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Asynchronous extraction of vanadium and chromium from vanadium slag by stepwise sodium roasting–water leaching

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ABSTRACT

A novel environment-friendly method based on stepwise roasting has been proposed to extract vanadium and chromium separately from vanadium slag with high chromium content (V–Cr slag), which consists of two stages of sodium roasting–water leaching. Fractional sodium roasting–water leaching is firstly conducted to extract vanadium from the V–Cr slag and 87.9% of vanadium is extracted in optimal conditions. Leaching residue of the fractional roasting stage is then roasted secondarily to extract chromium and 96.4% of chromium is extracted from the leaching residue in optimal conditions. Overall extractions of vanadium and chromium are 98.9% and 96.6%, respectively. Evolution mechanisms of V-bearing and Cr-bearing phases were elucidated by XRD, TG–DSC and SEM-EDS. It is elucidated that V(III) existing as V-spinels in the V–Cr slag is oxidized to water-soluble $NaVO_3$ while Cr(III) remains in the form of Cr-spinels or R_2O_3 phase (R: Cr, Fe) during the fractional roasting; in secondary roasting, Cr(III) existing as Cr-spinels and R_2O_3 phase in the leaching residue of fractional roasting stage is oxidized to water-soluble Na_2CrO_4. Vanadium and chromium have thus been extracted separately and thoroughly at the extraction procedure by controlling the roasting extent of V–Cr slag via the proposed stepwise roasting method. The established method provides new insights for comprehensive utilization of complex minerals containing multiple valuable elements.

1. Introduction

Vanadium is an important nonferrous metal element widely applied in metallurgical, material and chemical industries (Huang, 2000; Moskalyk and Alfantazi, 2003). Almost 88% of vanadium worldwide is extracted from vanadium titano-magnetite ore while the rest is extracted from other minerals (shale, stone coal, uranium ore, etc.) or secondary resources such as spent catalyst and petroleum residues (Bradbury, 2002; Moskalyk and Alfantazi, 2003; Tavakoli and Dreisinger, 2014a). During processing of vanadium titano-magnetite ore in the steelmaking industry, vanadium is reduced into hot metal and then oxidized and enriched into solid slag which is usually called *vanadium slag*. It contains 5–20 wt.% V_2O_3 and is the direct resource for vanadium extraction.

To extract vanadium, the vanadium slag is usually pretreated with sodium or calcium salts by roasting in oxidizing atmosphere before leaching (Jena et al., 1995; Li and Xie, 2012; Sadykhov, 2008). In common sodium roasting technique, V(III) in vanadium slag is oxidized by oxygen to maximal extent and transforms into sodium vanadates in the presence of sodium salts (Na_2CO_3, Na_2SO_4 or NaCl) during roasting. The produced sodium vanadates are leached by water and vanadium products are obtained from the vanadium-containing leaching liquor by precipitation and/or calcination (Barolin, 1982; He et al., 2007; Tavakoli and Dreisinger, 2014b; Van Vuuren and Stander, 2001). However, this process suffers from the emission of corrosive gases such as Cl_2, SO_2 and HCl due to the addition of Na_2SO_4 or NaCl (Barolin, 1982; Zhang et al., 2011). To avoid these toxic gases, roasting vanadium slag with pure soda (Na_2CO_3), followed by water leaching, is a clean way to extract vanadium. Although NaOH molten salt roasting has been reported to extract vanadium, it consumes large amount of NaOH which is more expensive than Na_2CO_3, leading to increased production cost (Chen et al., 2013). Calcium roasting combined with acid or alkaline leaching is another environment-friendly alternative to extracting vanadium from the vanadium slag (Li et al., 2012; Yang et al., 2014). Nevertheless, all these techniques produce tailings containing minor chromium. The toxic tailings cannot be properly disposed after vanadium extraction and cause potential threat to the environment.

Recently, researchers in the field of vanadium extraction have focused attention on the *Hongge* ore, which is a special kind of vanadium

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titano-magnetite ore with chromium reserved as large as vanadium in China (Liu et al., 2013a; Zhao et al., 2014). If the *Hongge* ore was utilized in steelmaking, vanadium slag with high chromium content (V–Cr slag) would be thus produced due to similar chemical characters of V and Cr elements. The contents of Cr_2O_3 and V_2O_3 in the V–Cr slag are predicted to be 8–20 wt.% according to material balance calculation. If the V–Cr slag was processed as common vanadium slag, tailings with high chromium content would be produced, which is a great threat to the environment. For considerations of resource utilization and environmental safety, both vanadium and chromium should be extracted from the V–Cr slag.

However, it is difficult to extract vanadium and chromium completely from the V–Cr slag by present techniques, although the existing forms of vanadium and chromium have already been speculated to be complex spinels $(Fe, Mg, Mn)_x(V, Cr)_{3-x}O_4$ $(0 < x < 1)$ (Diao et al., 2009; Huang, 2000; Moskalyk and Alfantazi, 2003; Zhang et al., 2012). Traditional sodium roasting technique can only extract vanadium but cannot extract chromium completely from the V–Cr slag due to that (1) chromium spinels (Cr-spinels) are more thermodynamically stable than vanadium spinels (V-spinels) and vanadium is thus oxidized prior to chromium (Zhao et al., 2014); (2) previously produced sodium salts including sodium vanadates ($NaVO_3$: 630 °C; $Na_4V_2O_7$: 660 °C) melt at the roasting temperature of 700–850 °C and then wrap the Cr-spinels, resulting in hindrance of the oxidation of all Cr(III) ions (Slobodin et al., 1979). NaOH molten salt roasting will also suffer from the problem of oxidation hindrance of Cr-spinels, leading to low extraction of chromium. Calcium roasting technique is not suitable to pretreat the V–Cr slag due to the possibility of forming hazardous calcium chromates (Tathavadkar et al., 2003). The method of submolten salts has been proposed to extract 93.7% of vanadium and 88.2% of chromium from the V–Cr slag by NaOH–$NaNO_3$ binary melts (Liu et al., 2013b) or to extract 95% of vanadium and 90% of chromium by NaOH submolten salt (Wang et al., 2014). The obtained solution contains vanadium and chromium in similar concentrations and it is difficult to separate them completely due to their chemical characters more similar in solution. Subsequent process is thus needed to separate vanadium and chromium, which increases the operation complexity and cost of production (Fan et al., 2013; Ning et al., 2014). To avoid the separation difficulty of vanadium and chromium in solution, it is wise to separate them during the extraction process. Therefore, it remains a major challenge to extract vanadium and chromium separately from the V–Cr slag.

