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Kinetics of titanium leaching with citric acid in sulfuric acid from red mud

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Abstract: The recovery of titanium with citric acid in sulfuric acid from red mud was put forward to strengthen acid leaching efficiency. The main factors on the recovery of titanium such as citric acid addition, sulfuric acid concentration, leaching temperature, time and liquid-to-solid ratio were studied. The kinetics analysis of titanium leaching from red mud was deeply investigated. The results show that the citric acid could increase the recovery of titanium and decrease the consumption of sulfuric acid. The recovery of titanium was increased from 65% to 82% and the consumption of sulfuric acid was decreased by about 30% with using 5% citric acid. The dissolution of perovskite, brookite, and hematite in red mud could easily be dissolved using citric acid. The acid leaching process was controlled by internal diffusion of shrinking core model (SCM) and the correlation coefficient was above 0.98. The apparent rate constant was increased from 0.0012 to 0.0019 with 5% citric acid at 90 °C. The apparent activation energy of titanium leaching decreased from 39.77 kJ/mol to 34.61 kJ/mol with 5% citric acid.
Key words: red mud; titanium; kinetics; citric acid; acid leaching

1 Introduction

Red mud is a kind of alkaline solid waste from the tailings during alumina production of bauxite [1−3]. About 0.8−1.5 t red muds are generated per ton of alumina and it is estimated that over 70 million tons of the waste are impounded annually in the world [4,5]. Meanwhile, the rising tendency of red mud output is increasing year by year. The disposal of damming up process on red mud is expensive and can cause environmental problems [6−8].

Red mud usually contains many kinds of metals such as Ti, Al, Ca, Na, V and Sc [9−11]. Titanium is a valuable metal which can be extracted from many kinds of minerals using direct acid leaching, alkaline leaching and activation roasting−acid leaching [12−14]. The recovery of titanium from Bayer process red mud was investigated with concentrated sulfuric acid [15]. The sulfuric acid concentration above 6 mol/L was needed and the recovery of titanium was lower than 70% [16]. For example, the extraction of titanium from red mud with sulfuric acid leaching under the condition of atmospheric pressure and without pretreatment was proposed by AGATZINILEONARDOU et al [17]. The recovery of titanium was 64.5% under the condition of sulfuric acid concentration of 6 mol/L, temperature of 60 °C and liquid-to-solid mass ratio of 20:1. Therefore, a lot of strong acid leaching solution was obtained due to the high sulfuric acid concentration and liquid-to-solid ratio [18,19]. However, there are few reports on the new effective agent and kinetics of titanium leaching from red mud.

In order to enhance leaching efficiency and decrease sulfuric acid consumption, the present research work was to investigate the recovery of titanium with citric acid from red mud. Furthermore, the process was scientifically explained using leaching kinetics to confirm titanium recovery from red mud.

2 Experimental

2.1 Materials

The red mud was collected from Henan Province, China. Its particle size distribution is shown in Fig. 1.

It is found that 50% of the red mud was smaller than 5 μm, whereas 100% of the sample was smaller than 33 μm. The sample was very fine and did not need to be

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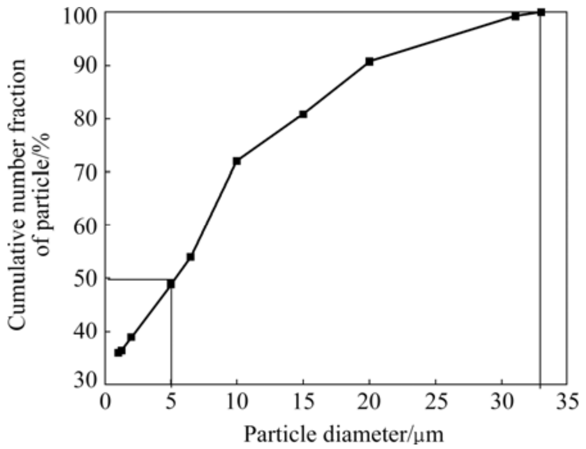

Fig. 1 Particle size distribution of red mud

crushed for acid leaching. The sample was assayed using inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the result is given in Table 1.

