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Kinetics on leaching of potassium from phosphorus−potassium associated ore in $HCl-H_3PO_4$ media

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Abstract: In order to relieve the equipment corrosion, reduce chlorine and increase phosphorus contents in leaching solution, the leaching behavior of potassium from phosphorus−potassium associated ore in the mixed acids of hydrochloric acid and phosphoric acid was investigated. The effects of various factors, such as mass fraction of hydrochloric acid, solid-to-liquid ratio, material ratio (CaF_2 dosage (g)/mass of ore (g)) and leaching temperature were comprehensively studied. It was found that the dissolution fraction of potassium can reach more than 86% under the optimum conditions of leaching temperature 95 °C, HCl concentration 10%, leaching time 6 h, solid/liquid ratio 1:5, and material ratio 0.1. In addition, the leaching kinetics of potassium was successfully modeled by a semi-empirical kinetic model based on the classic shrinking core model. The data showed that the leaching process of potassium was controlled by the product layer diffusion and the apparent activation energy for the process was found to be 54.67 kJ/mol over the temperature range from 65 to 95 °C.

Key words: kinetics; leaching; potassium; phosphorus−potassium associated ore; activation energy; K-feldspar

1 Introduction

Potassium is an essential ingredient in the fertilizers. At present, the global production of potash fertilizer is primarily based on the soluble potassium resources. While the soluble potassium resources is rare (<1% of world potassium storage) in China, the storage of insoluble potash ores, such as K-feldspar ($KAlSi_3O_8$), amounts to more than 10 billion tons [1]. Therefore, the economical and effective extraction of potassium from the insoluble potassium deposit has attracted many researchers' attention in China [2].

In recent years, the phosphorus−potassium associated ore with a reserve as much as 800 million tons has been found in Yichang City, China. The phosphorus−potassium associated ore generally contains P_2O_5 (6%−12%) and K_2O (5%−9%), and the simultaneous extraction of phosphorus and potassium to produce PK compound fertilizer may create economic value [3]. In order to prepare PK compound fertilizer, the phosphorus−potassium associated ore should be decomposed firstly. The phosphorus from phosphorus−potassium associated ore existed in the form of fluorapatite can be easily decomposed by acid, while potassium existed in the form of K-feldspar is very difficult to be decomposed by the ordinary acidic or alkaline media due to the high stability of the Al−Si−O tetrahedron structure [4]. As so far, several processes have been developed to extract soluble potassium from K-feldspar, mainly including the following methods: high temperature roasting process [5−7], hydrothermal process [8−12], microbial decomposition process [13,14], low temperature acidic leaching process [15−17]. Among these methods, low temperature acid decomposition method has received much attention in recent decades due to its lower leaching temperature (<120 °C) and higher potassium dissolution fraction (>85%).

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The previous research results have shown that the dissolution fraction of potassium from phosphorus−potassium associated ore in hydrochloric acid solution reached more than 90% by using low temperature acidic leaching process [18]. However, some problems still exist, especially the equipment corrosion, higher chlorine and lower phosphorus contents in leaching solution [3]. In order to alleviate the equipment corrosion, reduce chlorine and increase phosphorus contents in leaching solution, the use of the mixture of hydrochloric acid and phosphoric acid to leach potassium from phosphorus−potassium associated ore is of great interest. However, very limited studies involving the leaching of potassium from phosphorus−potassium associated ore in $HCl-H_3PO_4$ media have been reported. Therefore, it is necessary to investigate leaching kinetics of potassium from the ore in the mixed acids.

In this work, the leaching of potassium from phosphorus−potassium associated ore in $HCl-H_3PO_4$ media at low temperature was studied. The influence of various factors, viz., the mass fraction of hydrochloric acid (w(HCl)), leaching temperature, solid-to-liquid ratio (S/L) and material ratio (CaF_2 dosage (g)/mass of ore (g), M) were systematically investigated. Moreover, the leaching kinetics of potassium was modeled by a classical shrinking core model. Then, the kinetic parameters and activation energy were obtained.

2 Experimental

2.1 Experiment materials

Phosphorus−potassium associated ore was obtained from Yiling district of Yichang City, Hubei Province, China. The chemical analysis of the ore performed by X-ray fluorescence (XRF) is shown in Table 1. The main minerals in the ore determined by X-ray diffractometer (XRD) and XRF characterizations are potassium feldspar ($KAlSi_3O_8$), fluorapatite ($Ca_5(PO_4)_3F$), and silicon dioxide (SiO_2). In this study, hydrochloric acid and phosphoric acid were mixed, and the mass fraction of phosphoric acid was kept at 30% and that of hydrochloric acid was varied.

2.2 Experimental procedure

Leaching experiments were carried out in a round-bottomed split flask with a three-necked top, equipped with a water-cooled condenser. The flask was heated by a thermostat-controlled oil batch which can control the stirring speed with a magnetic stirring apparatus. A typical experimental procedure was performed as follows: the mixed acids of known mass fraction of hydrochloric acid were put into the flask, and then the system was heated to a desired temperature. When the desired temperature reached, 20 g phosphorus−potassium associated ore (0.0385−0.105 mm) and a certain amount of CaF_2 were added into the flask. In the whole experiment, the stirring speed was controlled at 1200 r/min. All the chemical reagents and samples were weighed with an uncertainly of ±0.002 g. Liquid samples (1−1.5 mL) were collected at predetermined time intervals, and filtered using 0.22 μm syringe filters. The clear filtrate was diluted and then analyzed for the concentrations of K^+. The dissolution fraction of K (x) was calculated through the following expression:

$$x=\frac{39\times 2\times V\times C_K}{94\times m\times w(K_2O)} \quad (1)$$

where C_K is the concentration of potassium in the leached solution, V is the volume of the diluted solution, 39 and 94 denote the mole masses of K and K_2O, respectively, m is the mass of the added ore, and $w(K_2O)$ is the mass fraction of K_2O in the ore.

Table 1 XRF analysis of phosphorus−potassium associated ore

Composition	Mass fraction/%
Na_2O	0.216
MgO	0.902
Al_2O_3	13.535
SiO_2	52.25
P_2O_5	5.581
SO_3	4.391
K_2O	8.723
CaO	7.256
MnO	0.0207
Fe_2O_3	3.308
NiO	0.0086
Rb_2O	0.00954
SrO	0.0311
ZrO_2	0.0803
BaO	0.183
Cl	0.034
Loss on ignition	2.568

The mineralogical phase and morphology of the ore were characterized by XRD and scanning electron microscopy (SEM), respectively. XRD patterns were recorded on a diffractometer (using Cu K_α radiation) operating at 40 kV/30 mA. A scanning rate of 0.02 (°)/s was applied to record the patterns in the 2θ angle range from 10 to 70°. The potassium concentrations in the leached solutions were analyzed by atomic absorption spectrometry (AAS, SOLAARM6, America).