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Selective leaching of vanadium from chromium residue intensified by electric field



ENVIRO

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ABSTRACT

Electro-oxidation was an environmentally-friendly technology, which could enhance the leaching process of vanadium. A novel process was developed for the selective leaching of vanadium from residue. The effects of reaction temperature, alkali-to-residue mass ratio, contact time and current intensity on leaching of vanadium were studied. Results showed that under the optimal reaction conditions (reaction temperature of 90 °C, initial NaOH-to-residue mass ratio of 0.5:1 g/g, contact time of 120 min, liquid to solid ratio of 4 mL/g and current intensity of 1000 A/m²), leaching efficiency of vanadium could reach up to 91.7%. The kinetics study revealed that leaching process of vanadium from chromium residue intensified with electric field was interpreted with shrinking core model under chemical reaction control. The apparent activation energy of vanadium dissolution was 10.08 kJ/mol.

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Introduction

Vanadium is an important strategic metal in the manufacturing of iron and steel, non-ferrous metals and petrochemical industry, *etc.*, due to its excellent physicochemical properties [1]. There are two important vanadium sources in China, called the vanadium and titanium magnetite ore and stone coal [2].

Many hydrometallurgical processes have been proposed to recover vanadium like salt-roasting, acid leaching, ammonia leaching, bioleaching and alkali leaching [3–9]. And some recycle technologies and impurity removal processes were conducted [10-14]. In the salt-roasting process, the vanadium slag was roasted with sodium salts. The vanadium(III) could be oxidized to high valence and form soluble phases like sodium vanadate, which could be easily leached out. However, some toxic gases emitted during the process were harmful for environment, such as hydrogen chloride, chlorine. Acid leaching was an efficient way for leaching vanadium from stone coals. However, it will not only lead to high acid consumption but also produce high concentrations of impurities for metallic ions in the leaching solution [8,15]. A novel method called sub-molten salt (SMS) technology has been successfully applied for treating amphoteric ores to extract valuable metals [16–19]. But the SMS was characterized by high alkaline concentration (usually above 50%), high process temperature and concentrated solution. It needed high alkaline consumption and energy cost.

In this regard, it is necessary to develop a new and cleaner production process to improve the vanadium leaching efficiency with low energy consumption. The present work focused on the alkaline leaching of vanadium from chromium residue intensified by electric field. The effects of reaction temperature, alkali-toresidue mass ratios, contact time and current intensity on leaching efficiency of vanadium were studied.

Materials and methods

Materials

The chromium residue used in this study was collected from Panzhihua city, Sichuan province, China. It was generated from the treatment of waste water from an iron and steel mill. The waste water contained chromium(VI) and vanadium(V). The residue was produced by firstly reducing chromium(VI) and vanadium(V) with Fe or FeSO₄, and then adding NH₃ to precipitate them. The XRF (Xray fluorescence) analysis of the chromium residue is as shown in Table 1. And the XRD (X-ray diffraction) analysis of the chromium residue is shown in Fig. 1. The vanadium and the chromium contained in the chromium were formed from low valence compounds like Fe(Cr,V)O₄, VOSO₄, Cr₂(SO₄)₃.

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Table 1

XRF analysis results of main composition in residue.

Component	0	Cr	Si	Na	S	V
Amount (wt.%)	41.09	14.36	12.02	9.76	12.02	1.63
Component	Ca	Cl	Fe	K	Mg	N
Amount (wt.%)	1.42	4.09	0.33	0.29	0.20	8.83

All the reagents including sodium hydroxide used for leaching and ammonium ferrous sulfate, urea, potassium permanganate, sodium nitrite and *N*-phenylanthralinic used in chemical analysis were of analytical grade.

Methods

The dried chromium residue was ground and sieved, and its particle size below 200 mesh was used in this study. During the leaching process, the entire suspension was stirred at an appropriate rate.

The leaching procedure was conducted in a stirred beaker which was placed in the water bath equipment. The NaOH solutions were prepared and then added into the beaker. The chromium residue would be added into the reactor once the expected temperature was reached. After the required contact time, the filtrate was separated from the residue by vacuum filtration.

Titration with ammonium ferrous sulfate was used to determine the concentration of vanadium and chromium in the filtrate [20].

Results and discussion

Alkaline leaching

The effect of NaOH-to-residue mass ratio on the leaching efficiency was studied under the following conditions: liquid to solid ratio of 4 mL/g, reaction temperature of $90 \degree \text{C}$, and contact time of 2 h. The results were shown in Fig. 2.

The leaching efficiency of vanadium was not good, which yielded to a best of 62.6%. This could be partially explained by the elution of some chemicals which were responsible for the alkaline consumption such as NH_4Cl and $(NH_4)_2SO_4$, as the presence of ammonium salts were confirmed by the smell of NH_3 during the



Fig. 1. XRD traces of the chromium residue.



Fig. 2. Effects of NaOH-to-residue mass ratio on the leaching efficiency of vanadium.

alkaline leaching process of the residue [21]. Also, some vanadium oxides in low valence were insoluble in NaOH solution, which leads to the low leaching efficiency of vanadium. The chromium could not be leached out as chromium(III) was insoluble in the NaOH solution.

Electro-oxidation-leaching

Some ways to improve the leaching efficiency of vanadium were studied. Oxidizing substances like MnO₂ and H₂O₂ were added to enhance the leaching of vanadium in low valence during the leaching process [3]. Electro-oxidation was also used to improve the leaching efficiency of vanadium in some ways [22,23].

The electro-oxidation technology was applied in processing the chromium residue in concentrated NaOH solution. The electrodes used were the Pb-Ag-Ca-Sr. The space between the anode and the cathode was 0.04 m and the working area of the electrode was 0.0008 m². And the experiments were carried out intensified with current intensity of 1000 A/m². The results were presented in Fig. 3.

Taken into account the optimized vanadium leaching efficiency by NaOH solution, the performance was intensified by electric field, which yielded to a best of 91.7%. During the leaching process, H_2O and OH^- around the metal anode would lost electron formed •OH and absorbed on the surface of the metal anode to generate



Fig. 3. Effects of NaOH-to-residue mass ratio on the leaching efficiency of vanadium and chromium intensified by electric filed.

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