Table 1 Main chemical composition of red mud (mass fraction, %)

TiO_2	Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	MgO	Sc_2O_3	V_2O_5
6.64	10.63	22.31	18.92	20.46	5.72	2.04	0.016	0.42

It is shown that the composition of this red mud complex contained many metallic oxides such titanium, aluminum, ferrum, calcium and vanadium oxides. The XRD pattern of the red mud sample is depicted in Fig. 2.

It is indicated that the main minerals in the red mud were perovskite, brookite, hematite, calcite, cancrinite, quartz and muscovite.

The analytical purity chemical reagent including citric acid and sulfuric acid from Dengke Chemical Reagent Technology Co., Ltd., was used. The water used in this work was distilled water.

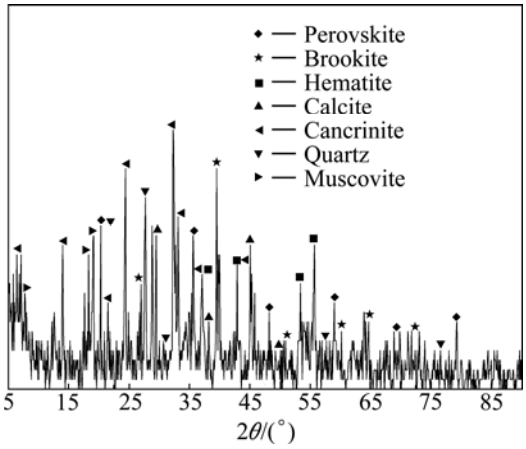

Fig. 2 XRD pattern of red mud sample

2.2 Methods

The sample was firstly dried at 95 °C for 12 h in a TE-DO130 drying oven (China), which was taken out of the drying oven and then cooled further to room temperature. Then 20 g dried sample was mixed citric acid with the sulfuric acid solution of different concentrations. Then, the ore slurry was stirred using a KX79-1 magnetic heating mixer (China) at the speed of 300 r/min under different conditions of time, temperature and liquid-to-solid ratio. The acid leaching solution was collected by filtration with a SHB-IIIA vacuum suction filter (China). The solid residue was dissolved in hydrofluoric acid solution and then the content of titanium was determined by ICP-AES. The recovery of titanium was calculated by the following equation.

$$\alpha = \frac{q-p}{q} \times 100\% \quad (1)$$

where α is the recovery of titanium, q is the titanium quantity of sample and p is the titanium quantity of final residue.

3 Results and discussion

3.1 Effect of citric acid

The effect of citric acid addition on the recovery of titanium is shown in Fig. 3 under the condition of sulfuric acid concentration of 5 mol/L, liquid-to-solid ratio of 5:1, temperature of 90 °C and reaction time of 60 min.

It can be observed that the recovery of titanium increased with increasing the citric acid addition. The increasing rate was sharp in low citric acid addition range, and became mild in citric acid addition ratio range. The recovery of titanium could reach 82% with adding 5% citric acid.

3.2 Effect of sulfuric acid concentration

The effects of sulfuric acid concentration without

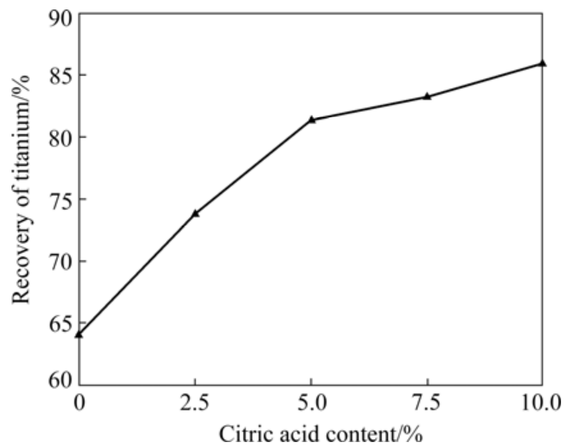

Fig. 3 Effect of citric acid addition on recovery of titanium

and with 5% citric acid on recovery of titanium are illustrated in Fig. 4 under the condition of liquid-to-solid ratio of 5:1, temperature of 90 °C and reaction time of 60 min.

