimizing the leaching process.

Leaching process of CMW with hydrochloric acid can be described as a non-catalytic fluid–solid reaction. The major models developed for these reactions include the first order, shrinking core, shrinking particle, homogeneous and grain models, among which the shrinking core model has been widely accepted in hydrometallurgy for the dissolution kinetics of fluid-solid systems [14–16].

Many studies have been carried out on aluminum dissolution kinetics from coal fly ash, kaolin and clay with shrinking core model [17–19]. Most of them concentrate on coal fly ash, which has the same chemical components as CMW but different mineral constitutes, influencing the

dissolution behavior. The acid leaching process of coal fly ash roasted with KF as assistant was modeled [14], indicating that the aluminum dissolution rate was controlled by chemical reaction and its dissolution percentage reached 92.46%. However, fluoride ions were easily introduced in the following acid leaching process, which has negative effect on the environment. Seidel and Zimmels investigated aluminum leaching mechanism and kinetics for coal fly ash using sulfuric acid [19]. The leaching process followed the shrinking core model. During sulfuric acid leaching process, calcium sulfate formed and precipitated within the pores and on the particle surface, resulting in a self-inhibition effect on mass transfer at the leaching sites. Iron leaching kinetics was also studied. For example, Lee et al. [20] used oxalic acid to dissolve iron oxides from a clay material and found that the dissolution rate increased with oxalate concentrations in the optimum pH range (2.5–3.0). Dissolution of fine pure hematite (105–140 μm) followed a diffusion-controlled shrinking core model. Leaching kinetics for the removal of iron from low grade gibbsite bauxite with HCl was studied [21]. The dissolution of iron followed the first order equation $-\ln(1-\alpha) = kt$, with an apparent activation energy of 81.0 kJ·mol^{-1}. Removal of more than 98% iron from hematite was achieved with about 10% aluminum loss from gibbsite phases of the ore by using 4 mol·L^{-1} acid. As a large and prospective aluminum source, the study on CMW leaching mechanism and kinetics is insufficient. Simultaneous dissolution kinetics of Al_2O_3 and Fe_2O_3 from CMW is rarely found, which is needed to optimize aluminum leaching process and purify aluminum products.

The present study is conducted to investigate Al_2O_3 and Fe_2O_3 dissolution kinetics from CMW using HCl as a leaching medium. The influence of acid concentration and leaching temperature on dissolution kinetics are investigated. Based on Al_2O_3 and Fe_2O_3 dissolution characteristics, a process for recovering Al_2O_3 and removal of Fe_2O_3 is proposed and tested experimentally.

2. Experimental

2.1. Materials

CMW was provided by Lu'an Coal Mining Group (Shanxi, China). The XRD analysis of raw material shows that kaolinite ($Al_2O_3·2SiO_2·2H_2O$) and quartz (SiO_2) are the major mineral phases (Fig. 1). The CMW was crushed and screened to the size fraction of 0.18–0.125 mm and calcined at 700 °C for 2 h for activation. The chemical composition of the calcined material based on XRF analysis is listed in Table 1.
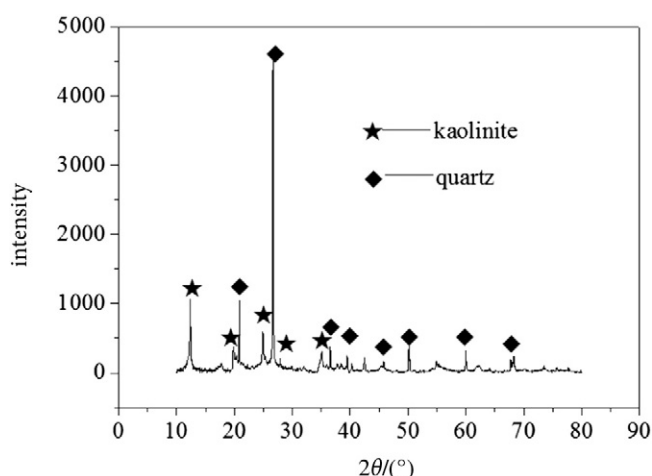

Fig. 1. XRD pattern of raw CMW material.

Table 1
Chemical composition of the calcined CMW sample used in the study

Compounds	Mass composition/%
Al_2O_3	33.89
Fe_2O_3	5.18
SiO_2	52.48
MgO	0.32
CaO	1.38
TiO_2	1.63
K_2O	1.83

Hydrochloric acid (37%, 1.18 g·ml^{-1}) was used as the leaching medium. Desired concentrations of HCl were prepared by dilution with de-ionized water for the leaching process.

2.2. Leaching process

CMW dissolution was carried out in a 500 ml four-necked round-bottom flask placed in a thermostatically controlled water bath, as shown in Fig. 2. A thermometer was fitted to one of the openings. 10 g of calcined CMW was added to 200 ml agitated HCl solution (solid/liquid ratio = 1/20 g·ml^{-1}) at certain temperature. The reaction mixture was stirred at 500 r·min^{-1} throughout the experiment to avoid diffusion of acid across the solid–fluid boundary layer [21,22]. At selected time intervals, 10 ml solution sample was taken using a syringe filter fitted with a membrane of 0.45 μm pore size. The filter residue returned to the flask with an addition of 10 ml HCl solution at the same concentration, so that the solid/liquid ratio was maintained constant at 1/20 g·ml^{-1}. The filtrate was analyzed to determine aluminum and iron contents in the solution by the wet chemical method and the dissolution percentages of Al_2O_3 and Fe_2O_3 were calculated.

2.3. Shrinking core model

The shrinking core model assumes that the reaction products and/or inert matters remaining in the solid phase form a layer of "ash" that encapsulates the unreacted core. The equations of shrinking core model can be expressed as [23]

$$1-3(1-R)^{2/3} + 2(1-R) = K_p t \quad \text{(diffusion controlled process)} \quad (1)$$

$$1-(1-R)^{1/3} = K_c t \quad \text{(chemical reaction controlled process)} \quad (2)$$

with diffusion rate constant $K_p = \frac{6MDC_0}{b\rho r_0^2}$ and reaction rate constant $K_c = \frac{kC_0^n M}{r_0 \rho}$, where R is the fraction of dissolution (%), t is the time (min), D is the diffusion coefficient (cm^2·min^{-1}), C_0 is the initial concentration of HCl solution (mol·L^{-1}), k is the chemical reaction rate constant (cm·min^{-1}), M is the molecular weight of mineral, r_0 is the initial average radius of particles (cm), ρ is the density of CMW (kg·m^{-3}), and b is the stoichiometric coefficient.

3. Results and Discussion

Leaching of CMW in HCl solution is a complicated process with following chemical reactions:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \quad (3)$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \quad (4)$$