A Novel Technology for Recovery and Separation of Vanadium and Chromium from Vanadium-Chromium Reducing Residue

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Received: 26 November 2019; Accepted: 20 December 2019; Published: 26 December 2019

Abstract: This paper was to develop an efficient process for efficient recovery and separation of vanadium and chromium. The vanadium-chromium reducing residue was conducted by oxidation acidic leaching with MnO$_2$, followed by selective adsorption of vanadium and precipitation of chromium, respectively. The results showed that 97.93% vanadium was leached out and then adsorbed by melamine at pH 1.8 at 90 °C for 60 min. Almost all chromium was leached out and efficiently recovered as Cr$_2$O$_3$. The leaching process was mainly controlled by surface chemical reaction, and its kinetic behaviors fitted well with the shrink core model. The apparent activation energy for vanadium and chromium leaching out was calculated as 19.93 kJ·mol$^{-1}$ and 21.26 kJ·mol$^{-1}$, respectively.

Keywords: vanadium; chromium; MnO$_2$; acid leaching

1. Introduction

Vanadium(V) and chromium (Cr) are key resources that have been widely used during the manufacturing of petrochemicals, catalysts, ferrous and non-ferrous alloys, and stainless steel [1–4]. Due to the similar chemical and physical properties, vanadium and chromium commonly co-exist in minerals. Industrial vanadium is usually extracted from vanadium titanomagnetite ore and stone coal, during which a large amount of wastewater containing V(V) and Cr(VI) is produced. To satisfy the discharge standard, Na$_2$SO$_3$ or iron scurf is added to reduce and precipitate Cr(III), V(IV), and V(III), with the solid named as vanadium–chromium reducing residue (VCRR). China produces over 500 thousand tons of VCRR every year, causing significant environmental pollution, therefore, proper and efficient VCRR management technologies are urgently required.

To date, various hydrometallurgy technologies, such as direct NaOH leaching [5] and electric field alkaline leaching [6,7] have been developed to recover vanadium from the VCRR. The “NaOH-H$_2$O$_2$” combined direct leaching and roasting alkaline leaching are commonly used for VCRR processing [8–10]. However, the recovery of chromium was rarely focused. For simultaneous vanadium and chromium recovery, a new process of using sodium carbon-aided oxidation roasting, followed by sulfuric acid leaching was proposed by Yang et al. [11]. The extraction efficiency of vanadium could reach 90%, while only around 60% chromium was recovered. To further improve the chromium extraction efficiency, ion exchange [12–14] and solvent extraction [15–17] for simultaneous vanadium and chromium recovery were conducted. However, those processes significantly increased the operational complexity, making it economically infeasible.

As the solubility of vanadium(III) is much lower than that of vanadium(V), vanadium recovery in the form of vanadium(V) precipitates is preferable. Wang [18–20] introduced MnO$_2$ to oxidize
vanadium(III) to vanadium(V), which was then hydrolyzed and separated from chromium(III). The overall vanadium recovery efficiency was 86.5%, which was lower than most industrial practices, therefore, more effort is required to improve the recovery efficiency. In this paper, MnO₂ was used to oxidize the low-valent vanadium during the acid leaching process, followed by selective adsorption for vanadium(V) and Cr(III) recovery. The effect of reaction time, reaction temperature, MnO₂ dosage, and liquid-to-solid ratio on vanadium and chromium leaching efficiency were investigated. The leaching kinetics, as well as the optimal conditions for vanadium and chromium recovery, were also examined.