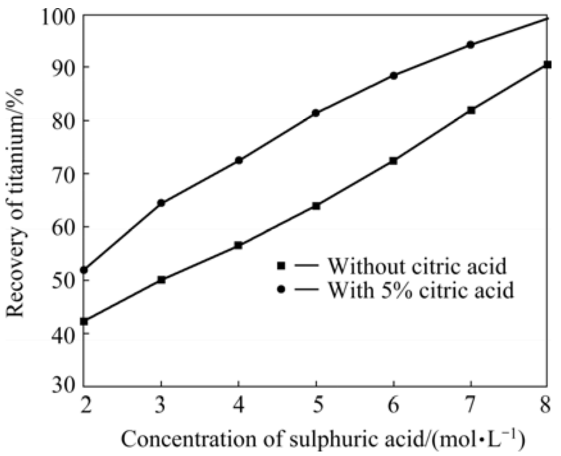

Fig. 4 Effect of sulfuric acid concentration on recovery of titanium

It can be seen from Fig. 4 that the 82% of titanium recovery could be obtained with 7 mol/L sulfuric acid, but only 5 mol/L sulfuric acid was needed with adding 5% citric acid. The recovery of titanium was increased and the increase tendency was symmetrical with increasing sulfuric acid concentration. Furthermore, the sulfuric acid consumption was decreased by 30% with adding 5% citric acid.

3.3 Effect of liquid-to-solid ratio

The effects of liquid-to-solid ratio on recovery of titanium at different leaching time without and with 5% citric acid are shown in Fig. 5 and Fig. 6, respectively under the condition of sulfuric acid concentration of 5 mol/L and temperature of 90 °C.

It is indicated that the recovery of titanium increased with increasing the liquid-to-solid ratio in Fig. 5 and Fig. 6. The increase tendency was sharp at low liquid-to-solid ratio and leaching time range. The recovery of titanium could increase from 45% to 60% with increasing liquid-to-solid ratio from 3:1 to 5:1 at leaching time of 60 min without citric acid. The recovery of titanium was 79% with liquid-to-solid ratio of 9:1 at leaching time of 60 min. The increase tendency of titanium recovery with 5% citric acid was similar to that without citric acid. The recovery of titanium was 82% at liquid-to-solid ratio of 7:1 with adding 5% citric acid. Therefore, the citric acid could not only decrease the sulfuric acid concentration, but also reduce the liquid-to-solid ratio in the acid leaching process.

3.4 Effect of leaching temperature

The effects of leaching temperature on recovery of titanium at different leaching time without and with 5% citric acid are given in Fig. 7 and Fig. 8, respectively under the condition of sulfuric acid concentration of 5 mol/L and liquid-to-solid ratio of 5:1.

It can be observed that the recovery of titanium increased sharply with increasing temperature from

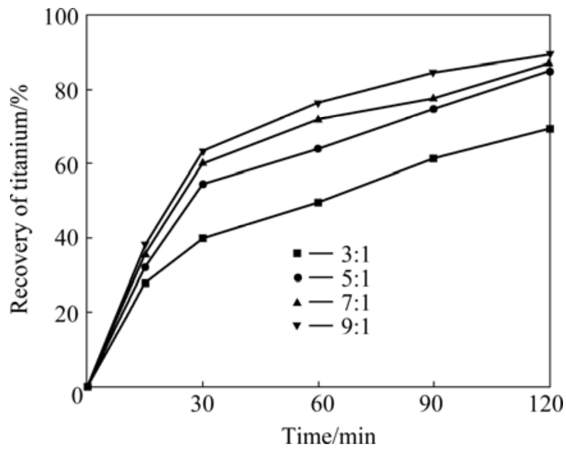

Fig. 5 Effect of liquid-to-solid ratio on recovery of titanium without citric acid

