



Separation and recovery of iron impurity from a vanadium-bearing stone coal via an oxalic acid leaching-reduction precipitation process



Pengcheng Hu^{a,b,c}, Yimin Zhang^{a,b,c,*}, Tao Liu^{a,b,c}, Jing Huang^{a,b,c}, Yizhong Yuan^{a,b}, Yadong Yang^{a,b,c}

^a College of Resources and Environment Engineering, Wuhan University of Science and Technology, Wuhan 430081, Hubei Province, China

^b Hubei Provincial Engineering Technology Research Center of High Efficient Cleaning Utilization for Shale Vanadium Resource, Wuhan 430081, Hubei Province, China

^c Hubei Collaborative Innovation Center for High Efficient Utilization of Vanadium Resources, Wuhan 430081, Hubei Province, China

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ABSTRACT

Sulfuric acid leaching solutions of vanadium-bearing stone coal usually contain massive iron impurity, which is detrimental to vanadium extraction because iron is easy to precipitate or co-extracted during the solvent extraction and ion exchange. Meanwhile, sulfuric acid in wastewaters is environmentally hazardous. In this paper, a vanadium-bearing stone coal was leached with oxalic acid, which has the advantages of cheap biological sources and good environmental compatibility. The iron impurity was separated from the oxalic-acid leaching vanadium-bearing solution (OLVS) via reduction precipitation. During the oxalic acid leaching, 80.5% of the vanadium can be recovered, and 50.2% of the iron impurity was leached with vanadium under the conditions: a CaF_2 addition of 5 wt%, an oxalic acid dosage of 60 wt%, a leaching time of 4 h, a leaching temperature of 95 °C and a water-mineral ratio of 1.0 mL/g. However, the concentrations of vanadium and iron were 1777.5 ppm and 6552.5 ppm, respectively, in the OLVS. By adopting reduction precipitation, 83.8% of the iron was precipitated as $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with only a 2.5% vanadium loss when an iron powder dosage was 2.5 times that of the stoichiometry for 90 min at 25 °C. The oxalic-acid leaching vanadium-bearing solution after reduction precipitation (OLVS-P) contained 1733.6 ppm of vanadium and only 1059.8 ppm of iron. Analyses indicated that the as-produced $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (P- $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) was in a high crystalline state with a purity of 98.2%. Therefore, the iron impurity can be separated and recovered from the vanadium-bearing stone coal via the oxalic acid leaching-reduction precipitation process.

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1. Introduction

Vanadium is an important rare metal that is widely applied in various technological fields, such as steel alloys, batteries and advanced materials [1–4]. Stone coal is widely distributed in China and occupies more than 87% of the domestic vanadium reserves; therefore, vanadium extraction from stone coal has attracted substantial attention [1,3].

Most vanadium in stone coal exists as an isomorphism in the crystal lattice of mica group minerals (including muscovite, illite and biotite) because vanadium can readily replace Al(III), making vanadium extraction from stone coal difficult [5,6]. Currently, blank roasting-acid leaching is an effective technique to recover vanadium from stone coal [3]. Sulfuric acid is widely used as a

leaching reagent, and some fluorides (e.g., CaF_2 , HF, and NH_4F) are introduced to the leaching process to enhance the vanadium leaching efficiency [5,7]. However, massive impurity ions, especially iron cations, are leached together with vanadium, resulting in a leaching solution that contains a high concentration of iron impurity [8,9], which has an adverse effect on vanadium extraction from leaching solutions. Solvent extraction and ion exchange are commonly applied to extract and concentrate vanadium from leaching solutions [8,10]. However, Fe(III) can easily be precipitated as colloidal $\text{Fe}(\text{OH})_3$ when the pH value is higher than the $\text{Fe}(\text{OH})_3$ hydrolysis pH value. As a consequence, not only is colloidal $\text{Fe}(\text{OH})_3$ detrimental to the ion exchange process but it also gives rise to a third phase and emulsification in the solvent extraction process [9,11]. Meanwhile, Fe(II) and Fe(III) can be partially extracted with vanadium [9,12,13], decreasing purity of the vanadium-rich solution and V_2O_5 product. Raffinate (wastewater), which is derived from the solvent extraction process, is discharged or used to prepare an acid solution for leaching without recycling iron at a high concentration [14,15]. It can be concluded that the

* Corresponding author at: School of Resource and Environmental Engineering, Wuhan University of Science and Technology, Wuhan 430081, Hubei Province, China.

E-mail address: zym126135@126.com (Y. Zhang).

iron impurity in vanadium-bearing leaching solutions negatively affect vanadium extraction. Therefore, it is essential to separate and recover iron impurity as a value-added product from leaching solutions before solvent extraction or ion exchange for vanadium enrichment and extraction.