2. Materials and Methodology

2.1. Materials

The VCRR was precipitated from wastewater containing vanadium and chromium(III) from an iron and steel mill from Pan Gang Group Co., Ltd., Panzhihua, Sichuan Province, China [8,21,22]. Before the experiment, the residue was first dried in an oven overnight, followed by dry-sieving to obtain particles through <200 mesh, and then characterized by XRF (XRF-1800, Shimadzu, Japan, shown in Table 1). The VCRR were measured by X-ray diffraction meter (XRD-6000, Shimadzu, Japan) with a Cu Kα radiation source under the conditions of λ = 0.15418 nm, 40 kV, and 40 mA at 10° to 90°, and the results are displayed in Figure 1.

| Component | O | Cr | Si | Na | S | V |
|-----------|---|----|----|----|---|---|
| Amount (wt.%) | 41.44 | 18.80 | 11.30 | 10.93 | 10.64 | 3.11 |
| Component | Ca | Cl | Fe | K |
| Amount (wt.%) | 1.94 | 1.06 | 0.37 | 0.17 |

Figure 1. The XRD pattern of the original residue.

2.2. Experimental Procedure

All reagents used in the experiments were analytical grade. VCRR oxidation acid leaching, selective adsorption of vanadium, and precipitation of chromium were integrated for efficient resource recovery and effluent management. A detailed process flowsheet is shown in Figure 2.
The oxidation acid leaching of vanadium was performed in a glass beaker with a thermostatic mixing water bath (±0.1 °C). A predetermined amount of VCRR and deionized water was added to the beaker to produce a homogeneous slurry under constant stirring. The slurry was heated to a predetermined temperature. Next, a predetermined amount of MnO₂ and concentration of sulfuric acid (H₂SO₄) were added to the beaker. After the required reaction time, the filtrate was separated from the VCRR by vacuum filtration. The concentration of vanadium and chromium in the filtrate was determined by inductively coupled plasma optical emission spectrometry (ICP-3000).

The leaching efficiencies of vanadium (ηᵥ) and chromium (η₇₆₆) were calculated using Equations (1) and (2), as shown below:

\[ ηᵥ = \frac{V \cdot Cᵥ}{m \cdot \omegaᵥ} \times 100\% \]  
\[ η₇₆₆ = \frac{V \cdot C₇₆₆}{m \cdot \omega₇₆₆} \times 100\% \]

where \( Cᵥ \) and \( C₇₆₆ \) are the concentration of vanadium and chromium in the filtrate, g/L; \( V \) is the volume of the filtrate, L; \( \omegaᵥ \) and \( \omega₇₆₆ \) are the mass fraction of vanadium and chromium in the vanadium–chromium reducing residue; \( m \) is the mass of VCRR used in the leaching experiments, g.

The selective adsorption of vanadium from the filtrate was achieved by adding an amount of the melamine under the pH of about 1.8 at 90 °C for 60 min. After reacting for the required time, the adsorption precipitation was obtained by vacuum filtration. Then, the \( V₂O₅ \) was obtained by roasting the adsorption precipitation at 550 °C for 150 min in a muffle furnace. The filtrate was then neutralized using NaOH to precipitate Cr (III) at pH 8.5 under 90 °C. After filtration, the precipitate was roasted and washed with distilled water to remove soluble impurities. \( Cr₂O₃ \) was then obtained by drying the refined material at 110 °C for 2 h [18,20]. The effect of various parameters on adsorption performance of vanadium with melamine had been examined by our previous researches [23,24], thus they were not reported here.
3. Results and Discussion

3.1. Leaching Process

3.1.1. Effect of H$_2$SO$_4$ Dosage

The effect of H$_2$SO$_4$ concentration on leaching efficiency of vanadium and chromium was investigated while keeping the reaction time at 180 min, reaction temperature of 90 °C, and liquid-to-solid ratio of 5:1 mL/g. The concentration of H$_2$SO$_4$ was set as 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, and 30 wt.%. The results are detailed in Figure 3.

![Figure 3](image-url)  
*Figure 3. Effect of concentration of H$_2$SO$_4$ on the leaching efficiency of vanadium and chromium.*

The vanadium and chromium were existed in low valence according to the results shown in Figure 1. The chromium was easy to leach out and the leaching efficiency of chromium was increased along the concentration of H$_2$SO$_4$. The leaching efficiency was 92.10% at 5 wt.% H$_2$SO$_4$ and up to 99.80% at 30 wt.% H$_2$SO$_4$.

