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Technical note

Treatment of tionite residue from titanium oxide industry for recovery of TiO_2 and removal of silica

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ABSTRACT

Solid waste tionite generated in the sulfate process for TiO_2 production is a secondary titanium resource with high silicon content. To recover titanium and remove silicon from the tionite, a process involving hydrothermal conversion, water washing, and acid leaching was proposed. To avoid Na_2O loss, the formation of Na_2TiSiO_5 by-product was prevented by adding CaO. XRD, ICP-OES and FT-IR were used to examine the transformation of the titanium and silicon. The optimum hydrothermal conditions are NaOH/tionite mass ratio of 4:1 and Ca/Si molar ratio of 1:1 in 45% NaOH solution at 240 °C for 1 h. Under these conditions, the titanium conversion was 97.3% with Na_2TiO_3 as the main titanium phase, while most silicon was converted to Ca_2SiO_4, and katoite, and $NaCaHSiO_4$, instead of Na_2TiSiO_5. About 97.5% of the Na_2O was recovered after washing the hydrothermal products with water, and 93.1% of the silicon retained in the washed solution was removed by adding CaO. After leaching the washed products with 40% H_2SO_4 solution at 60 °C, about 97% of the titanium was easily recovered, forming the titanyl sulfate solution that was employed for TiO_2 production. The Ca and Si components formed $CaSO_4$ and silica gel, which were then separated from the acid leaching solution.

1. Introduction

The understanding and control of the transformation of silicon minerals in the extractive metallurgy processes are significant issues (Queneau and Berthold, 1986). As an example, in the Bayer process for Al_2O_3 production, silicon reacts with alumina and soda to precipitate as insoluble sodium alumina silicate (e.g., sodalite), which is then discharged as red mud causing serious caustic and alumina losses (Abdulvaliyev et al., 2015; Liu and Li, 2015; Smith, 2009). Silicon also causes severe scale formation, which leads to less effective heat transfer (Zheng et al., 1997).

Efforts have been made to solve the problems caused by the silicon components in titanium hydrometallurgy when treating raw titanium minerals with high silicon contents (Chen et al., 2013; Mazzocchitti et al., 2009; Xiao et al., 2010). An undissolved residue known as "tionite" (Dondi et al., 2010; Hajjaji et al., 2012), generated during the digestion of titanium minerals in the sulfate process of TiO_2 production, is listed in the National Hazardous Waste List of China. The chemical composition of dry tionite is 35–50% TiO_2, 15–30% SiO_2, 10–15% Fe_2O_3, and small amounts of other impurities. It could be treated as a secondary titanium resource with high silicon content. However, the tionite is usually disposed of in landfills (Chen, 2009), giving rise to serious environmental risks and a loss of titanium resources. To date, many studies have focused on reusing tionite or recovering titanium from tionite. For example, tionite has been directly used in construction materials (Contreras et al., 2013; Dondi et al., 2010; Hajjaji et al., 2012; Labrincha et al., 2014). Furthermore, physical separation methods combining gravity concentration, flotation, and magnetic separation have been tested for recovering titanium minerals from tionite (Belardi et al., 1998; Jiang, 2012). The high Si content and other impurities, as well as the low titanium recovery efficiency, are the main obstacles facing these processes.

A new and eco-friendly process for the recovery of titanium from tionite was developed in our previous study (Qi et al., 2014). The flow sheet of this new process is shown in Fig. 1. In this process, the titanium in tionite can be converted into Na_2TiO_3 by NaOH hydrothermal conversion. Most of the NaOH medium can be recycled by washing the hydrothermal products with water. Titanium is recovered by leaching the washed products in H_2SO_4 solutions. However, the high silicon content in tionite reacts with the titanium and NaOH to precipitate as sodium silicotitanate (Na_2TiSiO_5). Like the behavior of sodalite in Bayer process,

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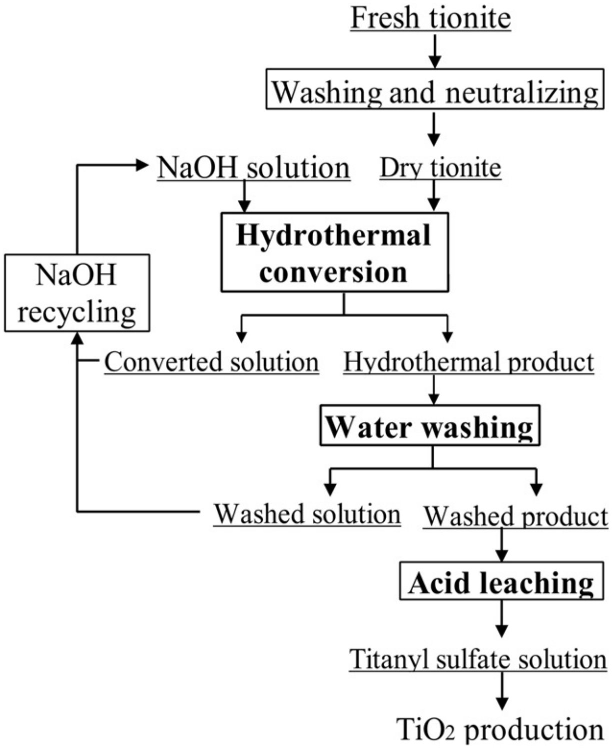

Fig. 1. Flow sheet of new process for recovering TiO_2 and removing silica from tionite.

the formed Na_2TiSiO_5 is stable in water which could lead to serious Na_2O loss in the process. Moreover, it gives rise to a serious scaling problem in the reactor. Thus, the formation of Na_2TiSiO_5 must be avoided.