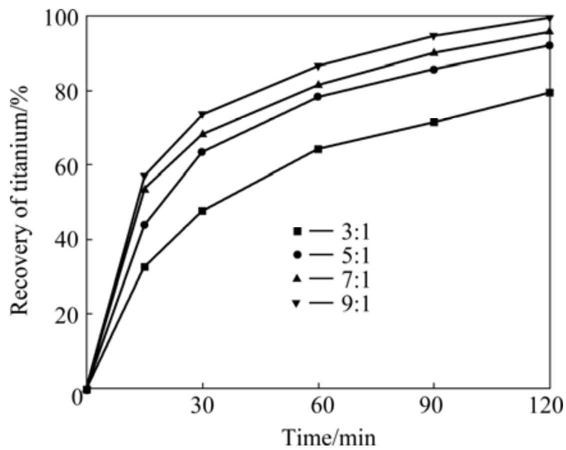

Fig. 6 Effect of liquid-to-solid ratio on recovery of titanium with 5% citric acid

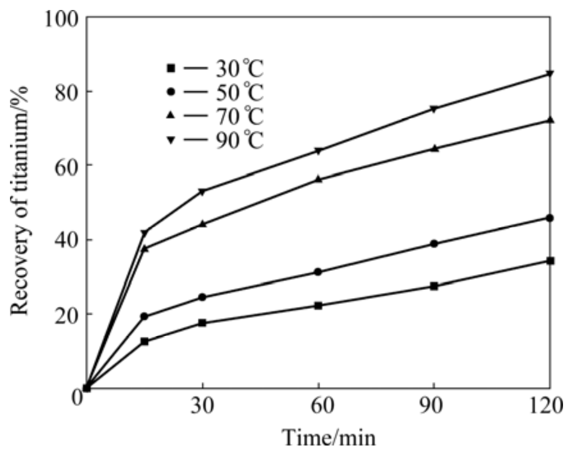

Fig. 7 Effect of leaching temperature on recovery of titanium without citric acid

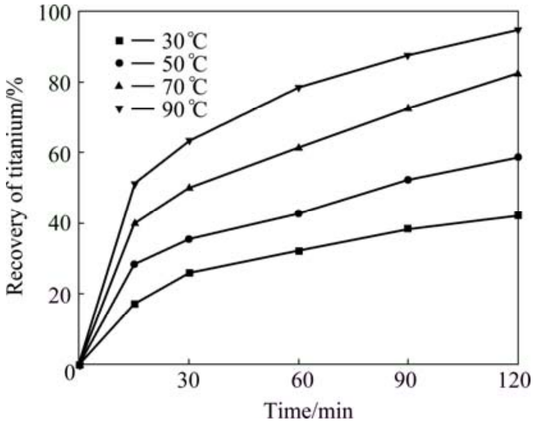

Fig. 8 Effect of leaching temperature on recovery of titanium with 5% citric acid

30 °C to 90 °C. The titanium recovery increased from 20% to 65% with increasing temperature from 30 °C to 90 °C at leaching time of 60 min, whereas the values were 30% and 82% at leaching temperature of 30 °C and 90 °C with adding 5% citric acid in Fig. 7 and Fig. 8. It can be also explained that the reaction rate of acid leaching with citric acid was quicker. Furthermore, the increasing rate of the recovery of titanium was rapid first and then became mild.

3.5 Kinetics analysis of titanium leaching

It is important to establish a quantitative measurement of the leaching kinetics and mechanism to confirm the leaching process. The XRD pattern of leaching residue of red mud is shown in Fig. 9.

It can be seen that perovskite, brookite and hematite have been dissolved and quartz was nearly not dissolved in red mud with sulfuric acid, where some anhydrites existed due to the dissolution of perovskite and brookite. However, in the leaching process with citric acid, the recovery of titanium was increased by accelerating the dissolution of perovskite and brookite, where the phase

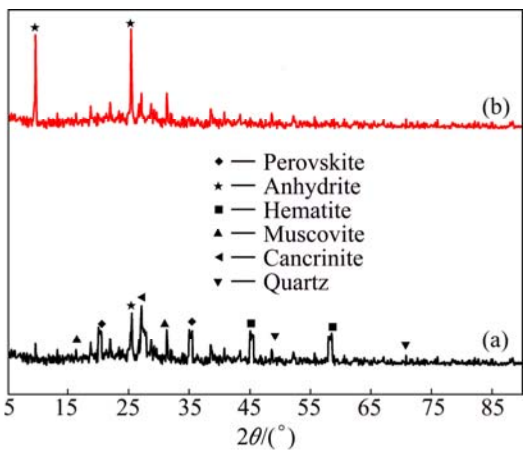

Fig. 9 XRD patterns of leaching residues: (a) Without citric acid; (b) With 5% citric acid

of anhydrite was enhanced with 5% citric acid. Furthermore, the residue existed after the leaching process. Therefore, the experimental data can be analyzed using the SCM [20].

