

Titanite processing by hydrobromic acid leaching and carbochlorination



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ABSTRACT

Two stage processing – acid leaching and carbochlorination – is proposed for titanium extraction from titanite (CaTiSiO_5). Calcium oxide and 40–60 wt.% of titanium oxide in titanite were dissolved by leaching in recyclable hydrobromic acid. Titanium dioxide of 99.5 wt.% purity was obtained by thermal hydrolysis of titanium containing acid solution. On the second stage, solid leaching residue was carbochlorinated at 1100 °C in a rotary tube furnace to produce titanium tetrachloride. An overall titanium extraction of 93.7% was obtained. Pyrohydrolysis of CaBr_2 at 1100–1200 °C was used for the hydrobromic acid recycling.

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1. Introduction

Rutile and ilmenite concentrates are used today as principal raw materials for the worldwide production of titanium metal and high purity titanium dioxide. However, there are deposits of low grade (5–7 wt.% TiO_2) sands and rock type titanium ores in China (Chen et al., 2013; China Zhongsheng Resources Holdings Limited, 2014) containing both ilmenite (FeTiO_3) and titanite (CaTiSiO_5) minerals, with up to 45 wt.% of total TiO_2 content in titanite. Such ores are beneficiated to produce 46 wt.% ilmenite concentrate with total titanium extraction of only 30–60% because of titanite is considered as a gangue mineral. Titanite is also a constituent of the Khibiny apatite-nepheline ores in Murmansk Region in Russia. During the process of concentrating the complex ores mined at the Khibiny field, titanite concentrate was produced by the Apatit joint-stock company on an experimental-industrial scale at volumes of approximately 1500 t/year (Lokshin et al., 2009, Gerasimova et al., 2009). The high calcium content in titanite containing concentrates makes impossible of their use in high temperature carbochlorination in fluidized bed (the most commonly used method for the rutile or titanium slag processing), and sulfuric or hydrochloric acid leaching for the ilmenite concentrates processing. Agglomeration of particles because of liquid CaCl_2 accumulation destroys the fluidized bed in the carbochlorination process. Moreover, the production of CaCl_2 or CaSO_4 in the acid leaching processes is followed by a dramatic increase in the consumption of acid and environment pollution due to high volume of wastewater.

The obvious way out is the two-stage titanite processing: extraction of calcium using recyclable acid, followed by high temperature

carbochlorination of the solid residue. Acid recycling gives an opportunity to the acid leaching methods to extract any metal from Ca-containing ores, and to make it more attractive from an economic point of view. Moreover, the volume of industrial wastewater will be greatly reduced.

No methods of acid recycling have been proposed up to now for the calcium ore processing, and titanite concentrate in particular. The main reason is impossibility to recycle these acids by the sulfur or chlorine extraction from calcium sulfate or chloride, without using other expendable chemicals.

Earlier, TiO_2 (and CaO as well) extraction from titanite by the acid leaching was studied (Lokshin et al., 2009, Gerasimova et al., 2009). Sulfuric, hydrochloric, nitric, and phosphoric acid leaching was investigated. It has been found, that HCl acid leaching gives the best results in a view of the economy and technology; 94.1% of titanite was decomposed after 5 h at $T = 105$ °C, $P = 0.1$ MPa. The acids were used as expendable chemicals without recycling.

In this paper a new method of TiO_2 extraction from titanite is proposed. Hydrobromic acid is used for titanite leaching, and a method for recycling the acid from CaBr_2 is proposed as well. Only carbon (coal) and air are used for hydrobromic acid recycling. Titanite is processed into synthetic rutile, titanium tetrachloride, silica, calcium oxide, or calcium silicate. This method is based on the “High-speed Metallurgy” concept (Kustov and Parfenov, 2015): no waste, no expendable chemicals (but coal and air), and universal technological approach for the most components of ore. For hydrobromic acid recycling from calcium bromide we used an earlier proposed method of calcium-containing minerals processing by bromine or hydrogen bromide (Kustov and Parfenov, 2012; Kustov et al., 2012; Zaitzeva et al., 2014). The process route includes: (1) titanite leaching in 48 wt.% hydrobromic acid solution at standard pressure to extract all calcium and part of titanium into solution, and the residue - mixture of titanium dioxide and silica;

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(2) selective carbochlorination of the solid residue (mixture of silica and part of titanium dioxide) to produce titanium tetrachloride; (3) hydrobromic acid recycling from calcium bromide.

2. Equipment, chemicals, methods and procedure

2.1. Synthesis of titanite

The principal purpose of this investigation is to study the behavior of pure titanite in hydrobromic acid solution. Therefore, a synthetic titanite was used for the experiments instead of natural ore or concentrate. Titanite was synthesized from the mixture of powdered (-0.074 mm) calcium carbonate, titanium dioxide and silica with the mole ratio of $[\text{CaCO}_3]:[\text{TiO}_2]:[\text{SiO}_2] = 1:1:1$. All chemicals were of analytical grade. Known method (Nerad et al., 2013) was used for the sintering procedure. The final sintered product contained 98.0 wt.% titanite and 2.0 wt.% cristobalite, with a total TiO_2 content of 40.0 wt.% (Fig. 1). For the leaching experiments synthetic titanite was milled to -0.074 mm.

2.2. Leaching equipment

A flat bottom glass flask of 200 mL equipped with a reflux condenser and an electric heater with magnetic stirrer were used for the leaching experiments. 20–50 mL of azeotropic hydrobromic acid solution (48 wt.%) and 2.0–2.5 g of titanite powder (-0.074 mm) were mixed at 120–125 °C, $P = 0.1$ MPa.

