A mechanism of calcium fluoride-enhanced vanadium leaching from stone coal

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ABSTRACT

A comparison between unassisted and calcium fluoride-enhanced leaching demonstrated that calcium fluoride can markedly boost the efficiency and accelerate the rate of vanadium leaching from stone coal. Analysis methods were adopted to identify the mechanism of calcium fluoride-enhanced vanadium leaching from stone coal, including Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), valence state of vanadium, X-ray Diffractometry (XRD), X-ray Photoelectron Spectroscopy (XPS), ^{19}F liquid Nuclear Magnetic Resonance (NMR), Scanning Electron Microscope (SEM) and thermodynamics. The whole calcium fluoride-enhanced vanadium leaching process was that calcium fluoride reacted with sulfuric acid and then generated $HF_{(aq)}$; calcite was dissolved into the acid; chlorite and phlogopite were thoroughly disintegrated and subsequently generated quartz, K^+, Mg^{2+}, $[SiF_6]^{2-}$, $[AlF_5]^{2-}$ and Al^{3+}; the released V(III) was oxidized to VO^{2+} by O_2 from the air. It is the procedure that fluorine combined with aluminum and silicon in the lattice of vanadium-bearing phlogopite to generate $[SiF_6]^{2-}$ and $[AlF_5]^{2-}$ that facilitated the vanadium leaching from stone coal. This generation decreased the $\Delta G°$ of phlogopite disintegration, declined the effect of chemical reaction on vanadium leaching, accelerated the leaching rate of vanadium and boosted the leaching efficiency of vanadium.

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1. Introduction

Vanadium is an important strategic resource that is almost exclusively used in ferrous and non-ferrous alloys (Moskalyk and Alfantazi, 2003) due to its physical properties, such as high tensile strength, hardness and fatigue resistance (Archana, 2005). China has the most abundant vanadium-bearing mineral reserves (USGS, 2012), and the reserves of vanadium in China occupy more than 35% the world reserves of vanadium. Furthermore, stone coal (also known as black shale) is an important vanadium-bearing resource in China (Li et al., 2012, 2013), and the gross reserves of vanadium in stone coal account for more than 87% of the domestic vanadium reserves (Bin, 2006). However, the amount of V_2O_5 extracted from stone coal only accounted for 30–40% of total V_2O_5 output of China in 2010, which is not commensurate with China's vanadium reserves in stone coal. It is estimated that the need for vanadium will continue to increase (Anjum et al., 2012; Denison Mines Corp., 2010; Yang et al., 2010) and that the world's increasing demand for vanadium can only be met by extracting vanadium from stone coal in the near future (X.Y. Zhang et al., 2011; Y.M. Zhang et al., 2011).

Stone coal is a type of inferior anthracite in which the grade of vanadium is low (less than 1% usually). Most of the vanadium in stone coal exists in the crystal lattice of the aluminosilicate minerals and

isomorphically replaces Al(III) in vanadium-bearing micas (Zhu et al., 2012; X.Y. Zhang et al., 2011; Y.M. Zhang et al., 2011; Bin, 2006). Thus, it is difficult to extract vanadium from stone coal by traditional beneficiation such as gravity concentration and magnetic concentration. Flotation is a better method of enrichment (Zafar and Ashraf, 2007), but the extraction efficiency is low and the grade of vanadium in the product is not sufficient to meet market requirements. Additionally, the flotation process is complex and lengthy. Therefore, it is necessary to use hydrometallurgical extraction to develop new processes for vanadium extraction from stone coal (Habbache et al., 2009).

