Treatment of tionite residue from titanium oxide industry for recovery of TiO₂ 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 $\text{Na}_2\text{TiSiO}_5$ 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, 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 $\text{Na}_2\text{TiSiO}_5$. 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.

Keywords: tionite; titanium recovery; silicon removal; hydrothermal conversion; water washing; acid leaching

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 ($\text{Na}_2\text{TiSiO}_5$). Like the

behavior of sodalite in Bayer process, the formed $\text{Na}_2\text{TiSiO}_5$ 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 $\text{Na}_2\text{TiSiO}_5$ 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 $\text{Ca}(\text{OH})_2$ 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 tiorite followed by an alkaline hydrothermal treatment. CaO was added to the NaOH hydrothermal system to prevent of the formation of $\text{Na}_2\text{TiSiO}_5$. 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 tiorite 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 tiorite 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 tiorite 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 O₂ were used in all of the experiments.

2.2. Experimental procedures

2.2.1. Hydrothermal conversion

To convert the titanium in tiorite into Na₂TiO₃, 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 tiorite and CaO were mixed in the NaOH solution in the autoclave. Then, O₂ 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 tiorite. 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 analysed.

2.2.2. Water washing

To recover Na₂O from the hydrothermal products and remove silicon, the 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 Na₂O and removal of Si were 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) H₂SO₄ solutions at 60°C with the H₂SO₄/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 $\text{Cu K}\alpha$ 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 $\text{Na}_2\text{TiSiO}_5$ 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 $\text{Na}_2\text{TiSiO}_5$ (JCPDS 086-1615) when the NaOH concentration falls to 45%, and no Na_2SiO_3 was not detected in the XRD pattern.

The titanium conversion with >50% and 45% NaOH solutions were almost the same (97.4% and 97.1%, respectively). Therefore, the use of 45% NaOH solution was considered to reduce the evaporation energy consumption of NaOH recycling. The results also indicate that it was basically impossible to extract the Na_2O from $\text{Na}_2\text{TiSiO}_5$ by water washing, and the formation of $\text{Na}_2\text{TiSiO}_5$ was calculated to result in a loss of about 0.2 tons of Na_2O of per ton of tionite in the process. Thus, the formation of $\text{Na}_2\text{TiSiO}_5$ in the hydrothermal reaction must be avoided.

The NaOH-CaO hydrothermal method was used to treat tionite to prevent the formation of $\text{Na}_2\text{TiSiO}_5$. Fig. 2c indicates that the addition of CaO into the 45% NaOH solution with the Ca/Si (in tionite) molar ratio of 1:1 at 240°C could effectively prevent the formation of $\text{Na}_2\text{TiSiO}_5$. Most silicon reacted with CaO to form Ca_2SiO_4 , NaCaHSiO_4 , and katoite ($\text{Ca}_{2.93}\text{Al}_{1.97}\text{Si}_{10.64}\text{O}_{2.56}(\text{OH})_{9.44}$), with less than 5% of the total silicon in tionite going into the solution. The main phase of titanium was Na_2TiO_3 , with minor amounts of CaTiO_3 also being observed in Fig. 2c. In this case, the titanium conversion was 97.3%. The Fe_2O_3 in the hydrothermal product may be of low crystallinity, and no peaks of iron phases were detected in the XRD patterns. Moreover, the addition of CaO inhibited the leaching of silicon into the solution in the form of Na_2SiO_3 , and the formed Ca_2SiO_4 , katoite, and NaCaHSiO_4 all immobilized the silicon in the solid phase. It improved the utilization rate of the highly concentrated NaOH solution when converting the titanium components in the hydrothermal conversion process.

As shown in Fig. 2d, $\text{Na}_2\text{TiSiO}_5$ continued to exist when the Ca/Si molar ratio decreased to 0.5:1, which indicated there was a strict requirement regarding the amount of CaO to be added. Since the Ca/Si molar ratio of 1:1 yielded acceptable results but a higher Ca/Si molar ratio would increase the

lime cost, the Ca/Si molar ratio was set to 1:1.

The theoretical NaOH/tionite mass ratio for the complete reaction in the hydrothermal conversion is about 0.7:1. In Fig. 2c, the NaOH/tionite mass ratio was 4:1, with the excess NaOH acting as a mineralizer to maintain the NaOH concentration. Compared with Fig. 2c, when the NaOH/tionite mass ratio decreased to 2.5:1 (Fig. 2e) from 4:1 or the temperature fell to 230°C (Fig. 2f) from 240°C, the XRD peaks of NaCaHSiO₄ were all intensified which indicated that more NaCaHSiO₄ were formed. These findings were in agreement with the results of the previous study (Chen et al., 2010). NaCaHSiO₄ requires only half of the CaO charge compared with Ca₂SiO₄. However, its formation was not preferred because special care must be applied to recover Na₂O from NaCaHSiO₄ in the subsequent process. The titanium conversion in Figs. 2e and 2f were 92.8% and 91.3%, respectively. In this case, the optimum conditions are a reaction temperature of 240°C, a NaOH/tionite mass ratio of 4:1, and a Ca/Si molar ratio of 1:1 in 45% NaOH solution for 1 h, as shown in Fig. 2c.