In order to extract vanadium and chromium separately, it is essential to focus on the difference of V-spinels and Cr-spinels in the V–Cr slag. According to the nucleation and growth kinetics of spinel crystals in common vanadium slag, Cr-spinels crystallize prior to V-spinels (Zhang et al., 2012). Hence, it is speculated that Cr-spinels should occupy the center of spinel grains in the vanadium slag while V-spinels should distribute more in the outer shell layer of spinel grains. The speculated layered core/shell distribution of Cr-spinels/V-spinels inspires the idea of controlling the oxidative roasting extent of V–Cr slags to asynchronously extract vanadium and chromium. In other words, at first, it can be controlled to roast the V–Cr slag fractionally by optimizing the roasting condition to extract vanadium alone in the outer shell layer of the spinel grain; the obtained leaching residue in which Cr-spinels are exposed can be roasted again to extract chromium. In this way, vanadium and chromium can be extracted separately and thoroughly from the V–Cr slag. Sodium roasting can be conducted in both roasting stages since soda roasting technique is suitable to both V-spinels and Cr-spinels (Fang et al., 2012, 2014; Tathavadkar et al., 2001, 2003).

Therefore, in this study, a stepwise roasting method has been proposed to extract vanadium and chromium separately from the V–Cr slag (Fig. 1). The stage of fractional sodium roasting–water leaching is aimed to extract vanadium while the stage of secondary sodium roasting–water leaching is aimed to extract chromium. By this method, vanadium and chromium in the V–Cr slag have been extracted asynchronously and thoroughly and thus been separated at the extraction stage. According to our knowledge, it is first time to separate vanadium and chromium at the extraction stage. With the proposed stepwise roasting method, the final leaching residue and waste solution of precipitation can both be recycled, leading to no toxic tailings or waste solution. Hence, the proposed stepwise roasting method is believed to be a novel environment-friendly method. This work is focused on the favorability and mechanism of stepwise roasting for asynchronous extraction of vanadium and chromium, which aims to provide new insights for clean comprehensive utilization of artificial or natural complex minerals containing multiple valuable elements.

2. Materials and experimental

2.1. Materials and apparatus

The V–Cr slag was obtained in an industrial test, in which the *Hongge* ore was directly reduced to hot metal in electric furnace, in Pan Steel, China. Chemical compositions of the Hongge ore and the V–Cr slag are shown in Table 1. Chemical compositions of samples were determined by X-ray Fluorescence (XRF, Shimadzu XRF-1800) or Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, PerkinElmer Optima-4300DV). Phase compositions of solid samples were identified by X-ray diffraction analysis (XRD, Rigaku D/MAX 2500PC) using Cu $K\alpha$ radiation. Thermal gravimetry (TG) and differential scanning calorimetry (DSC) analysis was carried out with NETZSCH STA 449C Thermal Analyzer, with a heating rate of 15 K/min in air and reference sample of Al_2O_3. Microscopic observation and analysis of element distribution in samples were conducted by scanning electron microscopy (SEM, TESCAN VEGA III) equipped with energy disperse X-ray spectrometry (EDS or EDX, INCA Energy 350). All chemical reagents used are of analytical grade and supplied by Chengdu Kelong Chemical Co. Ltd. Deionized water (Millipore Aquelix 5) was used in all experiments.

2.2. Experimental procedure

In the stage of fractional sodium roasting–water leaching, 5 g powder of V–Cr slag (<74 μm) was mixed with 0.762–6.096 g Na_2CO_3 in V/Na molar ratio of 0.40–0.05. The mixture was loaded in porcelain crucible and heated in Muffle furnace at 650–850 °C for 0.5–2.5 h. During the sodium roasting process, the door of the furnace was not closed completely to maintain the constant oxidizing atmosphere. Then the roasted mixture was taken out. After being cooled down to the room temperature, the roasted mixture was ground to powders, more than 60% of which can screen through 0.18 mm sieve. 3 g powder of ground roasted mixture was leached with 3–30 mL deionized water to extract water-soluble compounds in water-bath pot with a stirring speed of 200 r/min at 25–100 °C for 5–60 min. The slurry was filtrated (open-pore diameter 0.4 μm) to obtain leaching liquor and solid residues. The leaching liquor was diluted to 500 mL in volumetric flask, in which vanadium and chromium concentrations were determined by the standard ammonium ferrous sulfate titration method.

In the stage of secondary sodium roasting–water leaching, dried and ground leaching residue of the fractional roasting stage was the raw material. Similarly, 5 g powder of leaching residue was roasted with 1.545–4.119 g Na_2CO_3 in (V + Cr)/Na molar ratio of 0.40–0.15 at 850–1050 °C for 10–120 min. 3 g roasted powder was leached with 3–30 mL water at 25–90 °C for 2–60 min. The obtained leaching liquor was collected by filtration, in which vanadium and chromium concentrations were determined by the standard ammonium ferrous sulfate titration method.