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Reaction kinetics of roasting high-titanium slag with concentrated sulfuric acid

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Abstract: A novel method of roasting high-titanium slag with concentrated sulfuric acid was proposed to prepare titanium dioxide, and the roasting kinetics of titania was studied on the basis of roasting process**.** The effects of roasting temperature, particle size, and acid-to-ore mass ratio on the rate of roasting reaction were investigated. The results showed that the roasting reaction is fitted to a shrinking core model. The results of the kinetic experiment and SEM and EDAX analyses proved that the reaction rate of roasting high-titanium slag with concentrated sulfuric acid is controlled by the internal diffusion on the solid product layer. According to the Arrhenius expression, the apparent activation energy of the roasting reaction is 18.94 kJ/mol.

Key words: roasting kinetics; high-titanium slag; concentrated sulfuric acid; titania

1 Introduction

Titanium dioxide is an important inorganic chemical material, and is extensively used in white pigment, paper, plastics, rubbers, porcelain, and fibers, etc [1−4]. The main processes for the production of titanium dioxide are sulfate process and chloride process. In the sulfate process, titanium sulfate solution is subsequently hydrolyzed in highly acidic solutions, and then the precipitate of hydrous titanium oxides is obtained. The comprehensive management of waste acid and by-product of copperas are the most fatal weakness in the sulfate process [5−8]. On the other hand, the chloride process requires a feedstock of high TiO_2 grade and must satisfy the content limit of MgO+CaO less than 1.5%. Moreover, it is a high energy consuming process [9−11]. All the above-mentioned shortcomings prevent the development of the chloride process in industry. Therefore, it is significant to put forward novel technique and method for the production of titanium dioxide.

The reserve volume of vanadium−titanium magnetite resources is sufficient in Panxi region of Sichuan Province, China. In the course of the smelting of pig iron, titanium is discharged into the blast furnace slag, which pollutes the environment seriously [12−15]. High-titanium slag contains a large number of valuable metals, such as silicon, aluminium, calcium. Therefore, it is very meaningful to realize the comprehensive utilization of high-titanium slag. The procedure of extracting titanium dioxide from high-titanium slag can reduce a step of elimination of copperas and therefore the energy consumption is decreased consequently. It is apparent that the productivity is promoted and the pollution is relieved [16−18]. Hence, the high-titanium slag is adopted as the basic high-quality raw materials in titanium industry, which has a certain economic value.

The presented method of roasting high-titanium slag with concentrated sulfuric acid in this work has the advantages of saving time, low consumption of acid and high acidolysis rate. The more important term is that the waste sulfuric acid can be recycled. The effects of reaction conditions, such as roasting temperature, particle size and acid-to-ore mass ratio, on the reaction rate of roasting high titanium slag with concentrated sulfuric acid were considered sufficiently and analyzed. Furthermore, the appropriate kinetic equation and the rate-controlling step of roasting reaction were derived. Finally, the reaction mechanism was discussed in detail.

2 Experimental

2.1 Materials

Titanium slag after crushing and ball milling

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was used in the experiment. The chemical compositions of the high-titanium slag are listed in Table 1. The main component of titanium slag is TiO_2, and its content is 48.65%. All the chemical reagents were of analytical grade, and deionized water was used throughout the experimental process.

Table 1 Chemical compositions of high-titanium slag (mass fraction, %)

TiO_2	Al_2O_3	Fe	SiO_2	MgO	CaO	Mn
48.65	14.30	3.71	17.55	7.50	5.70	0.77

The mineralogical phases of the high-titanium slag were investigated by X-ray powder diffraction. The XRD pattern shown in Fig. 1 indicates that the main crystalline phases of the high-titanium slag are anosovite solid solution of magnesium and iron $(Mg_{0.5}Fe_{0.5})Ti_2O_5$ and complex silicate phase $Al_2Ca(SiO_4)_2$. FeO and MgO in titanium slag are beneficial to the increase of acidolysis rate of titanium slag.