3.2. Na₂O recovery and Si removal by water washing

After NaOH-CaO hydrothermal treatment, the solid product is washed with water to recover Na₂O from the Na₂TiO₃ phase. The Na⁺ in the Na₂TiO₃ easily underwent ion exchange with the H⁺ in the water (Eq. 2) (Liu et al., 2012).

XRD patterns of the water-washed products shown in Fig. 3 confirmed that Na₂TiO₃ was converted to an amorphous solid phase after water washing. Further experiments showed that about 80% of Na⁺ in the Na₂TiO₃ could be removed. Fig. 3 indicates that the Na₂TiO₃ peaks disappeared after water washing, and only weak peaks of the unreacted TiO₂ and FeTiO₃ were observed. The solubility of the Ti(IV) is less than 0.001 mol/L under the studied conditions (Huang et al., 2011; Li et

al., 2014b) which implies that nearly all of the titanium remained in the solid washed product.

NaCaHSiO₄ must be treated specially to recover the Na₂O. As shown in Figs. 3b and 3c, the major peak of NaCaHSiO₄ at 31.4° fell a little after washing with water, while the Ca₂SiO₄ and katoite peaks remained stable. Due to the existence of NaCaHSiO₄, the Na₂O recovery shown in Figs. 3b and 3c were lower than 95%. Previous studies revealed that NaCaHSiO₄ could be decomposed in the dilute NaOH solutions (Yang et al., 2014; You et al., 2014). To extract the Na₂O from the NaCaHSiO₄, the above hydrothermal products were first washed with water with the L/S ratio of 4:1 at 150°C for 2 h. As shown in Fig. 3d, NaCaHSiO₄ peaks disappeared, and further studies showed the overall recovery of the Na₂O after water washing process was 97.5%. The decomposition products were amorphous calcium silicate hydrates (CSH), which were more likely to be CaSiO₃·nH₂O or Ca₂SiO₄·nH₂O in our study (Zhang et al., 2011). The reaction could be described as follows:

Although most Si went into solid phases in NaOH-CaO hydrothermal system, some Si content remained in the washed solution. To remove this silicon, CaO with the Ca/Si molar ratio of 1.1:1 was added when the washed solution was heated to 95°C. This silicon in the solution reacted with CaO and was then precipitated as calcium silicate hydrates. Fig. 4 shows that silicon was removed very quickly, with about 93.1% of the silicon being removed from the solution in 2 h.

3.3. Recovery of titanium by sulfuric acid leaching

To compare the behaviors of the water-washed product and titionite, both of them were leached in H₂SO₄ solutions of different concentrations. Table 1 shows that the titanium leaching percentages of the washed products were all in excess of 94%, which was much higher than the direct leaching of

tionite. Because the rutile content in tionite barely dissolved in the H_2SO_4 solution, the leaching percentage of titanium was only 77.8% in the extreme digestion condition of the sulfate process.

The compositions of the titanyl sulfate solutions obtained from the washed products are listed in Table 2. After leaching with a 20% H_2SO_4 solution, the silicon content in the titanyl sulfate solution was found to be much higher than that obtained from the 40% H_2SO_4 solution, and this was not favorable for the purity of the final TiO_2 products. Most of silicon went into the leaching residue after leaching with the 40% H_2SO_4 solution.

Fig. 5 shows the results of the XRD and FT-IR analyses of the leaching residues obtained after leaching the water-washed products shown in Figs. 3a and 3b by the 40% H_2SO_4 solution. There were very small amounts of unreacted titanium minerals such as rutile, anatase, and ilmenite in both solid residues. In the acid leaching experiments, the silicon components could react with H_2SO_4 to form colloidal silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Fig. 5b shows that the characteristic IR absorption bands of silica gel at around 1100 cm^{-1} and 470 cm^{-1} are all observed in both residues (Mikushina et al., 2008), which indicates that most of the colloidal silica tends to form silica gel in the 40% H_2SO_4 solution. Fig. 5a indicates that the calcium components (e.g., Ca_2SiO_4 and katoite) decomposed in the H_2SO_4 solution, and the main calcium phase was CaSO_4 . The IR spectrum shown in Fig. 5b also shows the absorption bands of CaSO_4 , e.g., antisymmetric stretching vibration (1158 and 1122 cm^{-1}), bending vibration (675 , 616 , and 595 cm^{-1}), and symmetric stretching vibration (1026 cm^{-1}) (Lane, 2007).