2.3. Carbochlorination equipment

The carbochlorination method that had been used earlier (Kustov et al., 2014), was modified. Instead of a fixed bed reactor, a rotary (3 min^{-1}) quartz tube in a tube electric furnace (Fig. 2) was used for the selective titanium extraction from leaching residue. Our experiments have shown that the rotating reactor increased the carbochlorination efficiency by 25–35% in comparison to the fixed bed reactor due to better reagent mixing. Another advantage of rotating reactor is the possibility to arrange a “gas–solid” countercurrent flow for improving the yield of the heterogeneous chemical reactions, and the continuous input of reagents and output of products.

Samples for carbochlorination were placed in a hot reaction zone between two porous mullite-wool stoppers. The air-cooled and expanded exit zone of the quartz tube was used as a condenser for liquid titanium tetrachloride collection. Argon was used as a transport gas and a diluent for chlorine, at flow rate of 2.0 L/h. Chlorine was used at flow rate of 1.0 L/h.

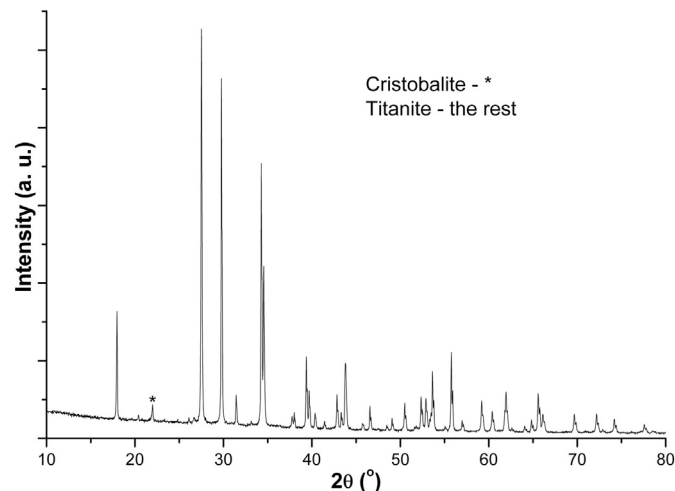


Fig. 1. XRD pattern of synthetic titanite. Cu K_α radiation.

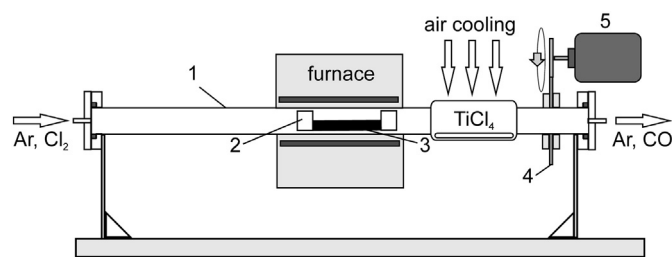


Fig. 2. Carbochlorination equipment. 1 – rotating quartz tube, 2 – mullite-wool stoppers, 3 – granules of leaching residue and carbon powder mixture, 4 – gear, 5 – electric motor.

2.4. HBr acid recycling equipment

The experiments on the recycling of hydrobromic acid from calcium bromide were performed in a horizontal tube reactor (Fig. 3). Anhydrous calcium bromide was mixed with calcium oxide at a molar ratio of 1:4 to prevent salt particles agglomeration at high temperature. A granulated mixture of calcium bromide and calcium oxide was placed into the tube and heated under argon atmosphere up to 1150 °C. After that, steam was injected into the reactor to produce hydrogen bromide by the pyrohydrolysis of calcium bromide. The output gas mixture of hydrogen bromide and steam was condensed and absorbed by water to produce hydrobromic acid solution.

2.5. Analytical equipment and methods

The X-ray diffraction (XRD) measurements of the powders were carried out by using PANalytical X'Pert PRO diffractometer with CoK_α radiation. The quantitative phase analysis was performed using the full-profile Rietveld method (Rietveld, 1969) and the derivative difference minimization technique (Solovyov, 2004).

Images of products were made on electron scanning microscope Hitachi TM3000.

Equilibrium calculations of chemical composition were made using the global free energy minimization method (Kustov et al., 2014).

3. Results and discussion

The flowsheet of titanite processing (Fig. 4) includes three main processes: acid leaching, carbochlorination of the solid residue, and HBr acid recycling. Carbon dioxide produced on the carbochlorination stage is the main environment pollution substance in the flowsheet.

3.1. Leaching experiments

Hydrobromic acid leaching of titanite (CaO 28.61 wt.%, TiO_2 40.74 wt.%, SiO_2 30.65 wt.%) can be described by the reaction:

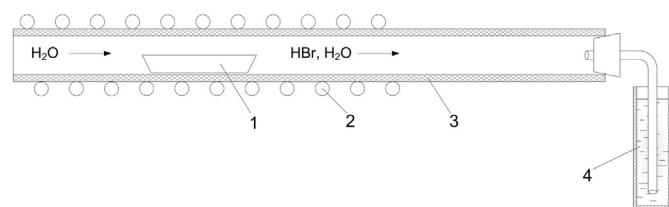
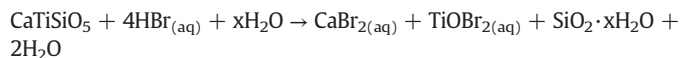


Fig. 3. Reactor for calcium bromide pyrohydrolysis. 1 – corundum crucible with granulated mixture of anhydrous calcium bromide and calcium oxide, 2 – electric heater, 3 – corundum tube, 4 – absorber with hydrobromic acid solution.

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