Hydrometallurgy 154 (2015) 40–46

Contents lists available at ScienceDirect

Hydrometallurgy

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

Solvent extraction of vanadium from a stone coal acidic leach solution using D2EHPA/TBP: Continuous testing

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A R T I C L E I N F O

Article history:
Received 14 January 2014
Received in revised form 10 November 2014
Accepted 19 November 2014
Available online 20 November 2014

Keywords:
Solvent extraction
Vanadium
D2EHPA
Stone coal

A B S T R A C T

This paper reports on continuous testing of a process for the recovery of vanadium from a H_2SO_4-HF solution, generated from the leaching of stone coal, by solvent extraction using a D2EHPA/TBP mixture as the extractant. Three unit processes are included: fully continuous countercurrent solvent extraction and stripping; oxidation and precipitation; and calcination. The solvent-extraction circuit was operated for 96 h. With six stages of countercurrent extraction, 97.7% vanadium, 98.3% molybdenum, and 97.9% titanium were extracted, while the sodium, potassium, fluorine, and nickel impurities were barely extracted. Scrubbing removed co-extracted and aqueous-entrained zinc, magnesium, silicon, and arsenic impurities. Most co-extracted impurities were scrubbed in two stages. Using five stages of stripping, more than 99.8% of the vanadium was stripped, yielding a vanadium concentration in the loaded strip solution of 34.1 g/L. Co-extracted molybdenum(VI), titanium(IV), and iron(III) remaining in the stripped organic phase were removed by a saturated sodium carbonate solution and the regenerated organic was reused for vanadium extraction. Vanadium was selectively precipitated with 98.5% efficiency from the loaded strip solution by oxidation and precipitation with ammonium sulfate. A high-purity V_2O_5 (99.61%) product was successfully produced by this flowsheet.

1. Introduction

Vanadium is always found in combination with various minerals, such as carnotite, roscoelite, vanadinite, mottramite, and patronite, which are important vanadium sources (Perron, 2001). In China, stone coal is an important vanadium resource, which is widely distributed in the southern provinces of Hunan, Hubei, Guangxi, Jiangxi, Zhejiang, Anhui, Guizhou, Henan, and Shanxi. The gross vanadium reserves are estimated at 118 million tons (in terms of V_2O_5), accounting for more than 87% of the Chinese domestic reserves of vanadium (Bin, 2006). Vanadium contained in stone coal generally ranges from 0.13% to 1.2% (Cai, 2001). Besides vanadium, about 60 different metallic and nonmetallic elements have been identified in stone coal, including molybdenum, nickel, uranium, copper, selenium, gallium, and precious metals (Xu et al., 2012; Pan et al., 2004; Pi et al., 2013): stone coal is therefore regarded as a complex resource. Because of its relatively high vanadium grade and abundant deposits, the extraction of vanadium from stone coal has been extensively studied.

Traditionally, extraction of vanadium from stone coal has used roast–leach technologies, including sodium chloride roasting followed by water leaching (Xu, 1988; Xu et al., 1990; Lin and Fan, 2001; Fan and Lin, 2001), blank roasting with acid or alkali leaching (Chen, 2010; He et al., 2007), and calcine roasting followed by acid leaching (Zou et al., 2001; Ma and Zhang, 2007). These technologies are based on the principle of oxidizing the lower valence state of V(III) to higher valence states of V(IV) and V(V) at a high temperature (Chen et al., 2008). The soluble V(IV) and V(V) compounds are then leached by water and/or sulfuric acid. A vanadium product is obtained by direct precipitation and refining of the leach solution. Negative aspects of the traditional roast–leach technologies are that the roasting efficiency is about 45 to 55% and the overall vanadium recovery is below 60% (Fan and Lin, 2001; Bin, 2006). In recent years, the use of direct acid leaching is gradually predominating for recovery of vanadium from stone coal in China (Lu, 2002; Li et al., 2009; Deng et al., 2010; C. Li et al., 2010; M. Li et al., 2010a). The principle of direct leaching is based on the fact that vanadium in certain stone coals can be leached by sulfuric acid and/or sulfuric acid with the addition of fluoride (Zhou et al., 2009; M. Li et al., 2010b; Wei et al., 2010; X.Y. Zhang et al., 2011; Tavakoli and Dreisinger, 2014). Direct acid leaching is characterized by high vanadium leach efficiencies and no air pollution (Y.M. Zhang et al., 2011). However, because acid leaching is non-selective, many impurities, such as iron, aluminum, molybdenum, sodium, potassium, and silicon, can also report to the leach solution with vanadium. Extraction and separation of vanadium from such multi-element stone coal acidic leach solutions are important in developing the direct acid leaching technique.

