Hydrometallurgy 149 (2014) 106–109

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Technical note

A novel method to extract iron, titanium, vanadium, and chromium from high-chromium vanadium-bearing titanomagnetite concentrates

Longsheng Zhao [a,b,c], Lina Wang [a,b,*], Tao Qi [a,b,**], Desheng Chen [a,b], Hongxin Zhao [a,b], Yahui Liu [a,b]

[a] *National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Beijing 100190, China*
[b] *Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China*
[c] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Article history:
Received 29 January 2014
Received in revised form 20 July 2014
Accepted 26 July 2014
Available online 7 August 2014

Keywords:
Titanomagnetite concentrates
Partial reduction
Hydrochloric acid leaching
Alkaline desilication
Titanium-rich slag

ABSTRACT

A novel process for the extraction of iron, titanium, vanadium, and chromium from high-chromium vanadium-bearing titanomagnetite concentrates is proposed. This process involves several steps: partial reduction of the concentrates, magnetic separation, hydrochloric acid leaching of the titanium-bearing tailing, and alkaline desilication of the HCl leach residue. The partial reduction ensures that the vanadium and chromium are predominantly concentrated in the titanium-bearing tailing. Subsequently, magnetic separation is used to recover an iron concentrate with a total iron content of 94.57%. During acid treatment, 90.8% vanadium leaching and 93.4% chromium leaching were obtained, with titanium losses of less than 0.3%. 96.3% of the silicon was removed by alkaline desilication, and titanium-rich slag with a purity of 93.39% was produced. The total recoveries of iron, titanium, vanadium, and chromium under the experimental conditions were 88.3%, 93.7%, 81.7%, and 84.4%, respectively.

1. Introduction

The Hongge mineral deposit in the Panzhihua–Xichang region is the biggest vanadium-bearing titanomagnetite deposit in China, with titanomagnetite reserves of 3.55 billion tons. It is a giant iron-polymetallic deposit containing titanium, vanadium, chromium, and other valuable elements (Chen et al., 2011).

At present, the two main routes for the utilization of vanadium-bearing titanomagnetite concentrates are blast furnace and direct reduction processes. In the blast furnace process (Fu et al., 2011; Zhou et al., 2012), the concentrates are sintered or pelletized, with subsequent smelting in the blast furnace to produce hot metal and blast furnace slag with 22–25% TiO_2. However, it is difficult to use this slag efficiently because of the dispersed distribution of titanium components in various fine-grained mineral phases with complex interfacial combinations, resulting in resource depletion and environmental degradation (Zhang et al., 2006, 2007).

The direct reduction process involves pelletization, direct reduction of the pellets in a rotary hearth furnace, and removal of the titanium slag from the vanadium-bearing molten iron in an electric smelting furnace (Deng et al., 2007; He et al., 2014; Roshchin et al., 2010, 2011). The molten iron is then oxidized to produce semi-steel and vanadium slag before decarburization in a BOF converter (Moskalyk and Alfantazi, 2003; Xiao et al., 2010). The vanadium slag is most commonly treated by sodium salt roasting (Liu et al., 2013). Generally, vanadium spinel in the vanadium slag is roasted with sodium salts at 750–850 °C to form water-soluble sodium metavanadate ($NaVO_3$). However, multiple-stage roasting is usually employed because of the very low vanadium conversion for single-stage roasting, giving rise to an over-consumption of energy and resources (Hukkanen and Walden, 1985; Liu et al., 2013).

Existing research on the utilization of high-chromium vanadium-bearing titanomagnetite concentrates is still focused on the traditional processes, in which chromium-bearing vanadium slag is produced after a BOF process (Diao et al., 2009; Fang et al., 2012). The vanadium and chromium are strongly embedded in the slag with a stable spinel structure, and sodium salt roasting is employed to extract the vanadium and chromium (Fang et al., 2012; Liu et al., 2013). However, chromium spinel is more difficult to break down due to its thermodynamically more stable structure (Liu et al., 2013). Moreover, the release of hazardous compounds containing V^{5+} and Cr^{6+} from the leach residue in the roast–leach process could cause serious environmental degradation in soil and water (Mayes et al., 2008; Xu et al., 2008).

The absence of a cleaner, low-energy production process for the efficient utilization of high-chromium vanadium-bearing titanomagnetite concentrates provided the impetus for this work. In this work, the partial reduction of the titanomagnetite concentrates, magnetic separation,

---

* Correspondence to: L. Wang, National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Beijing 100190, China. Tel.: +86 10 82544848; fax: +86 10 82544949.

** Correspondence to: T. Qi, National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Beijing 100190, China. Tel./fax: +86 10 62631710.

E-mail addresses: linawang@ipe.ac.cn (L. Wang), tqgreen@ipe.ac.cn (T. Qi).

http://dx.doi.org/10.1016/j.hydromet.2014.07.014
0304-386X/

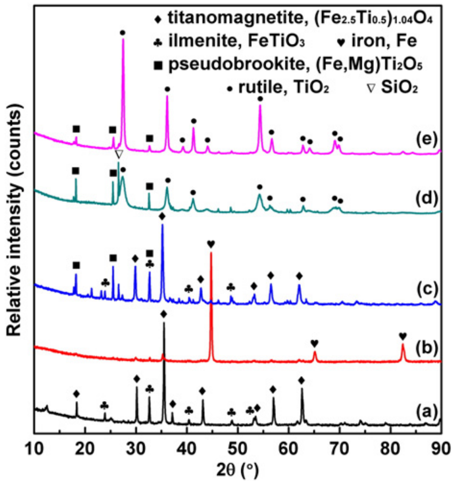

Fig. 1. XRD patterns of the solid samples, (a) high-chromium vanadium-bearing titanomagnetite concentrates; (b) iron concentrate; (c) titanium-bearing tailing; (d) HCl leach residue; and (e) titanium-rich slag.

acid leaching of the titanium-bearing tailing, and alkaline desilication were investigated.

