Secondary leaching of vanadium from vanadium tailing intensified with CaF₂

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Abstract. Vanadium in the vanadium tailing existed in different valence wrapped by metasilicate was difficult to leach out. CaF₂ was added to intensify the leaching process, which was aimed at destroying the metasilicate and releasing vanadium out to achieve high leaching efficiency and low residual content in the tailing. The parameters were studied. Results showed that CaF₂ could destroy the metasilicate and exposed vanadium out, which was beneficial for vanadium leaching. The vanadium in the vanadium tailing could be secondary leaching out and the residual content of vanadium was decreased to 0.84 wt. % under the optimal conditions: concentration of sulfur acid of 50 wt. %, reaction temperature of 90 ℃, reaction time of 150 min, liquid-to-solid ratio of 5.0 mL/g, and addition of CaF₂ at 10 wt. %.

1. Introduction

Vanadium is an important metal widely used due to its excellent properties, like batteries [1-6], catalysts [7], nano-materials [8-10], membrane [11], etc. The main vanadium-source is stone coal [12-14], vanadium titan-magnetite and other vanadium-contained sources, including fly ashes [15-17], spent catalysts [18-20], vanadium residue [21-24].

Vanadium in the mineral was mainly existed in the spinel with low valence. Liquid-oxidation technologies had been conducted to oxidize and leach out vanadium. Sub-molten salt (SMS) technology [25, 26, 27] had been successfully applied to treat amphoteric ores to extract valuable metals, while it needed high alkaline consumption and energy cost. Electro-oxidation was a new environmental-friendly technology [23, 28-30] used to leach out valuable metal, while the reaction principle was still unsolved and used limited. The most commonly used technologies were roasting technologies. Sodium roasting technology [31-33] was an efficient way to recover vanadium accompanied with toxic gases and amount of waste water. In order to overcome the problem associated in sodium roasting technologies, CaO was used to replace sodium salts during the roasting process [13, 21, 34]. Vanadium was converter to calcium vanadate and being efficiently leached out with sulfur acid during the process. Also non-salt roasting technology [22, 35, 36] was conducted.

Though many efficient technologies were applied to leach out vanadium, and leaching efficiency was high enough, there were still some vanadium remained in the tailing. In this paper, the vanadium tailing contained 3.11 wt. % V₂O₅ was used as vanadium source for secondary leaching. CaF₂ was added to intensify the leaching process and improve the leaching efficiency of vanadium. The effects of solid-to-liquid ratio, concentration of sulfur acid, reaction temperature, reaction time, liquid-to-solid ratio and addition dosage of CaF₂ on leaching efficiency of vanadium and residual content of vanadium were examined.
2. Experimental

2.1 Experimental Materials

The chemical composition of vanadium tailing was listed in Table 1. It can be seen that this vanadium tailing contained 3.11wt% V$_2$O$_5$, 10.67wt% CaO, 14.41wt% MnO$_2$ and 24.94wt% Fe$_2$O$_3$. The SEM graph amount of vanadium tailing sample was shown in Figure 1.

H$_2$SO$_4$ (98 wt. %), HCl (38 wt. %), and H$_3$PO$_4$ (85 wt. %) were purchased from Kelong Chemical Reagent Co., Ltd., China. Deionized water used in the experiments was produced by water purification system (HMC-WS10).

| Compounds | Fe$_2$O$_3$ | SiO$_2$ | CaO | SO$_3$ | V$_2$O$_5$ |
|-----------|-------------|---------|-----|--------|------------|
| amount    | 24.94       | 25.22   | 10.67 | 12.03  | 3.11       |
| Compounds | MnO$_2$ | Na$_2$O | P$_2$O$_5$ | Al$_2$O$_3$ |
| amount    | 14.41 | 0.19 | 0.78 | 2.42 |

Table 1 The component of vanadium tailing

2.2 Methods

All experiments were performed in a glass beaker with thermostatic mixing water bath pot equipment [23, 28, 37, 38]. The temperature was controlled by the bath pot, with a precision of ±0.1 °C. A predetermined amount of sulfur acid (H$_2$SO$_4$) and deionized water were added to beaker to make a homogeneous solution under constant stirring. And then the vanadium tailing was added after the temperature of the solution stabilization. After the leaching process, the solution was separated by vacuum filtration. The experiment conducted with CaF$_2$ was also carried out in the batch reactor.

After the required reaction time, the concentration of vanadium in the filtrate was determined by inductive couple plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 6300DV) [22, 35, 39]. The leaching efficiency ($\eta$) of vanadium for each experiment was calculated in Equation (1):

$$\eta = \frac{V \times C}{M \times W_x}$$

Where, $V$ is the volume of leaching solution, $L$; $C$ is the concentration of vanadium in the filtrate, g/L; $M$ is the initial mass of the vanadium tailing added into the reactor, g; $W_x$ is the mass percentage of vanadium in the vanadium tailing, wt%.

