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Technical note

Beneficiation of titania by sulfuric acid pressure leaching of Panzhihua ilmenite

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A B S T R A C T

The beneficiation of titania (TiO_2) by sulfuric acid (H_2SO_4) pressure leaching of Panzhihua ilmenite was investigated. The reaction temperature, H_2SO_4 concentration, and concentration of ferrous ions (Fe^{2+}) had significant effects on the enrichment of TiO_2. With increasing reaction temperatures, the dissolution of iron from ilmenite was enhanced, while the titanium loss was reduced. Increasing the concentration of Fe^{2+} had an adverse effect on the beneficiation of TiO_2. In contrast, the dissolution of iron from ilmenite was accelerated by increasing concentrations of H_2SO_4, up to 40 wt.% H_2SO_4. SEM analyses of the leach residues under different leaching conditions indicated that severe agglomeration occurred among the primary hydrolysate particles at high concentrations of H_2SO_4 or with the addition of ferrous sulfate ($FeSO_4$). Furthermore, a compact layer was formed on the surface of unreacted ilmenite particles, thus retarding the ilmenite leaching. The agglomeration might have resulted from the adsorption of H_2SO_4 on the primary particle surfaces, as revealed by energy-dispersive X-ray spectroscopy (EDX) and thermogravimetric analysis (TGA). The optimal conditions for the beneficiation process were as follows: H_2SO_4 concentration 40 wt.%, acid/ore mass ratio 2:1, reaction temperature 150 °C, and reaction time 3 h. Thus, a Ti-rich material with a TiO_2 content of ~85 wt.% was obtained. Moreover, the results demonstrated the technical feasibility of upgrading Panzhihua ilmenite in 40 wt.% sulfuric acid obtained by concentrating the diluted acid waste discharged from the sulfate TiO_2 process.

1. Introduction

Titania (TiO_2) is the most important white pigment and is widely used in coatings, plastics, paper, printing ink, chemical fibers, and the cosmetics industry (McNulty, 2007). There are two different commercial processes for the production of TiO_2, i.e., the chloride process and sulfate process. The current annual production capacity of titanium oxide pigment worldwide is approximately 6.5 million tonnes. More than 60% of TiO_2 is produced by the chloride process, while the rest is produced by the sulfate process (Li and Liang, 2007). The chloride process requires Ti-enriched feedstocks with high TiO_2 contents, including natural rutile, synthetic rutile, and titanium slag. Generally, synthetic rutile and titanium slag are derived from ilmenite. The sulfate process can directly employ titaniferous ores with low titanium contents, such as ilmenite, as feedstocks. However, more than 30% of the sulfate TiO_2 production factories recently shifted to using Ti-enriched feedstocks to reduce $FeSO_4$ and hydrolytic spent acid discharge (Sahu et al., 2006). Ilmenite and natural rutile are two primary natural titaniferous ores. However, natural rutile reserves constitute less than one-tenth of those of ilmenite (Itoh et al., 2006). Therefore, the development of various processes to upgrade the TiO_2 from ilmenite is of great importance.

Several processes including the smelting process, the reduction and corrosion process (also called the Becher process), and the acid leaching process have been developed for the beneficiation of TiO_2 from ilmenite. Among them, the smelting process is an energy-consuming process that can only remove iron impurities (Natziger and Elger, 1987). The product derived from the smelting process is called titanium slag and usually has a TiO_2 content of >85%. On the other hand, the products obtained by the other processes are called synthetic rutile and typically have a TiO_2 content of >92%. The Becher process is an inexpensive and environmentally friendly process. However, it is only suitable to upgrade beach sand ilmenite with low calcium and magnesium contents (Bracanin et al., 1980; Cassidy et al., 1986; Farrow et al., 1987; Hoecker, 1994; Reaveley, 1980).

