Recovery and Separation of Vanadium and Chromium by Two-Step Alkaline Leaching Enhanced with an Electric Field and H₂O₂

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ABSTRACT: This paper focused on the treatment of vanadium–chromium reducing residue with a two-step alkaline leaching process: electro-oxidation leaching of vanadium and H₂O₂ as well as oxidation leaching of chromium in an alkaline medium. The effects of experimental parameters on the leaching performance of vanadium and chromium were investigated. The experimental data showed that in the first alkaline leaching in stage I, the leaching efficiency of vanadium reached up to 95.32% under optimal conditions, while most of the chromium could not leach out (about 4% of chromium was leached out). Chromium was easily oxidized to high valence (CrO₄²⁻) with H₂O₂ in the second alkaline leaching stage II. Under optimal conditions, 96.24% chromium was leached out.

1. INTRODUCTION

Vanadium, chromium, and their oxides are widely used in many fields due to their excellent properties.¹–⁵ In a vanadium plant, wastewater containing CrO₄²⁻ and VO₄³⁻ is generated and the vanadium–chromium reducing residue is formed via the reducing treatment of these wastewaters. Thus, vanadium and chromium in the residue exist almost as V(III) and Cr(III). Handling of the vanadium chromium reducing residue has become a thorny problem in many plants in China.⁶,⁷ Many hydrometallurgy technologies have been investigated to improve the leaching efficiency of vanadium and chromium. Nowadays, the most common and commercial technology for recovery of vanadium and chromium is the roasting–leaching process, which includes sodium-roasting–water leaching⁸ and calcium-roasting–acid leaching.⁹–¹¹ Unfortunately, a series of problems of the sodium salt roasting technology are still unsolved, such as emission of hazardous gases, fusion agglomeration at a high roasting temperature, and utilization difficulty of tailings. The calcium-roasting–acid leaching process appears to be an environmental method for leaching of vanadium while not an efficient technology for recovery of chromium.¹¹–¹³ The so-called submolten salt technology introduced by the Chinese Academy of Sciences is an efficient technology for vanadium leaching out but the process consumes much energy and is uneconomical.¹⁴,¹⁵ Some oxidation–alkaline leaching technologies have been adopted, such as NaOH–H₂O₂ leaching¹⁶,¹¹ or NaOH and electro-oxidation.⁷,¹⁸–²¹ Vanadium could be leached out efficiently, but chromium could not be leached out. As a result, the vanadium–chromium reducing residue had not been treated effectively, resulting in wasting the vanadium and chromium resources as well as causing environmental pollution.

This paper focused on the treatment of the vanadium–chromium reducing residue with a two-step alkaline leaching process. In the first step, an electric field was applied to oxidize the low-valence vanadium. The effects of experimental parameters including the current density, the reaction temperature, the reaction time, and the dosage of NaOH on the selective oxidation of the low-valence vanadium were studied. After selective leaching, chromium(III) was oxidized by H₂O₂ in an alkaline medium. The effects of experimental parameters on the leaching performance of chromium were also investigated. Optimal leaching conditions of vanadium and chromium were also developed.

2. RESULTS AND DISCUSSION

The results shown in Figure 14 indicate that vanadium and chromium in the residue were of low valence, and hence they could not be directly leached out easily in the alkaline medium. It was found that E⁰ (V(V)/V(IV)) and E⁰ (Cr(VI)/Cr(III)) were 1.00 and 1.33 V, respectively.²² In other words, special oxidation treatment of the vanadium–chromium reducing residue is necessary.
residue could achieve selective oxidation of low-valence vanadium and chromium(III) not oxidized. The \( E-pH \) diagrams for the \( V-H_2O \) system and the \( Cr-H_2O \) system at 0.1 mol/L vanadium.

Figure 2. \( E-pH \) diagram of the \( Cr-H_2O \) system at 0.1 mol/L chromium.

Figure 3. Schematic of the leaching process of the vanadium–chromium reducing residue.

Figure 4. Effect of the dosage of NaOH on the leaching efficiency of vanadium and chromium (\( T = 90 ^\circ C, t = 120 \) min, \( L/S = 4 \) mL/g and \( r = 500 \) rpm).