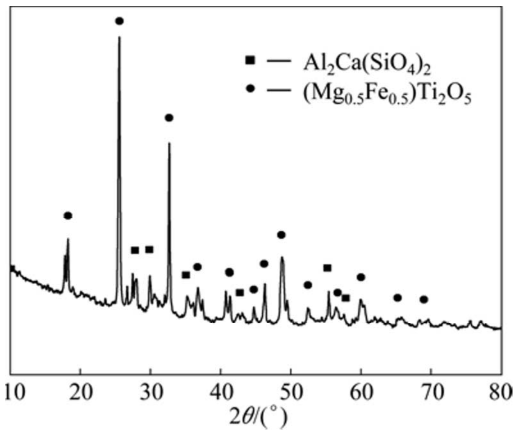

Fig. 1 XRD pattern of high titanium slag

2.2 Procedure

Experiments were performed in a resistance wire heating furnace. The concentrated sulfuric acid and high-titanium slag were homogeneously mixed in the porcelain crucibles. Then the crucibles were put into the resistance wire heating furnace and heated. When the temperature reached the predetermined temperature, we began to activate the timing device. The porcelain crucible was taken out at specified time and cold water was added quickly in order to stop the reaction immediately, with free access to air in the whole process. The temperature of the resistance wire heating furnace was controlled by a programmable temperature controller, with a precision of ±1 °C. The roasting product was leached by water (leaching conditions: temperature 70 °C, solid-to-liquid ratio 1:4, and stirring time 1 h). The extraction rate of TiO_2 was determined by the ammonium ferric sulfate dodecahydrate titration. The calculating formula of the extraction rate of TiO_2 is expressed as

$$x(TiO_2)=\frac{m'(TiO_2)}{m(TiO_2)} \tag{1}$$

where $x(TiO_2)$ is the extraction rate of TiO_2; $m'(TiO_2)$ is the mass of TiO_2 in the filtrate; $m(TiO_2)$ is the total mass of TiO_2 in high-titanium slag.

3 Results and discussion

3.1 Effect of temperature

The influence of roasting temperature on the reaction rate of high-titanium slag with concentrated sulfuric acid was investigated in the temperature range of 250−310 °C, with acid-to-ore mass ratio of 2:1 and particle size of 45−48 μm. Figure 2 shows that temperature has a significant effect on the reaction rate of roasting high-titanium slag. The extraction rate of TiO_2 increases rapidly with the increase of temperature.

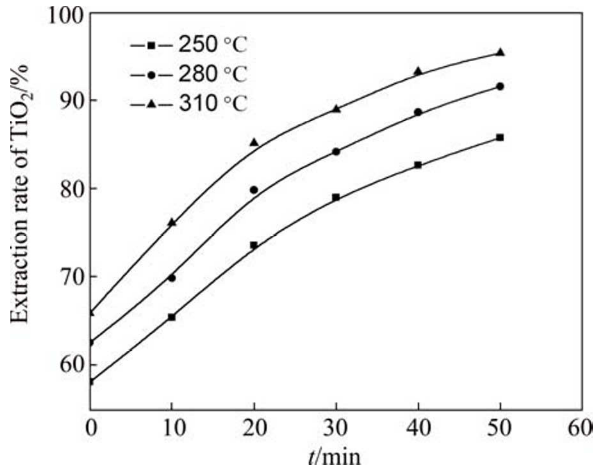

Fig. 2 Relationship between extracting rate of TiO_2 and time at different temperatures

In order to determine the kinetic parameters and rate-controlling step for roasting high-titanium slag with concentrated sulfuric acid, the experimental data presented in Fig. 2 were analyzed on the basis of the shrinking-core model. The experimental data were substituted into the Crank−Ginsting−Braunshtein's kinetic equation [19−22]:

$$1+2(1-x)-3(1-x)^{2/3}=Kt \tag{2}$$

where x is the extraction rate of TiO_2; K is the apparent rate constant; t is the reaction time. The corresponding relationship between the value of $1+2(1-x)-3(1-x)^{2/3}$ and the roasting time t is described in Fig. 3, which shows that the linear relationship between $1+2(1-x)-3(1-x)^{2/3}$ and roasting time t is significant. The results indicate that