An efficient means of controlling the silicon components in the Bayer process is the introduction of desilication additives such as CaO or $Ca(OH)_2$ into the digestion process (Cao and Dong, 2008; McCormick et al., 2002; Smith, 2009). The addition of lime could prevent the formation of sodium alumina silicate and promote the digestion of the high-silica bauxite ore. In another process, in which alumina was extracted from coal fly ash, a mixed-alkaline hydrothermal method, whereby CaO was added into the NaOH solution, was designed to prevent the leaching of silicon into the solution (Li et al., 2014a). There have been no reports on the use of CaO to control the silicon components in the NaOH hydrothermal conversion of titanium minerals.

The aim of this study was to devise a means of recovering TiO_2 and removing silica from tionite followed by an alkaline hydrothermal treatment. CaO was added to the NaOH hydrothermal system to prevent the formation of Na_2TiSiO_5. XRD, ICP-OES and FT-IR were used to investigate the transformation of the titanium and silicon components in the whole process.

2. Experimental

2.1. Materials

Fresh tionite was supplied by Shandong Dongjia Group Co., Ltd. It was washed with water, neutralized with the dilute alkali solution, and then dried. This study used dry tionite with the following chemical compositions: TiO_2 46.4%, SiO_2 21.1%, Fe_2O_3 14.8%, CaO 3.14%, Al_2O_3 2.81%, MgO 1.44%, MnO 0.83%. The main phases of the dry tionite were rutile, anatase, ilmenite, sphene, quartz, and some titanium and silicon oxides in amorphous forms.

Analytically pure NaOH and CaO, deionized water, and commercially pure O_2 were used in all of the experiments.

2.2. Experimental procedures

2.2.1. Hydrothermal conversion

To convert the titanium in tionite into Na_2TiO_3, the hydrothermal conversion experiments were performed in a 1 L nickel autoclave at 240 °C thermostatically controlled to within ±2 °C. A mechanical agitator was used to keep the slurry suspended. The tionite and CaO were mixed in the NaOH solution in the autoclave. Then, O_2 of 0.25 MPa was injected into the autoclave before the start of each experiment to promote the decomposition of the ilmenite and rutile phases in tionite. After the reaction, the pulp was filtered and the hydrothermal product (filter cake) was sampled and dried, then its X-ray diffraction (XRD) pattern and titanium conversion were analyzed.

2.2.2. Water washing

To recover Na_2O from the hydrothermal products and remove silicon, the hydrothermal products were washed in water with a liquid/solid mass (L/S) ratio of 2:1 at 60 °C. This procedure was performed three times in a 250 mL flask heated by an oil bath. To remove the residual silicon in the washed solution obtained from water washing, CaO was added when the washed solution was heated to 95 °C. The recovery of Na_2O and removal of Si was calculated from the compositions of the washed solutions.

2.2.3. Acid leaching

To recover titanium from the water-washed products, the washed products were leached in 20% to 60% (mass fraction) H_2SO_4 solutions at 60 °C with the H_2SO_4/solid mass ratio of 2.5:1. This was done for 2 h in a 250 mL flask heated by an oil bath. After leaching, the mixture was filtered to obtain the titanyl sulfate solution, which was then used to prepare TiO_2. The titanium leaching percentage (titanium recovery) was calculated from the titanium concentration of the titanyl sulfate solution.

2.3. Characterization

The XRD analysis was conducted on an X'Pert Empyrean instrument (PANalytical, Netherlands) with Cu Kα radiation. The chemical compositions of the solid samples and aqueous solutions were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optimal 5300DV, Perkin-Elmer, USA). The Fourier transform infrared (FT-IR) spectrum of the solids was acquired using KBr tablets (Spectrum GXI, Perkin-Elmer, USA).

To determine the titanium conversion of the hydrothermal reaction, the hydrothermal product was leached with 3.1 wt.% HCl solution at 25 °C for 24 h. The titanium that converted into Na_2TiO_3 and Na_2TiSiO_5 was dissolved while the titanium in the unreacted titanium minerals stayed in suspension. Subsequently, the titanium conversion was calculated from the titanium content in the leaching solution as determined by the ICP-OES analysis.

3. Results and discussion

3.1. Conversion of tionite using NaOH–CaO hydrothermal method

Fig. 2a indicates that the main phases of the hydrothermal product were Na_2TiO_3 and Na_2SiO_3 when tionite was treated in >50% NaOH solution. Na_2TiO_3 (JCPDS 028-1152) is the target intermediate product that facilitates the recycling of NaOH and the leaching of titanium in the subsequent processes to produce TiO_2 (Liu et al., 2012; Meng et al., 2014). Only 16.5% of the original silicon went into the converted solution after the hydrothermal reaction, which was due to the low solubility of Na_2SiO_3 in the highly concentrated NaOH solution (Baker et al., 1950). Fig. 2b indicates that most silicon tended to combine with titanium to form Na_2TiSiO_5 (JCPDS 086-1615) when the NaOH