According to the SCM, assuming that the leaching process is controlled by the internal diffusion, the following expression of leaching kinetics can be used:

$$K_a t=[1-2\alpha/3-(1-\alpha)^{2/3}] \quad (2)$$

However, assuming that the leaching process is controlled by the chemical reaction, the following expression can be applied for the leaching kinetics:

$$K_b t=[1-(1-\alpha)^{1/3}] \quad (3)$$

where t is reaction time, α is titanium recovery, K_a is rate constant of internal diffusion, K_b is rate constant of chemical reaction.

Two controlling steps of the SCM were investigated under different liquid-to-solid ratios without citric acid. The results are shown in Fig. 10.

According to Figs. 10(a) and (b), the control of internal diffusion fitted the leaching data well at different liquid-to-solid ratios. As the leaching process was controlled by internal diffusion, the main factor was the internal diffusion rate of sulfuric acid into particles

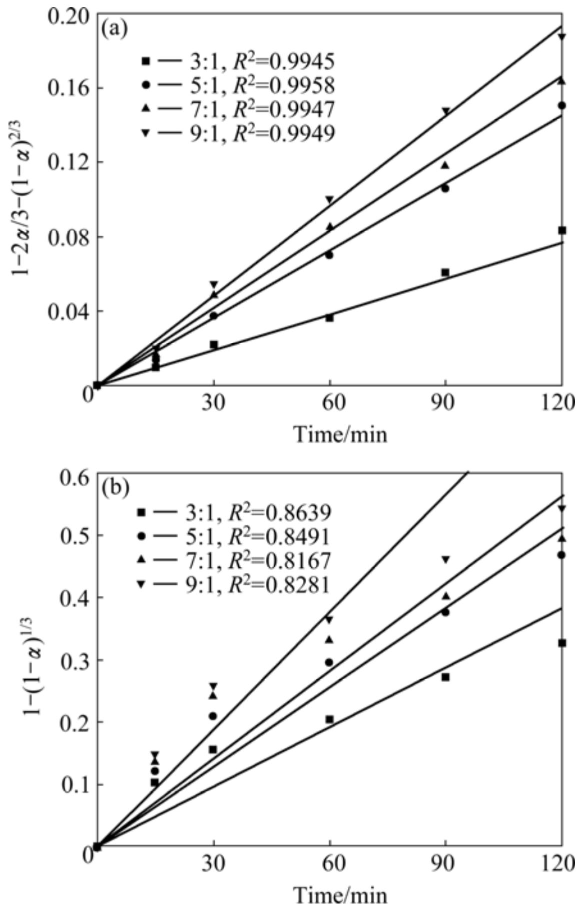

Fig. 10 Plots of $1-2\alpha/3-(1-\alpha)^{2/3}$ (a) and $1-(1-\alpha)^{1/3}$ (b) versus time at different liquid-to-solid ratios without citric acid

interior. The internal diffusion rate increased with increasing sulfuric acid and leaching temperature.

Two controlling steps of the SCM were investigated under different liquid-to-solid ratios with adding 5% citric acid. The results are indicated in Fig. 11.

