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Highly selective separation of vanadium over iron from stone coal by oxalic acid leaching

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ABSTRACT

In this paper, a novel method was proposed to selectively extract vanadium from stone coal by oxalic acid leaching. Vanadium was leached, but the iron impurity was maintained in the leaching residue. The effects of leaching conditions on the leaching efficiency of vanadium and iron were investigated for oxalic and sulfuric acid leaching, respectively. For oxalic acid leaching, 71.5% of the vanadium can be recovered with only 3.4% of the iron impurity leached under the leaching conditions: a dosage of H^+ of 12 mol/kg, a leaching time of 6 h, a leaching temperature of 368 K (95 °C) and a water–mineral ratio of 1.5 L/kg. However, under the same conditions, 74.1% of the vanadium and 13% of the iron were leached during sulfuric acid leaching. The XRD and FTIR analyses showed that both oxalic and sulfuric acid leaching can destroy the crystal lattice structure of muscovite, resulting in the leaching efficiency of vanadium without much difference. Further, the SEM-EDS and XPS analyses indicated that very little pyrite dissolved during oxalic acid leaching, but that much more pyrite dissolved during sulfuric acid leaching. Therefore, oxalic acid leaching can achieve a highly selective separation of vanadium over iron from stone coal.

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Introduction

Vanadium is a significant rare metal that is widely applied in ferrous and nonferrous alloys because of its physical properties such as high tensile strength, hardness, and fatigue resistance [1–3]. In China, stone coal (also called black shale) is a special vanadium-bearing resource, and the gross reserve of vanadium in stone coal accounts for more than 87% of the domestic reserve of vanadium [4,5].

In general, most vanadium in stone coal exists in the crystal lattice of the aluminosilicate minerals and isomorphically replaces Al(III) in vanadium-bearing mica group minerals (such as illite, muscovite and biotite), so it is difficult to extract vanadium from stone coal [6,7]. Traditional techniques of additives roasting-water leaching or low acidity leaching have been developed to extract vanadium from stone coal [2,8–10]. These techniques are either inefficient or release hazardous gases (such as HCl and Cl_2). Hence, the eco-friendly and high-efficiency technique of direct sulfuric acid leaching, together with some fluoride (such as HF and CaF_2) as assisted leaching reagent, has been proposed in recent years [6,11,12]. However, the sulfuric acid leaching process for vanadium extraction is not selective because numerous impurity ions, especially iron cation, are inevitably leached along with vanadium, which is detrimental to the selective extraction of vanadium from acid leaching solutions [13,14]. Solvent extraction and ion exchange are commonly adopted to recover and enrich vanadium from acid leaching solutions [13,15–17]. However, because sulfuric acid leaching solutions contain a high concentration iron impurity, Fe(III) can hydrolyze and precipitate as colloidal $Fe(OH)_3$ when the pH value is higher than the $Fe(OH)_3$ hydrolysis pH value. As a result, not only does colloidal $Fe(OH)_3$ affect the process of ion exchange, but it also leads to emulsification and a third phase in the solvent extraction process [8,18–21]. Moreover, the stripping of Fe(III) from the organic phase is known to be extremely difficult, so the accumulation of Fe(III) hinders the reutilization of extractant [22–24]. Fe(II) can also be co-extracted in the solvent extraction process [17,23,25,26], reducing the purity of vanadium-rich

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solution and vanadium pentoxide. From the above, it can be seen that the sulfuric acid leaching process is of poor selectivity for vanadium extraction from stone coal, so it is necessary to improve the selectivity for vanadium extraction in the leaching process.

At present, numerous researchers use watersoluble organic acids to recover valuable elements [27–32]. Oxalic acid is the most promising organic acid as a leaching reagent because of its cheap biological sources, acid strength and good complexing effects [33]. It was reported that oxalic acid can be used as a complexing agent to selectively extract vanadium from the spent catalyst [34]. Lee et al. [35] studied the recovery of metals (including vanadium) from a spent catalyst and compared oxalic acid to citric acid as leaching reagents. The results showed that the vanadium concentrations were 21,000 ppm and 18,000 ppm in the citric and oxalic acid leaching solutions, respectively. In addition, the citric acid leaching solution contained iron of 2650 ppm, but the iron concentration in the oxalic acid leaching solution was only 20 ppm, indicating that the oxalic acid leaching process can selectively extract vanadium from a spent catalyst. On this basis, it is possible to use oxalic acid to achieve a selective separation of vanadium over iron from stone coal during the leaching process. However, the studies focusing on the vanadium extraction from stone coal using oxalic acid as a leaching reagent have not been reported in the published literature.