The acid leaching processes include HCl and H_2SO_4 leaching. Normally, a high-temperature pretreatment of ilmenite, either by carbothermic reduction or by sequential oxidation and reduction, is an indispensable step prior to the leaching treatment. The beneficiation of TiO_2 by HCl leaching (the so-called Benelite process) has been widely studied. In this process, ferric irons (Fe^{3+}) are carbothermically reduced to ferrous iron (Fe^{2+}) and are subsequently dissolved in dilute hydrochloric acid (Sinha, 1978; Walpole, 1997). Lasheen (2005) and Mahmoud et al. (2004) both studied the effect of metallic iron reductants on the HCl leaching of ilmenite and found that the leaching of iron and the hydrolysis of titanium ions were substantially enhanced. To moderate the

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leaching conditions, Akhgar et al. (2010) and our group (Li et al., 2008b) investigated the effect of mechanical activation on the HCl leaching of ilmenite. We ascertained that mechanical activation facilitated the leaching of iron from the ilmenite matrix. The TiO_2 content of the resultant synthetic rutile was more than 91 wt.%. Industrial usage of the HCl leaching process is limited because HCl corrodes the production equipment, despite the advantages of the process including high efficiency, easy regeneration, and recyclability of HCl.

The H_2SO_4 leaching process is less efficient in removing impurities from ilmenite than the HCl leaching process. However, the H_2SO_4 waste discharged from the sulfate TiO_2 process can be utilized. Moreover, H_2SO_4 corrodes the production equipment to a lesser degree than HCl. An example of a typical H_2SO_4 leaching process is the Kataoka process (Kataoka and Yamada, 1973) in which Fe^{3+} ions in ilmenite are carbothermically reduced to the Fe^{2+} form at 900–1000 °C, followed by pressure leaching using ~20 wt.% H_2SO_4 at 120–130 °C. To circumvent the energy-consuming reduction step at high temperatures, a mechanical activation pretreatment of Panzhihua ilmenite was utilized as an alternative (Li and Liang, 2007). An iron extraction over 90% was achieved with 5–20 wt.% H_2SO_4 under atmospheric pressure to prepare high-grade synthetic rutile. However, the conditions of the mechanical activation included ball milling times of at least 4 h under an oxygen-free atmosphere, resulting in an overall uneconomic process.

The TiO_2 output in China reached 1.89 million tons in 2012 (Deng, 2013), of which more than 95% was manufactured using the sulfate process (Deng et al., 2003). Approximately 12 million tons of hydrolytic waste H_2SO_4 with a concentration of ~20 wt.% was discharged annually (Tang, 2000). Consequently, it is a great challenge to utilize the waste H_2SO_4 in the TiO_2 industry in China. Panzhihua deposits are one of the world's largest rock-type ilmenite reserves, and they account for approximately 93% of the titanium reserve in China (Liang et al., 2010). Compared to beach sand ilmenite, rock ilmenite has a better acid solubility due to the absence of rutile and pseudorutile ($Fe_2Ti_3O_9$), which stem from the weathering of ilmenite ($FeTiO_3$). In this study, the beneficiation of TiO_2 from Panzhihua ilmenite through sulfuric acid pressure leaching was investigated. Specifically, the effect of reaction temperature, H_2SO_4 concentration, acid/ore ratio, leaching time, and the concentration of Fe^{2+} on the pressure leaching process were systematically examined. The resulting Ti-rich materials were characterized, and the reaction mechanism was discussed.

2. Experimental

2.1. Materials

An ilmenite concentrate was provided by the Titanium Company of Pangang Group Corp. (Panzhihua, China). The chemical composition of the ilmenite is shown in Table 1. X-ray diffraction (XRD) analysis of the ore powder confirmed that the major mineral constituent of the ore was hexagonally structured $FeTiO_3$. The −45 μm fraction of the ore was utilized. All chemicals, including sulfuric acid and ferrous sulfate, were of analytical reagent grade and were used as received without further purification.