Figure 3 indicates that the low-valence vanadium was hard to leach out. Only 10.24% of vanadium was leached out at 5 wt.% H$_2$SO$_4$. Even when the concentration increased to 30 wt.%, the leaching efficiency of vanadium only reached 57.8%, nearly half of the vanadium was retained in the residue. The vanadium in low valence was hard to leach out [5], in order to improve the leaching of vanadium, some enhanced technology was needed [9,25].

3.1.2. Effect of MnO$_2$ Dosage

Based on the above discussion, the oxidation of low-valence vanadium is of great importance to further improve its leaching efficiency. It is known that $E^{0}_{\text{MnO}_2/\text{Mn}^{2+}} = 1.21$ V and $E^{0}(\text{VO}_2^{+}/\text{VO}^{2+}) = 1.00$ V, and therefore MnO$_2$ could be used for the oxidation of V(IV) during the leaching process [26,27]. With a summarization of the potential-pH diagram of vanadium and manganese shown in Figure 4, it was clear that the position of MnO$_2$ was always higher than that of V(IV) and V(III), indicating that the electrode potential of MnO$_2$ was higher than that of V(IV) and V(III). Therefore, MnO$_2$ could oxidize V(IV) and V(III) into V(V). The effect of MnO$_2$ dosage on the leaching efficiency of chromium and vanadium was investigated under the following reaction conditions: reaction time of 180 min, reaction temperature of 90 °C, liquid-to-solid ratio of 5:1 mL/g, and concentration of H$_2$SO$_4$ at 30 wt.%. The results are detailed in Figure 5.
Chromium leached out much easier in acidic medium, with the leaching efficiency increasing to 99.80% at the selected reaction conditions. The leaching efficiency of vanadium was increased linearly with the increase of dosage of MnO₂. The vanadium in low valences, like V(IV) and V(III), was oxidized to V(V) by MnO₂, and then dissolved in acidic medium and achieved high leaching efficiency. The results confirmed that MnO₂ could oxidize low-valence vanadium ion of V(IV) and V(III) into V(V).

3.1.3. Effect of Reaction Temperature

Reaction temperature played an important role in the diffusion process. The higher temperature increased the activity of atoms and molecules, and the reaction rate. Figure 6 summarizes the effect of reaction temperature on the leaching process under standard conditions: reaction time of 180 min, liquid-to-solid ratio of 5:1 mL/g, dosage of MnO₂ at 50 wt.%, and concentration of H₂SO₄ at 30 wt.%. The leaching efficiency of vanadium and chromium was improved by increasing the reaction temperature. At a reaction temperature of 90 °C, 99.80% of chromium and 97.93% of vanadium could leach out and therefore, 90 °C was chosen for optimal reaction temperature in further experiments.
3.1.4. Effect of Reaction Time

Figure 7 shows the leaching efficiency of vanadium and chromium by varying the reaction time from 30 min to 180 min under selected conditions: reaction temperature of 90 °C, liquid-to-solid ratio of 5:1 mL/g, dosage of MnO₂ at 50 wt.%, and concentration of H₂SO₄ at 30 wt.%. Increasing of reaction time could promote the reaction between H₂SO₄ and vanadium–chromium reducing residue and achieve high leaching efficiency. Almost all chromium was leached out at a reaction time of 180 min, and the leaching efficiency of vanadium was increased from 86.43% at 30 min to 97.93% at 180 min, which indicated that 180 min was enough to leach out chromium and vanadium.