In this study, a stone coal was leached with oxalic acid and sulfuric acid, respectively. The effects of the leaching conditions on the leaching efficiency of vanadium and iron were investigated. In addition, the mechanisms of the leaching behavior of vanadium and iron were analyzed. A novel leaching method was proposed to achieve a highly selective separation of vanadium over iron from stone coal.

Experimental

Materials

Vanadium-bearing stone coal was obtained from Tongshan, Hubei Province, China. The ore was crushed to a grain size of 0–3 mm by a jaw crusher (model XPC-60×100) and a double-roll crusher (model HLXPS-φ250×150). Then the ore was ground to less than 0.074 mm by a vibration mill (model XZM-100), accounting for 75% of the total. The ground ore is referred to as raw ore throughout this study. All reagents (calcium fluoride, oxalic acid and sulfuric acid) used in this study were of analytical grade.

The chemical composition of the raw ore was analyzed by ICP-AES and is shown in Table 1. The grade of V_2O_5 and Fe_2O_3 is 0.74% and 4.8%, respectively. The mineral composition of the raw ore was obtained by XRD, electron microscopy and chemical composition analysis and is shown in Table 2. The results of the electron probe analysis (EPMA) of the raw ore are shown in Table 3. From Tables 2 and 3, it can be seen that the main mineral phases of the raw ore are quartz, mica, calcite, feldspar and pyrite. Most vanadium is in mica minerals (including muscovite, illite and biotite), and most iron is in pyrite. In addition, some Fe exists in the

Table 1
Chemical composition of the raw ore (wt.%).

Element	V_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	C
Content	0.74	71.93	9.22	4.80	5.82	2.45	1.09	10.30

Table 2
Mineral composition of the raw ore (wt.%).

Mineral	Mica minerals	Feldspar minerals	Quartz	Pyrite	Calcite	Kaolinite	Coal	Else
Content	15	10	37	7	11	5	13	2

Table 3
EPMA result of the raw ore (wt.%).

Minerals	V_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O
Pyrite	0.00	0.06	0.00	65.69	0.00	0.00
Calcite	0.00	0.00	0.00	0.00	69.94	0.00
Quartz	0.00	98.35	0.00	0.00	0.00	0.00
Muscovite	4.22	51.08	27.22	0.26	0.02	9.52
Illite	5.01	39.95	23.25	0.16	0.15	8.55
Biotite	1.59	40.78	17.63	1.51	0.02	8.47
Albite	0.11	49.43	6.92	0.09	0.21	0.99

crystal lattice of the silicate minerals in the stone coal. The vanadium valences of the raw ore were measured on an automatic potentiometric titrimeter (model ZDJ-4A) using the ammonium ferrous sulfate method [36], and the result show that V(III) is dominate accounting for 61.8%, V(IV) accounts for 38.2% and V(V) is not found in the raw ore, as shown in Fig. 1.

From the analyses above, the raw ore used in this study is a representative and typical mica type vanadium-bearing stone coal, from which it is highly difficult to extract vanadium.

Procedure and test methods

The leaching experimental set-up is showed in Fig. 2 and the procedure was carried out as follows: the same mass of 0.05 kg raw ore was leached by oxalic acid or sulfuric acid under the condition of 5% (w/w) calcium fluoride addition in a round-bottom flask equipped with a temperature-controlled magnetic stirrer (SZCL-2A). There was a glass condenser to prevent solution loss because of evaporation. The effects of dosage of H^+, leaching time, leaching temperature and water–mineral ratio on the leaching efficiency of V and Fe were both investigated by oxalic and sulfuric acid leaching. At the end of each leaching experiment, the leaching solution and the leaching residue were obtained after solid–liquid separation by vacuum filtration (model SHB-III).

The dosage of H^+ and the water–mineral ratio were defined as follows:

$$\text{Dosage of } H^+ = \frac{\text{Integral molar quantity of } H^+ \text{ in the leaching reagent, mol}}{\text{The mass of the raw ore in the leaching experiment, kg}} \quad (1)$$

$$\text{Water–mineral ratio} = \frac{\text{Volume of water used in the leaching experiment, L}}{\text{The mass of the raw ore in the leaching experiment, kg}} \quad (2)$$

The leaching efficiency of vanadium and iron were calculated as follows:

$$\beta_V = \frac{C_V \times V}{\omega_V \times m} \times 100\% \quad (3)$$

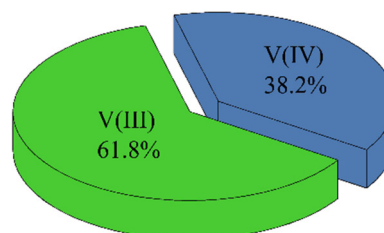$$\beta_{Fe} = \frac{C_{Fe} \times V}{\omega_{Fe} \times m} \times 100\% \quad (4)$$

Fig. 1. Vanadium valences of the raw ore.