2.2. Leaching experiments

Ilmenite was leached in a 700-mL lead-lined stainless steel pressurized reactor. It was stirred with a magnetic agitator and heated using an electric furnace. Its temperature was well controlled by an intelligent temperature control device. In each experiment, 100–200 mL of H_2SO_4 and a given amount of ilmenite were added to the reactor. For the experiment of effect of concentration of Fe^{2+} ions, a certain amount of $FeSO_4$ was introduced at the same time. The reactor was then sealed and heated to the desired temperature at 2 °C/min with stirring at 300 rpm. Subsequently, the reactor was kept at this temperature for a given period of time with a temperature fluctuation of ±2 °C. Following the pressure leaching, the autoclave was cooled to approximately 80 °C. The reactor was opened, and the slurry was filtered and washed. The filtrate was diluted to a set volume to determine the concentration of Ti and Fe ions. To avoid the possible hydrolysis of titanium ions, washing and dilution were conducted with 10 wt.% H_2SO_4. The leach residues were washed thoroughly with copious amounts of distilled water and dried at 100 °C for 2 h prior to characterization. A titanium-rich material was obtained by calcination of the leach residues at 1000 °C for 1 h.

Table 1
Chemical composition of the ilmenite used in this study (wt.%).

TiO_2	FeO	Fe_2O_3	SiO_2	MgO	Al_2O_3	CaO	V_2O_5	MnO_2
46.8	37.6	5.1	4.9	1.5	1.6	1.4	0.1	0.9

2.3. Analysis and characterization

The concentrations of titanium and iron ions in the filtrate were determined by redox titrations of ammonium ferric sulfate ($NH_4Fe(SO_4)_2$) and potassium dichromate ($K_2Cr_2O_7$), respectively. For the determination of titanium and iron contents in the leach residues, the residues were melted with sodium dioxide (Na_2O_2) at 700 °C and then leached with dilute hydrochloric acid. The resulting solution was then analyzed by the aforementioned redox titration method.

XRD was performed using a DX-2007 X-ray diffraction spectrometer (Danton, China) operating with a Cu Kα radiation source filtered with a graphite monochromator at a frequency of $\lambda = 1.54$ nm. The continuous scanning mode with a 0.03-s interval and 0.05-s set time was used to collect the XRD patterns. The voltage and anode current were 40 kV and 30 mA, respectively.

The surface morphologies of the ilmenite samples were observed before and after leaching using a Hitachi S-4800 scanning electron microscope (SEM) at an accelerating voltage of 5 kV. To reduce agglomeration, the samples were ultrasonically dispersed in water for 15 min prior to the analysis.

An X-ray fluorescence (XRF) spectrometer (Swiss ARL Advant'XP +-405) was used to analyze the chemical composition of the Ti-rich materials.

The relative elemental abundance of the leach residues was determined with a Hitachi S-450 SEM equipped with an energy-dispersive X-ray spectrometer (EDX, Thermo Electron V4105).

Thermal analyses were performed on a thermogravimetric analyzer (TG) (Seiko, Japan, EXSTAR6000) with a heating rate of 10 K/min and nitrogen flow rate of 30 mL/min.

3. Results and discussion

3.1. H_2SO_4 pressure leaching of Panzhihua ilmenite

3.1.1. Effect of reaction temperature

The effect of reaction temperature on the dissolution of Ti and Fe from Panzhihua ilmenite was studied under the following experimental conditions: H_2SO_4 concentration of 20 wt.%, acid/ore ratio of 2:1 (*w*/*w*) (100% H_2SO_4/ore mass ratio), and leaching time of 3 h. The results are shown in Fig. 1. The temperature significantly affected the leaching of both iron and titanium from ilmenite. The extraction of Fe gradually increased with leaching temperatures. The extraction curve of Fe leveled off with temperatures above 140 °C, and a maximum Fe extraction of ~76% was achieved. However, the extraction of titanium exhibited an opposite trend and underwent a monotonic decrease with increasing temperatures. The extraction of Ti was less than 1% at 150 °C.

It has been widely accepted that there is no selectivity in the acid leaching of ilmenite, as Ti and Fe dissolve at their stoichiometric ratios (Chen, 1997; Sinha, 1978). The Ti/Fe molar ratio of Panzhihua ilmenite is close to 1:1. However, the Ti/Fe ratio in the leachate obtained in this study was much less than 1, indicating that the hydrolysis of the dissolved