However, the present technologies and equipment for extracting vanadium from stone coal are relatively laggard. Most traditional processes neither are inefficient (Li et al., 2011; M.T. Li et al., 2009; Z. Li et al., 2009; Li et al., 2010a, 2010b) nor produce serious environmental pollutants such as HCl and Cl_2 (Ye et al., 2012). Recently, an eco-friendly and hopeful process known as direct acid-leaching solvent extraction was developed (M.T. Li et al., 2009; Z. Li et al., 2009; Li et al., 2010a, 2010b). Specifically, fluorine-bearing aid-leaching reagents (e.g., HF, NH_4F, H_2SiF_6 and CaF_2) are introduced into the leaching system to improve the efficiency of vanadium leaching (He et al., 2008). So far, a few researchers have researched the fluoride-assisted vanadium leaching. Zhou et al. (2009) used sulfuric acid with NH_4F to investigate the direct acid-leaching parameters and attempted to discover the mechanism of fluoride-assisted leaching. They found that only the limonite was dissolved in the absence of NH_4F while both micas and limonite were dissolved in the presence of NH_4F. Li et al. (2010a, 2010b)

researched the optimum parameters for the direct acid-leaching process using sulfuric acid, HF and NaClO. They found that HF can promote the decomposition of the micaceous minerals and increase the vanadium leaching efficiency. X.Y. Zhang et al. (2011) and Y.M. Zhang et al. (2011) studied the optimum parameters in the H_2SiF_6 leaching process. They preliminarily ascribed the function of H_2SiF_6 to the generation of $HF_{(aq)}$ and the destruction of the illite structure by comparing leaching by H_2SO_4 with leaching by H_2SiF_6. He et al. (2008) investigated the effects of HF acid, NaF and CaF_2, and demonstrated that fluoride can facilitate the breakage of the crystal structure of aluminosilicate minerals. Besides, He (2009) researched the sulfuric acid leaching process of blank-roasted residue by calculating the standard free energies of the dissolution of pure illite, hematite and kaolinite at specific temperatures. This study discovered that the dissolution of vanadium-bearing illite was spontaneous. However, the mechanism about how vanadium-bearing micas break down and how fluoride enhances the vanadium leaching still remains unknown. It is more regrettable that there are few studies (Zhou et al., 2011) about the thermodynamics analyses of vanadium leaching from stone coal.

The main purpose of this work is to analyze the mechanism of calcium fluoride-enhanced vanadium leaching from stone coal by thermodynamic analyses and the comparison between unassisted and calcium fluoride-assisted vanadium leaching.

2. Experimental

2.1. Materials

The stone coal used in this study was obtained from Jiangxi province in China. Prior to the leaching tests, the ore was crushed to a grain size of 0–3 mm and subsequently ground to a particle size of <74 μm accounting for 75%. The obtained ore was called raw ore throughout this work. The chemical composition of the raw ore determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) is shown in Table 1. The mineral analysis by X-ray Diffractometry (XRD) method is shown in Fig. 1. The main minerals were quartz, pyrite, chlorite and phlogopite. The valence state analyses (Table 2) which depended on the method of potentiometric titration (Hu et al., 2012; Zhang, 1992) showed that vanadium of the raw ore was composed of V(III) and V(IV). There was no V(V). Phlogopite was the main vanadium-bearing mineral. The calcium fluoride was supplied by Shanghai Shanpu Chemical Co., Ltd. All other reagents and chemicals used were of analytical reagent grade.