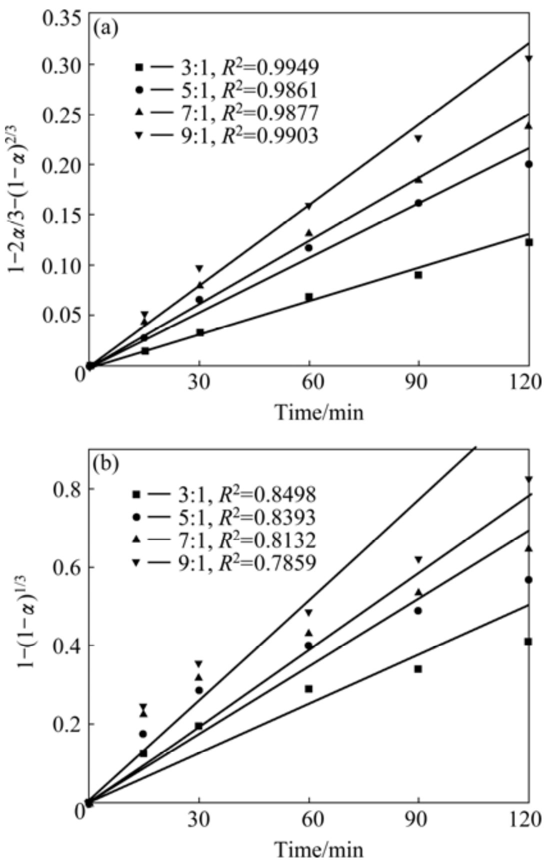

Fig. 11 Plots of $1-2/3\alpha-(1-\alpha)^{1/2}$ (a) and $1-(1-\alpha)^{1/3}$ (b) versus time at different liquid-to-solid ratios with 5% citric acid

According to Figs. 11(a) and (b), the control of internal diffusion still fitted the leaching data well at different liquid-to-solid ratios with adding citric acid. Therefore, the apparent activation energy and reaction rate constant of titanium leaching were needed to investigate to illustrate the effect of citric acid on titanium extraction from red mud.

3.6 Reaction rate constant and apparent activation energy of titanium leaching

The internal diffusion controlling steps of the SCM were investigated under different temperatures without and with adding 5% citric acid. The results are shown in Fig. 12.

It can be seen that the control of internal diffusion also fitted the leaching data well and the correlation coefficient (R^2) was larger than 0.98 at different temperatures. The apparent rate constants of acid leaching process were 0.0001, 0.0002, 0.0008 and 0.0012 at 30, 50, 70 and 90 °C, respectively. However, those were 0.0002, 0.0005, 0.0011 and 0.0019, respectively with adding 5% citric acid. The apparent rate constant increased with increasing the leaching temperature, and the apparent rate constant of acid leaching with citric acid was higher than that without citric acid.

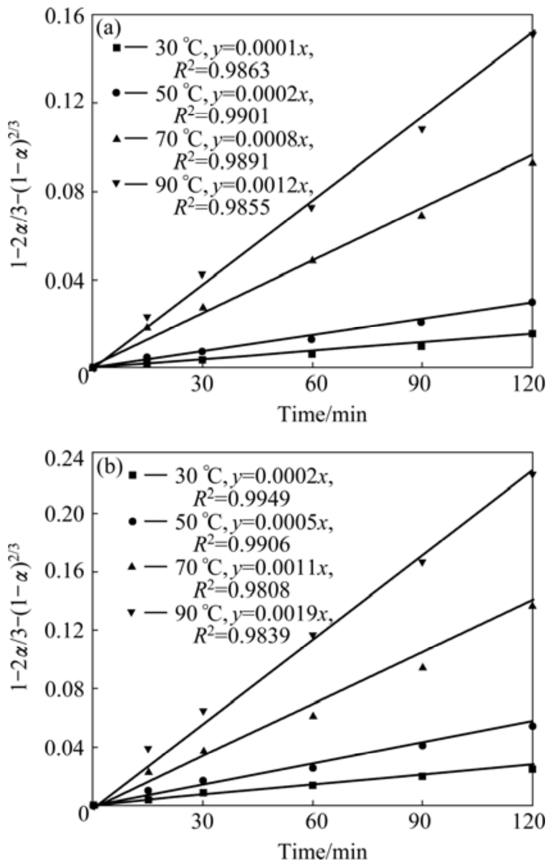

Fig. 12 Plots of $1-2\alpha/3-(1-\alpha)^{2/3}$ versus time at different temperatures without (a) and with 5% citric acid (b)

According to the speed constants at different temperatures without and with citric, the plots of ln K_a versus temperature were investigated. The results are indicated in Figs. 13 and 14, respectively.