3.1.5. Effect of Liquid-To-Solid Ratio

The liquid-to-solid ratio showed a significant effect on the volume of filtrate and concentration of purpose product in the leaching process. A series of experiments were conducted to evaluate an optimal liquid-to-solid ratio to achieve high leaching efficiency of vanadium and chromium. The liquid-to-solid ratio was set as 3:1 mL/g, 4:1 mL/g, 5:1 mL/g, 6:1 mL/g, and 7:1 mL/g, and other reaction conditions were kept as constant: reaction temperature of 90 °C, reaction time of 180 min, dosage of MnO₂ at 50 wt.%, and concentration of H₂SO₄ at 30 wt.%. The results are shown in Figure 8.
The leaching process was inefficient for low liquid-to-solid ratio as the viscosity of reaction medium was large, just 88.64% of chromium and 80.45% of vanadium were leached out in liquid-to-solid at 3:1 mL/g. The leaching process favored higher liquid-to-solid ratio, where the chromium and vanadium of 99.80% and 97.93% were obtained at a liquid-to-solid ratio of 5:1 mL/g. Further increase of the liquid-to-solid ratio only improved the leaching efficiency slightly, therefore, a liquid-to-solid of 5:1 mL/g was recommended for future use.

Based upon the above experimental results, the optimal reaction conditions for vanadium and chromium leaching out were reaction temperature of 90 °C, reaction time of 180 min, dosage of MnO2 at 50 wt.%, concentration of H2SO4 at 30 wt.%, and liquid-to-solid at 5:1 mL/g. The leaching efficiency of vanadium and chromium was up to 99.80% and 97.93% under optimal reaction conditions.

3.2. Kinetic Analysis

The shrink core model is often used to described the kinetic behaviors of leaching processes [6,28–31], wherein a reaction between solid and fluid reactants occurs on the outer surface of the solid. The typical three kinetic models [32–34] are represented as followed:

(1) if diffusion through a liquid was the controlling step

\[ K_1t = \eta \]  

(3)

(2) if diffusion through a product layer was the controlling step

\[ K_2t = 1 - \frac{2}{3}\eta - (1 - \eta)^{2/3} \]  

(4)

(3) if a surface chemical reaction was the controlling step

\[ K_3t = 1 - (1 - \eta)^{1/3} \]  

(5)

which, \( \eta \) is the leaching efficiency, \( K_1 \) is the apparent rate constant for diffusion through the fluid film, min\(^{-1}\); \( K_2 \) is the apparent constant for the diffusion through the product layer, min\(^{-1}\); \( K_3 \) is the apparent rate constant for surface chemical reaction, min\(^{-1}\); \( t \) is the reaction time, min.

The apparent rate constants obtained from the plots and correlation coefficients of each experimental parameter are provided in Table 2. The results indicated that the regression coefficient of surface chemical reaction was maximum among the three kinetic models, indicating that surface chemical reaction was the rate-controlling step. Therefore, Equation (5) was used to express the kinetic behavior of leaching process following the shrinking core model.
The leaching reaction rates of vanadium and chromium at different temperatures were fitted (Figure 9), and the value of $K_3$ was obtained, where $K_3$ is the reaction rate constant corresponding to the slopes of the straight lines. Then, the specific apparent activation energy could be calculated based on the Arrhenius equations, the results are shown in Figure 10.

$$\ln K = \ln A - \frac{E_a}{RT}$$

where $E_a$ is the apparent activation energy, $A$ is the pre-exponential factor, and $R$ is the molar gas constant.