2.2. Methods

2.2.1. Leaching tests

Leaching tests were carried out to determine the effects of sulfuric acid and time on the unassisted and calcium fluoride-assisted vanadium leaching from stone coal. The tests about the effect of sulfuric acid concentration on the efficiency of calcium fluoride-assisted vanadium leaching were carried out in magnetic temperature-controlled stirrers (SZCL-2A) at liquid/solid ratio (L/S) of 1 mL/g, 368 ± 1 K and 5% (w/w) calcium fluoride for 4 h. The H_2SO_4 concentration was in the range of 5%–25% (v/v). Similarly, the effect of leaching time on the efficiency of calcium fluoride-assisted vanadium leaching was determined in magnetic temperature-controlled stirrers (SZCL-2A) at 15% (v/v) H_2SO_4, 1 mL/g, 368 ± 1 K and 5% (w/w) calcium fluoride. The leaching time was in the range of 0–6 h. Leaching tests in the absence of calcium fluoride were carried out under the same conditions except for
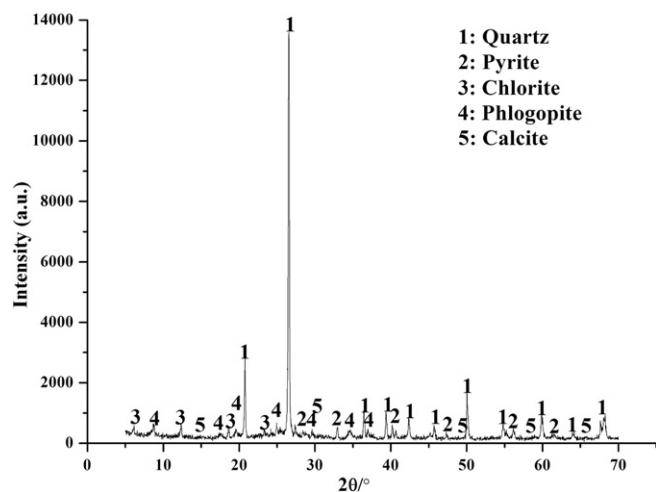

Fig. 1. XRD patterns of the raw ore.

5% (w/w) calcium fluoride. Each leaching test consumed 100 g raw ore. The slurry was then divided into the leachate and residue via vacuum filtration.

2.2.2. Analyses

The leachate and residue obtained from the leaching tests at 15% (v/v) H_2SO_4, 1 mL/g and 368 ± 1 K for 4 h were used for analyses. The chemical composition of the leachate was analyzed by ICP-AES. The ICP-AES was performed on the IRIS Advantage ER/S instrument (Thermo Elemental, USA). The forms of fluorine in the leachate were determined by ^{19}F liquid Nuclear Magnetic Resonance (NMR) and X-ray Photoelectron Spectroscopy (XPS). The NMR analysis was performed on the Avance-III-500 instrument (Bruker, Germany). The XPS analysis, which consisted of loading anion resin 201 × 7 (commercial Chinese name) with the leachate with fluorine and subsequent vacuum drying of the resin, was performed on the VG Multilab 2000 instrument (Thermo Electron, USA). The mineral composition and morphology of the obtained residue was analyzed by XRD and Scanning Electron Microscope (SEM) respectively. The XRD analysis was performed on the D/max-III instrument (Rigaku, Japan), and the SEM analysis employed the JSM-5610LV instrument (JEOL, Japan). In addition, the valence state of vanadium was determined by potentiometric titration performed on the ZDJ-4 automatic potentiometric titrator from INESA Scientific Instrument Co., Ltd.

The vanadium concentration in the aqueous phase was determined by ferrous ammonium sulfate titration using 2-(phenylamino)-benzoic acid as an indicator (GB/T 8704.5, 2007). The fluorine concentration was determined by fluorine ion selective electrode (GB/T 7484, 1987) and the iron concentration was determined by 1,10-phenanthroline spectrophotometry (HJ/T 345, 2007). The content of other elements in the aqueous phase was analyzed using ICP-AES.

By comparing the analyses of the raw ore with those of the leachate and residue, it is possible to infer the whole leaching process. Furthermore, comparing calcium fluoride-assisted and unassisted leaching behaviors can identify the mechanism of calcium fluoride-enhanced vanadium leaching from stone coal. Thermodynamic analyses were conducted to further confirm the reactions that described calcium fluoride-assisted vanadium leaching from stone coal and the associated mechanism.

Table 1
The composition of the raw ore.

Element	V	Al	TFe	K	Ca	Mg	Ba	Si	C	S
Content/wt.%	0.57	3.39	2.18	1.41	0.31	0.90	0.043	29.10	16.16	2.58

Table 2
The valence state of vanadium in the raw ore.

Valence state	V(III)	V(IV)	V(V)
Content/%	64.84	35.16	0