Solvent extraction offers an attractive method for producing high-purity nonferrous metal products from complex leaching solutions. Previous studies (Lu, 2002; Li et al., 2009; Deng et al., 2010; Li et al., 2012) have shown that vanadium can be effectively extracted

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http://dx.doi.org/10.1016/j.hydromet.2014.11.008
0304-386X/

by di(2-ethylhexyl)phosphoric acid (D2EHPA) from acidic solutions. Furthermore, some studies (Li et al., 2011; Tavakoli and Dreisinger, 2014) indicate that vanadium can be selectively extracted over iron from sulfuric acid leach solutions using a D2EHPA and tri-*n*-butylphosphate (TBP) mixed solvent system diluted in sulfonated kerosene. Although a few papers (Rakib and Durand, 1996; Chagnes et al., 2010; Zeng et al., 2010; Yan et al., 2013; Li et al., 2013) are concerned with the extraction of vanadium from an acidic solution, there is no information on the extraction behaviors of common impurities in the solvent-extraction process, which is very important for the practical application of this technology. In the present study, results of continuous testing of a process including solvent extraction, oxidation, precipitation, and calcination for extraction and separation of vanadium from a multi-element stone coal acidic leach solution are presented and the behaviors of common impurities are discussed.

2. Experimental

2.1. Materials

Stone coal (from Hunan province, China) was the vanadium source employed. The acidic leach solution was generated by direct leaching in 160 g/L H_2SO_4 and 25 g/L HF solution at 90 °C, using a liquid-to-solid ratio of 2 mL/g and a reaction time of 6 h. The leach solution contained Fe(III), which has a negative influence on extraction by D2EHPA. Previous research (Li et al., 2011) has shown that it is necessary to reduce Fe(III) to Fe(II) before vanadium extraction. The leach solution was therefore treated by addition of sodium sulfite, using a mole ratio of Na_2SO_3/Fe(III) of 0.8 at 30 °C for 2 h. After the reduction pretreatment, the resulting solution was used as the feed to solvent extraction. The chemical analysis is shown in Table 1.

Commercial D2EHPA, TBP, and sulfonated kerosene (as diluent) were purchased from Shanghai Rare-Earth Chemical Co., Ltd. Sodium sulfite, sulfuric acid, ammonium hydroxide, sodium carbonate, and hydrogen peroxide were purchased from the local market. All reagents were used as received.

2.2. Test procedures

The trial included three unit processes: 1) Fully continuous countercurrent solvent extraction and stripping; 2) oxidation and precipitation; and 3) calcination. A flowsheet schematic is shown in Fig. 1.

2.2.1. Fully continuous countercurrent extraction, scrubbing, and stripping

The fully continuous countercurrent solvent-extraction operation comprised of six extractions, two scrubbing, and five stripping stages. Each stage consisted of an individual square box-type mixer and a settling compartment. The active mixer volume was 500 mL and the settler volume was 1200 mL. Peristaltic pumps, used for controlling the solution flow rates, were supplied by Changzhou Co., Ltd., Zhejiang, China. A PHS-3C digital pH meter was used to measure the pH of the aqueous solutions.