3. Results and Discussions

3.1 Effect of concentration of sulfur acid

The effect of concentration of sulfuric acid on the leaching efficiency of vanadium and the residual content of vanadium in the residue was preferentially examined under the following conditions: the liquid-to-solid ratio of 5.0 ml/g, tailing particle size of < 200 mesh, reaction temperature of 90 °C,
reaction time of 150 min. The results were summarized in Figure 2. The results indicated that the leaching efficiency of vanadium was increased with the increasing of concentration of sulfur acid. And also the residual content of vanadium was decreased. During the leaching process, the vanadium oxide was reacted with sulfur acid and being leached out [12, 40-42]. Also, the vanadium was easy to dissolve in acid solution at low concentration. In view of the cost of acid cost during the leaching process, the concentration of 50 wt. % would be the optimum concentration.

![Figure 2](image2.png)

Figure 2 The effect of concentration of sulfur acid on leaching efficiency and residual content of vanadium (wt. %) in the residue

3.2 Effect of reaction temperature

The reaction temperature was another important parameter that had significant influence on the leaching process of vanadium from both thermodynamic and kinetic consideration. Figure 3 summarized the effect of reaction temperature on leaching efficiency of vanadium and residual content of vanadium in the residue under the standard conditions: the liquid-to-solid ratio of 5.0 ml/g, tailing particle size of < 200 mesh, the concentration of sulfur acid of 50 wt. %, reaction time of 150 min.

It was shown that the reaction temperature had an obvious effect on the residual content of vanadium. When the reaction temperature increased from 30 °C to 90 °C, the residual content of vanadium decreased greatly from 1.31 wt. % to 1.05 wt. %. This indicated that a higher temperature could facilitate the reaction. The temperature of 90 °C was chosen to study the effect of other factors in the subsequent experiments.

![Figure 3](image3.png)

Figure 3 The effect of reaction temperature on leaching efficiency and residual content of vanadium (wt. %) in the residue

3.3 Effect of reaction time

The effect of reaction time on the leaching process was preferentially studied under the following conditions: the liquid-to-solid ratio of 5.0 ml/g, tailing particle size of < 200 mesh, the concentration
of sulfur acid of 50 wt. %, reaction temperature of 90 °C. The leaching efficiency of vanadium and residual content of vanadium over reaction time were summarized in Figure 4.

It could be clearly seen that the residual content of vanadium decreased slightly from 1.30 wt. % to 0.94 wt. % with the reaction time increasing from 30 min to 150 min. This indicated that vanadium could be more easily and quickly leached out from the vanadium tailing. In view of the cost of electric energy during the leaching process, the reaction time of 150 min would be the optimum reaction time.

Figure 4 The effect of reaction time on leaching efficiency and residual content of vanadium (wt. %) in the residue

3.4 *Effect of liquid-to-solid ratio*

The solid-to-liquid ratio was an important parameter affected the volume of filtrate and concentration of purpose product in the leaching process. Some experiments were conducted to evaluate an optimal solid-to-liquid ratio for high leaching efficiency of vanadium. The solid-to-liquid ratio was set as 3.0 mL/g, 4.0 mL/g, 5.0 mL/g, 6.0 mL/g and 7.0 mL/g, respectively. And other conditions were kept constant, such as the concentration of sulfur acid of 50 wt. %, reaction temperature of 90 °C, reaction time of 150 min and tailing particle size of < 200 mesh. The results were shown in Figure 5.

It could be seen from Figure 5 that with the liquid to solid ratio increasing from 3.0 mL/g to 7.0 mL/g and the residual content of vanadium was kept stable as 1.05 wt. %. This indicated that the liquid-to-solid ratio had no significant influence on the leaching process of vanadium.

Figure 5 The effect of liquid-to-solid ratio on leaching efficiency and residual content of vanadium (wt. %) in the residue

3.5 *Effect of addition of CaF₂*

Some ways to improve the leaching efficiency of vanadium were studied. Oxidizing substances like MnO₂ and H₂O₂ and electro-oxidation technology were applied to enhance the leaching process [23, 28, 29, 43-45]. CaF₂ was used to destroy the metasilicate and intensified the leaching process. The effect of addition of CaF₂ on the leaching process was summarized in the Figure 6.Seeed from Figure 7,
the metasilicate was destroyed with the addition of CaF$_2$, the vanadium in different valence exposed out and reacted with sulfur acid, and then dissolved in the solution, which aimed at improving the leaching efficiency of vanadium and decreased the residual content of vanadium in the tailing. When the addition of CaF$_2$ was 10 wt. %, the residual content of vanadium was decreased to 0.84 wt. %, which was acceptable in industrial application.

Figure 6 The effect of addition of CaF$_2$ on leaching efficiency and residual content of vanadium (wt. %) in the residue

Figure 7 The leaching model with the addition of CaF$_2$

4. Conclusions
In this paper, CaF$_2$ was used as an addition to intensify the leaching process and improve the leaching efficiency of vanadium. The addition of CaF$_2$ could destroy the metasilicate and exposed vanadium out, which was beneficial for vanadium leaching. The vanadium in the vanadium tailing could be secondary leaching out and the residual content of vanadium was 0.84 wt. % under the optimal conditions: concentration of sulfur acid of 50 wt. %, reaction temperature of 90 °C, reaction time of 150 min, liquid-to-solid ratio of 5.0 mL/g, and addition of CaF$_2$ at 10 wt. %.

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