2. Experimental

2.1. Experimental materials

The high-chromium vanadium-bearing titanomagnetite concentrates were obtained from Hongge, SW China. The concentrates were ground to pass a 100-mesh screen after drying. X-ray diffraction analysis revealed that the concentrates consisted mostly of titanomagnetite, with a small amount of ilmenite (Fig. 1a). The chemical composition of the concentrates is given in Table 1.

The reductant used in this work was pulverized anthracite, with the industrial and ash fusibility analyses listed in Table 2. All the other reagents used were of analytical grade.

2.2. Experimental procedure

The partial reduction experiments were conducted in a temperature-controlled muffle furnace (±5 °C). 120 g titanomagnetite concentrates were first mixed with pulverized coal and minor amounts of Na_2CO_3 additive. The presence of Na_2CO_3 facilitates the carbon gasification reaction and induces the growth of metallic iron particles (Basumallick, 1995; Huang et al., 2010; Zhou and Zeng, 2010). The mixture was placed in a sealed silicon carbide crucible, and the crucible was then heated to the preset temperatures in the muffle furnace. After the reduction experiments finished, the reduced samples were immediately quenched with water to avoid re-oxidation and then ground at room temperature in a stainless steel rod mill with hardened stainless steel rods for 30 min. The milled samples were then separated by a low-intensity magnetic separator with a glass tube (50 mm in diameter, 700 mm in length), which was placed between the bobbins at an angle of 45°, with a magnetic field intensity of 48 kA/m. The grades of magnetic concentrate and titanium-bearing tailing were chemically analyzed. The recoveries of iron (the ratio of the amount of Fe in the iron concentrate to that in the titanomagnetite concentrates), titanium, vanadium, and chromium (the ratio of the amount of Ti, V, or Cr in the titanium-bearing tailing to that in the titanomagnetite concentrates) were deduced according to the mass balance.

Table 1
Chemical composition of the high-chromium vanadium-bearing titanomagnetite concentrates (mass fraction, %).

TFe	FeO	TiO_2	V_2O_5	Cr_2O_3	CaO	MgO	Al_2O_3	SiO_2	MnO
55.14	27.33	13.60	0.58	1.10	1.10	4.24	3.36	3.12	0.32

The leaching experiments were carried out in a 0.25 L Teflon autoclave with a stainless steel shell. The titanium-bearing tailing was first mixed with a hydrochloric acid solution using an appropriate liquid-to-slag ratio. The admixture was transferred into the Teflon autoclave, and the autoclave was affixed and sealed completely. Subsequently, the autoclave was kept at the preset temperature for a certain time, and then cooled quickly after the reaction. The slurry was filtered, and the HCl leach residue was washed with distilled water. The compositions of the HCl leach residue and the lixivium were chemically analyzed. The elemental leaching efficiencies were then calculated.

The alkaline desilication experiments were conducted in a three-necked round-bottom flask with a Teflon-coated stirrer. The HCl leach residue was mixed with a dilute NaOH solution, and the admixture was then heated at the preset temperature for a certain time. The slurry was filtered, and the residue was washed, and subsequently dried at 110 °C and calcined at 750 °C for 2 h, forming titanium-rich slag. The composition of the titanium-rich slag was chemically analyzed.

2.3. Analysis

The composition of the solutions and solid samples was determined by ICP-OES (Optima 5300DV, Perkin Elmer, USA). The determination of metallic iron (MFe) content and FeO content in the samples was performed using the potassium dichromate volumetric method, and the metallization degree (the ratio of MFe content to total iron content in the reduced sample) was then calculated. The phase compositions of the solid samples were performed on a Smartlab-9 X-ray diffractometer (Rikagu, Japan).

3. Results and discussion

To avoid high temperature processes such as converter smelting and caustic roasting, vanadium and chromium should be concentrated in the phases where titanium is concentrated. It is well established that vanadium and chromium are very strong carbide-forming elements (Bratberg and Frisk, 2004). Thus, the C/Fe molar ratio influences the metallization degree and the recovery rates of metals during the isothermal reduction and magnetic separation (Fig. 2). At C/Fe molar ratios higher than 1.0, vanadium and chromium carbides are expected to be formed at 1200 °C because of the excess amount of carbonaceous reductants. The newly formed carbides are then dissolved in the austenite with a face-centered cubic structure (Villars et al., 1994), resulting in a

Table 2
Industrial and ash fusibility analyses of pulverized anthracite.

Industrial analysis (mass fraction, %)[a]				Ash fusibility (°C)[b]				S (mass fraction, %)
FC_{ad}	A_d	V_{daf}	M_{ad}	DT	ST	HT	FT	
87.10	8.83	4.07	2.08	1288	1305	1322	1327	0.376

[a] FC_{ad}: fixed carbon in air dried sample, A_d: ash in air dried sample, V_{daf}: volatiles in air dried sample, M_{ad}: moisture in air dried sample.
[b] DT: distortion temperature, ST: softening temperature, HT: hemispherical temperature, FT: flowing temperature.