| Table 2. Apparent rate constants $K_1$, $K_2$, and $K_3$ for the kinetic models and correlation coefficients. |
|---------------------------------------------------------------|
| **Parameter** | **Diffusion through the Liquid Film** | **Diffusion through the Product Layer** | **Surface Chemical Reaction** |
| | $\eta$ | $1 - 2/3\eta - (1 - \eta)^{2/3}$ | $1 - (1 - \eta)^{1/3}$ |
|----------|----------|-----------------|-----------------|
| **Chromium** | | | |
| 30 °C | $K_1$ (min$^{-1}$) | $R^2$ | $K_2$ (min$^{-1}$) | $R^2$ | $K_3$ (min$^{-1}$) | $R^2$ |
| 0.0004279 | 0.9596 | 0.000675 | 0.9350 | 0.000682 | 0.9887 |
| 0.0005409 | 0.9699 | 0.000605 | 0.9251 | 0.000877 | 0.9897 |
| 0.0007514 | 0.9428 | 0.000635 | 0.9316 | 0.001250 | 0.9951 |
| 0.0012200 | 0.9524 | 0.000800 | 0.9199 | 0.002100 | 0.9991 |
| 0.0014200 | 0.9434 | 0.000795 | 0.9276 | 0.002530 | 0.9880 |
| **Vanadium** | | | |
| 30 °C | | | |
| 0.000754 | 0.9837 | 0.000728 | 0.9340 | 0.00124 | 0.9913 |
| 0.001140 | 0.9681 | 0.000868 | 0.9152 | 0.00194 | 0.9826 |
| 0.001500 | 0.9608 | 0.000901 | 0.9263 | 0.00272 | 0.9982 |
| 0.001900 | 0.9735 | 0.000948 | 0.9369 | 0.00366 | 0.9988 |
| 0.002380 | 0.9863 | 0.000965 | 0.9200 | 0.00459 | 0.9894 |

Figure 9. Plot of leaching kinetics of vanadium at various reaction temperatures in different leaching processes.
The apparent activation energies of vanadium and chromium leaching out were calculated as 19.93 kJ·mol$^{-1}$ and 21.26 kJ·mol$^{-1}$, respectively. The low value of apparent activation energy indicated that vanadium and chromium were easy to leach out in acidic medium. And, the vanadium was easier than chromium to leach out within the addition of MnO$_2$.

4. Conclusions

This paper focused on the separation and recovery of vanadium and chromium from vanadium–chromium reducing residue. The following conclusions were obtained:

(1) Vanadium and chromium could be efficiently leached out, and the leaching efficiency of vanadium and chromium are up to 99.80% and 97.93% under optimal reaction conditions: reaction temperature of 90 °C, reaction time of 180 min, dosage of MnO$_2$ at 50 wt.%, concentration of H$_2$SO$_4$ at 30 wt.%, and liquid-to-solid at 5:1 mL/g.

(2) The leaching process of vanadium and chromium were controlled by surface chemical reaction, and the leaching kinetic behaviors followed the shrink core model, and the apparent activation energies for vanadium and chromium leaching out are 19.93 kJ·mol$^{-1}$ and 21.26 kJ·mol$^{-1}$, respectively.

(3) Vanadium and chromium in the leaching solution could be separated by selective adsorption and precipitation. The melamine acted as an efficient absorbent, and nearly 99.99% vanadium was adsorbed by melamine under the initial pH of leaching solution about 1.8 at 90 °C for 60 min. Then, the V$_2$O$_3$ was obtained by roasting the precipitation at 550 °C for 150 min in a muffle furnace. The chromium retained in the leaching solution was precipitated as Cr(OH)$_3$ in pH about 8.5 at 90 °C. And, the product of Cr$_2$O$_3$ was obtained by drying the refined Cr(OH)$_3$ at 110 °C for 2 h.

Author Contributions: Conceptualization, H.P.; Methodology, H.P.; Validation, H.P.; Formal Analysis, L.Y. and Y.C.; Investigation, L.Y. and Y.C.; Resources, H.P.; Data Curation, J.G.; Writing—Original Draft Preparation, H.P.; Project Administration, H.P.; and Funding Acquisition, H.P. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Science and Technology Research Program of Chongqing Municipal Education Commission (No. KJQN201901403) and the Chongqing Science and Technology Commission (No. cstc2018jcyjAX0018).

Conflicts of Interest: The authors declare no conflict of interest.

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