Our previous work (Li et al., 2011) identified the optimum organic-phase composition as containing 10% (v/v) D2EHPA and 5% (v/v) TBP in sulfonated kerosene: this organic composition was used in the present study. Stripping was carried out using 1.5 mol/L sulfuric acid. The solvent-extraction trial operated continuously for 96 h. The main extraction, scrubbing, and stripping parameters, obtained in previous experiments and adopted for this work, are listed in Table 2. During continuous operation, a 20% bleed of the stripped organic phase was regenerated using a saturated sodium carbonate solution. The regenerated organic was then mixed with the remaining unregenerated organic and reused for vanadium extraction.

Table 1
Chemical analysis of the feed solution.

Composition	Concentration (g/L)	Composition	Concentration (g/L)
V	3.56	Zn	1.05
Fe	13.10	Cu	0.45
Al	8.75	Mg	1.25
K	3.50	As	0.06
Na	3.42	Ni	1.22
Ti	0.65	P	3.15
Mo	0.58	SO_4^{2-}	130.5
Ca	1.01	F	18.90

Prior to starting continuous operation, all extraction compartments (EX1 to EX6) were proportionally filled with feed solution and fresh organic phase, before initiating the pumping of feed solution into EX1 and organic phase into EX6. The aqueous solution flowed from EX1 to EX6, while the organic phase flowed from EX6 to EX1. The two phases were fully mixed in each mixer, and separation of the aqueous and organic phases was observed during settling. Samples collected from each settling compartment and the final raffinate were analyzed.

2.2.2. Oxidation and precipitation

The oxidation and precipitation processes were conducted at atmospheric pressure in a 2000-mL glass stirred reactor placed in a temperature-controlled water bath. Vanadium(IV) was oxidized to vanadium(V) using H_2O_2. Aqueous ammonia was used to control the pH and to precipitate ammonium polyvanadate. Ammonia hydroxide (20 wt.%) (NH_3 184.6 g/L) was slowly added until the pH reached 1.5 to neutralize the free sulfuric acid. H_2O_2 (30 wt.%) was then added into the pre-neutralized solution until vanadium(IV) was completely oxidized. Finally, ammonium polyvanadate was precipitated at conditions of pH of 1.8 to 2.2, 92 °C, and a reaction time of 120 min. Ammonium polyvanadate was separated by vacuum filtration (0.7 atm) and washed twice with distilled water.

2.2.3. Calcination

The ammonium polyvanadate was dried at 60 °C for 24 h in a laboratory oven at constant temperature. The dried ammonium polyvanadate was calcined in a muffle furnace at 500 to 550 °C for 3 h to obtain the V_2O_5 product.

2.3. Chemical analysis

Vanadium concentrations in the aqueous phase were determined by ferrous ammonium sulfate titration using 2-(phenylamino)benzoic acid as an indicator (Method GB/T 8704.5-2007) and the iron concentration was determined by potassium dichromate titration using sodium diphenylamine sulfonate as an indicator (Zheng and Tao, 2010). Fluoride was determined by ion-selective electrode measurements. Other elements were analyzed by inductively coupled plasma optical-emission spectroscopy (ICP-OES).

The percentage extraction (%*E*) was calculated from:

$$\%E = \frac{C_{\text{init}} - C_{\text{raffinate}}}{C_{\text{init}}} \times 100\% \tag{1}$$

where C_{init} and $C_{\text{raffinate}}$ represent the concentrations of the particular element in the feed solution and raffinate, respectively. The distribution ratio (*D*) was calculated as the ratio of concentration of metal present in the organic phase to that in the aqueous phase at equilibrium. From *D* values, the separation factor (β) was calculated as:

$$\beta_{V/Me} = \frac{D_V}{D_{Me}} \tag{2}$$

where the subscripts V and Me represent vanadium and the common metal impurities, respectively.