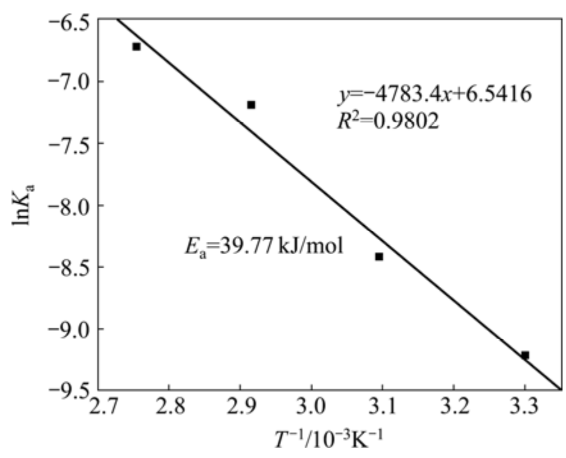

Fig. 13 Plots of ln K_a versus temperature of titanium leaching without citric acid

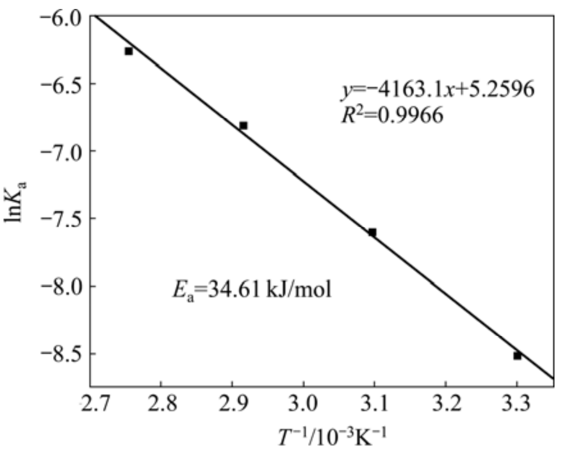

Fig. 14 Plots of ln K_a versus temperature of titanium leaching with 5% citric acid

It can be observed that the correlation coefficient (R^2) was above 0.98 at different temperatures. The apparent activation energies (E_a) of titanium leaching without and with citric acid were 39.77 kJ/mol and 34.61 kJ/mol by the calculation. The decrease of apparent activation energy can effectively enhance the leaching process based on the theory of kinetics.

4 Conclusions

1) The recovery of titanium reached 82% under the conditions of citric acid of 5%, sulfuric acid concentration of 5 mol/L, temperature of 90 °C, liquid-to-solid ratio of 5:1 and time of 60 min. The XRD patterns of red mud and leaching residue showed that the citric acid could enhance the dissolution of perovskite and brookite.

2) The acid leaching process was controlled by internal diffusion and the correlation coefficient was above 0.98 using SCM. The speed constant and E_a of titanium leaching were 0.0019 and 34.61 kJ/mol with 5% citric acid at 90 °C, which resulted in the increase of titanium recovery.

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柠檬酸助浸提取赤泥中钛的动力学

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摘　要：在硫酸体系中，采用柠檬酸助浸提取赤泥中的钛，以提高钛的浸出效率。考察柠檬酸用量、硫酸浓度、浸出温度、反应时间和液固比等因素对钛浸出率的影响。研究赤泥浸出提钛过程的动力学理论。结果表明：在赤泥浸出过程中添加柠檬酸可显著提高钛的回收率和降低硫酸消耗。通过添加 5%的柠檬酸，钛的浸出率从 65%提高至 82%，硫酸消耗降低 30%，赤泥中的钙钛矿、板钛矿和赤铁矿更容易溶解溶出。动力学研究表明：赤泥助浸酸浸提钛过程受未反应收缩核模型的扩散步骤控制，线性相关系数大于 0.98。通过添加 5%的柠檬酸，可使赤泥酸浸提钛表观速率常数从 0.0012 提高至 0.0019，表观活化能由 39.77 kJ/mol 降至 34.61 kJ/mol。

关键词：赤泥；钛；动力学；柠檬酸；酸浸

(Edited by Yun-bin HE)