Currently, environmentally acceptable organic acids (e.g., oxalic acid, citric acid and others) have been studied as alternative leaching reagents for metal extraction [16–27]. Organic acids may dissolve minerals via the following two mechanisms: (1) acid attack and displacement of metal ions by H⁺ (acidolysis) and (2) formation of soluble metal-ligand complexes and chelates (complexolysis) [16,26]. Oxalic acid has attracted particular interest because of its strong acidity, cheap biological sources and good complexing ability [19–21]. Moreover, oxalic acid is a solid-state acid, making it easy to use in the leaching process. At present, oxalic acid can be produced from the bio-fermentation of carbon sources, making the production of oxalic acid economical [16,19,20]. Meanwhile, the remaining oxalic acid in wastewater can be readily removed via bio-degradation without pollution [27]. Therefore, the use of oxalic acid as a leaching reagent provides an environmentally friendly leaching process. Extensive studies have been performed to efficiently extract vanadium from spent catalysts using oxalic acid [17,18,22–24]. However, there are very few published studies on vanadium extraction from stone coal using oxalic acid. Our previous study indicated that oxalic acid can be used as an alternative leaching reagent to recover vanadium from stone coal [25], but the vanadium leaching efficiency was only 71.5% from a direct leaching process. To further improve the vanadium leaching efficiency further, the stone coal should be roasted and then leached with oxalic acid. It has been reported that the iron oxides can be dissolved by oxalic acid and exist as $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ and $\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$ in solutions [19–21,28,29]. Therefore, iron oxides in the roasted stone coal may also be leached during the leaching process, resulting in a complex leaching solution that contains a massive iron impurity. Several researchers have successfully separated and recovered iron from solutions in the form of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ($K_{sp} = 3.2 \times 10^{-7}$), which has potential applications as a raw material for magnetite, as a solid electrolyte and as an absorbent [20,21,30,31].

Based on the above, it is possible to efficiently extract vanadium from roasted stone coal via oxalic acid leaching, which is eco-friendly, and the iron impurity can be separated and recovered as $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ from the leaching solution. In this paper, a novel technology of oxalic acid leaching-reduction precipitation process was proposed. A vanadium-bearing stone coal was leached with oxalic acid and the iron impurity was successfully precipitated as a value-added product of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ from the oxalic-acid leaching solution.

2. Experimental

2.1. Materials

The vanadium-bearing stone coal, which was obtained by blank-roasting in an industrial fluidized bed reactor at 750–850 °C for 50–60 s, was collected from Teng-da Mining and Metallurgy Co. Ltd., Hubei, China. The vanadium-bearing stone coal was crushed to a grain size of 0–3 mm by a jaw crusher and a double-roll crusher. Then the ore was ground to minus 0.074 mm with a vibration mill, accounting for 75% of the total. The ground ore is referred to as raw ore throughout this study. All reagents used in this study were of analytical grade. All water used in this study was deionized water.

The main chemical composition and mineral composition of the raw ore were obtained by ICP-AES (Table 1) and XRD (Fig. 1) analyses, respectively. As shown in Table 1, the grades of V_2O_5 and

Fe_2O_3 are 0.97% and 4.61%, respectively. The XRD pattern of the raw ore shown in Fig. 1 indicates that the main mineral phases are quartz, muscovite, hematite and anhydrite. Most iron exists in the hematite. As discussed above, vanadium in stone coal can replace Al(III) as an isomorphism in the structures of mica group minerals. To develop a visual understanding of the vanadium occurrence state in the raw ore, SEM-EDS analysis was conducted. Fig. 2 shows that the relevance of V, O, Al, Si and K was quite good, meanwhile, the atom percentages of O, Al, Si and K at the pointed area “M” were similar to those of muscovite, indicating that the vanadium was within the muscovite. Therefore, the raw ore used in this study is a typical and representative mica-type vanadium-bearing stone coal, and it is highly difficult to extract vanadium from this stone coal.

2.2. Oxalic acid leaching-reduction precipitation process

2.2.1. Oxalic acid leaching step

Leaching experiments were performed to systematically study the optimal conditions for vanadium leaching efficiency. The experiments were performed as follows: 50 g of the raw ore was leached by oxalic acid with a constant amount of 5 wt% CaF_2 addition in a three-necked glass flask, which was heated with a temperature-controlled water bath magnetic stirrer and fitted with a glass condenser to prevent solution loss due to evaporation. Several leaching experiments were performed with varying oxalic acid dosages, leaching times and leaching temperatures at different water-mineral ratios. After the leaching experiment, the leaching solution and the leaching residue were obtained by vacuum filtration.

The vanadium leaching efficiency (E_V) was calculated by the following Eq. (1).

$$E_V = \frac{C_V \times V}{\omega_V \times m} \times 100\% \quad (1)$$

where C_V , V , ω_V and m refer to the concentration of vanadium in the leaching solution (g/L), volume of the leaching solution (L), grade of vanadium in the raw ore and mass of the raw ore used in the leaching experiment, respectively.

The vanadium leaching efficiency (E_{Fe}) was calculated by the following Eq. (2).

$$E_{Fe} = \frac{C_{Fe} \times V}{\omega_{Fe} \times m} \times 100\% \quad (2)$$

where C_{Fe} , V , ω_{Fe} and m refer to the concentration of iron in the leaching solution (g/L), volume of the leaching solution (L), grade of iron in the raw ore and mass of the raw ore used in the leaching experiment, respectively.

2.2.2. Reduction precipitation step

The oxalic-acid leaching vanadium-bearing solution (OLVS) was obtained under the optimal leaching conditions according to the oxalic acid leaching step. Precipitation experiments were conducted to systematically investigate the optimal conditions for the separation and recovery of the iron impurity from the OLVS. The experiments were performed as follows: a required iron powder dosage was added to 50 mL of the OLVS, which was stirred for 90 min at a required precipitation temperature. Several precipitation experiments were performed with varying iron powder dosages at different precipitation temperatures. At the end of each precipitation experiment, the precipitate was obtained by vacuum filtration, washed with deionized water and dried in a vacuum oven. The precipitate and the oxalic-acid leaching vanadium-bearing solution after reduction precipitation under the optimal reduction precipitation conditions were called as-produced $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (P- $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and OLVS-P, respectively.

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