The titanyl sulfate solution obtained from the 40% H_2SO_4 solution was hydrolysed by being heated to the boiling point after concentration, and the obtained H_2TiO_3 hydrolysis product was then washed and calcinated to prepare TiO_2 . The chemical composition of the obtained product was TiO_2 99.3 wt.%, SiO_2 0.031 wt.%, MgO 0.047 wt.%, MnO_2 0.009%, $\sum\text{Fe}$ 0.004 wt.%, and SO_3 0.102 wt.%. Very low

amounts of silicon and other impurities remained in the final TiO_2 product.

4. Conclusion

To recover titanium and remove silicon from tionalite, a process consisting of alkaline hydrothermal conversion, water washing, and sulfuric acid leaching for TiO_2 production was proposed. The $\text{Na}_2\text{TiSiO}_5$ by-product formed due to the high silicon content in tionalite lead to Na_2O loss, but its formation was prevented by adding CaO during the hydrothermal conversion, forming Ca_2SiO_4 , NaCaHSiO_4 , and katoite. The optimum hydrothermal conditions were NaOH /tionalite mass ratio of 4:1 and Ca/Si molar ratio of 1:1 in the 45% NaOH solution at 240 °C for 1 h. The titanium conversion was 97.3% with Na_2TiO_3 as the main titanium phase in these conditions. In the water washing process, most Na_2O in the Na_2TiO_3 and NaCaHSiO_4 was extracted from the hydrothermal products, and the total recovery of Na_2O was 97.5%. About 93.1% of the silicon retained in the NaOH solution after water washing was removed by adding CaO . After leaching the washed products with the 40% H_2SO_4 solution at 60°C for 2 h, the Ca and Si components in the water-washed product formed CaSO_4 and silica gel. The titanium was easily leached with the titanium recovery of about 97%. The obtained titanyl sulfate solution was used to prepare TiO_2 product.

Acknowledgments

The authors gratefully acknowledge the foundations from the projects supported by the National Basic Research Program of China (973 Program, 2013CB632604), the National Science Foundation for Distinguished Young Scholars of China (Grant No. 51125018), the Key Research Program of the Chinese Academy of Sciences (Grant No. KGZD-EW-201-2), and the National Natural Science Foundation of China (Grant Nos. 51374191 and 51402303).

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Table 1

Titanium leaching percentages under different conditions.

Conditions	Tionite				Water-washed product		
C _{H₂SO₄} (wt.)	98% ^a	60%	40%	20%	60%	40%	20%
Temperature (°C)	200	60	60	60	60	60	60
Ti leaching (%)	77.8	7.03	5.64	4.21	97.4	96.9	94.1

^a 98% H₂SO₄ and 200°C was the extreme digestion condition in sulfate process.

Table 2

Composition of titanyl sulfate solutions leaching from different H₂SO₄ solutions (g/L).

C _{H₂SO₄}	Ti(IV)	H ₂ SO ₄	Si(IV)	Na(I)	ΣFe	Mg(II)	Mn(IV)	Ca(II)	Al(III)
40 wt. %	102.3	340.3	0.12	15.7	30.9	2.87	2.58	1.01	0.55
20 wt. %	44.8	149.2	3.43	6.8	13.6	1.29	1.33	0.64	0.23

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

Fig. 2. XRD patterns of hydrothermal products obtained from different NaOH concentrations, reaction temperatures, NaOH/tiorite mass ratios, and Ca/Si molar ratios. (a) >50%, 240°C, 4:1, 0; (b) 45%, 240°C, 4:1, 0; (c) 45%, 240°C, 4:1, 1:1; (d) 45%, 240 °C, 4:1, 0.5:1; (e) 45%, 240°C, 2.5:1, 1:1; (f) 45%, 230°C, 4:1, 1:1.

Fig. 3. XRD patterns of water-washed products. (a), (b), and (c) were obtained by washing the hydrothermal products in Figs. 2a, 2c, and 2f, respectively (washing condition: 55°C, L/S ratio of 2:1; 30 min, 3 times). (d) was obtained by washing the product in Fig. 2f (washing condition: 150°C, L/S ratio 4:1, 2 h).

Fig. 4. Effect of time on silicon removal from washed solution by adding CaO.

Fig. 5. XRD patterns and FT-IR spectra of acid leaching residues. (A) Leaching residue of water-washed product shown in Fig. 3a. (B) Leaching residue of water-washed product shown in Fig. 3b.