Figure 5. Effect of current density on the leaching efficiency of vanadium and chromium (\( T = 90 ^\circ C, m(\text{NaOH})/m(\text{residue}) = 1.0 \) g/g, \( t = 120 \) min, \( L/S = 4 \) mL/g and \( r = 500 \) rpm).
25 °C are shown in Figure 1\textsuperscript{6,23} and Figure 2, respectively. It could be seen that the potential for Cr(VI) was much higher than that for V(V) in the alkaline medium. When the pH > 10, the potential remained about 0.25 V and vanadium existed as VO\textsubscript{3}\textsuperscript{−}, while chromium was still in the Cr(III) form. Thus, a suitable potential could be applied as vanadium existed as V(V) and chromium existed as Cr(III), according to the results shown in Figures 1 and 2. A recent study\textsuperscript{7} indicated that a selective leaching process could be achieved by enhancing the electric field in the alkaline medium. Therefore, in this paper, vanadium and chromium were separated and recovered by a two-step leaching process: electro-oxidation leaching of vanadium and H\textsubscript{2}O\textsubscript{2} as well as oxidation leaching of chromium in an alkaline medium. The schematic is shown in Figure 3.

### 2.1. Leaching of Vanadium

#### 2.1.1. Effect of Dosage of NaOH

As the main reactant, the dosage of NaOH...
investigate the effect of the dosage of NaOH on the leaching process. Other reaction conditions were kept constant: liquid-to-solid ratio (L/S) of 4 mL/g, reaction temperature (T) of 90 °C, reaction time (t) of 120 min, and stirring rate (r) of 500 rpm.

The results shown in Figure 4 indicate that the dosage of NaOH had a positive effect on the leaching efficiency of vanadium. The leaching efficiency of vanadium could increase 19.32% under optimal reaction conditions and increased with the increase in the electric field. At the same time, the leaching efficiency of chromium was 4.2% at its maximum.

2.1.2. Effect of Current Density. An electric field was introduced to enhance the leaching process, and the effect of current density (J) on the leaching process was studied while the other reaction conditions were kept constant: T = 90 °C, m(NaOH)/m(residue) = 1.0 g/g, t = 120 min, L/S = 4 mL/g, and r = 500 rpm, respectively.

The results shown in Figure 5 indicate that the current density had a positive effect on the leaching efficiency of vanadium. Vanadium existed in low valence as V(III) and V(IV) in the residue, as seen from Figure 14. During the leaching process, the H₂O molecule or OH⁻ was oxidized to *OH by the electric field.²¹,²²,²³ Then it migrated toward the bulk solution and reacted with the low-valence vanadium in the residue and oxidized it to high-valence vanadium (V(V)), which highly dissolved in the alkaline medium. The reactions during the leaching process can be expressed by the model shown in Figure 6 and the equations as follows:⁷,¹⁸

\[ MO_x(\text{OH}) \rightarrow MO_{(x+1)} + H^+ + e^- \]  
(1)

\[ MO_{(x+1)} + V(\text{III})/V(\text{IV}) \rightarrow MO_x + V(V) \]  
(2)

\[ OH + V(\text{III})/V(\text{IV}) \rightarrow V(V) + H_2O \]  
(3)

\[ MO_x(\text{OH}) \rightarrow 1/2O_2 + MO_x + H^+ + e^- \]  
(4)

\[ MO_{(x+1)} \rightarrow 1/2O_2 + MO_x \]  
(5)

\[ O_2 + V(\text{III})/V(\text{IV}) + OH^- \rightarrow V(V) + H_2O \]  
(6)

where MOₓ stands for the metal electrode.

2.1.3. Effect of Reaction Temperature. Figure 7 describes the effect of the reaction temperature on the leaching process while the other reaction conditions were kept constant: t = 120 min, m(NaOH)/m(residue) = 1.0:1.0 g/g, L/S = 4 mL/g, J = 0.25 A/cm², L/S = 4 mL/g, and r = 500 rpm. The results showed that the leaching efficiency of vanadium increased linearly with the reaction temperature. Therefore, a reaction temperature of 90 °C was chosen as the optimal condition for further experiments.

2.1.4. Effect of Reaction Time. To investigate the effect of reaction time, several experiments based on the reaction time from 30 to 150 min were carried out, and the results are shown in Figure 8. The leaching efficiency of vanadium increased with the increase of reaction time from 30 to 120 min. A prolonged reaction time had a negative effect on the leaching efficiency of vanadium. As the time increased from 30 to 120 min, the oxidation of low-valence vanadium tended to balance and the leaching efficiency increased from 60.02% at 30 min to 95.32% at 120 min. Therefore, the reaction time of 120 min was chosen as the optimal time.

2.1.5. Composition of Vanadium and Chromium Residue after Leaching in Stage I. The composition of the leaching
residue in stage I is detailed in Table 1, which was obtained after selective leaching of vanadium under optimal conditions: \( m(\text{NaOH})/m(\text{residue}) = 1.0:1.0 \text{ g/g}, J = 0.25 \text{ A/cm}^2, L/S = 4 \text{ mL/g}, T = 90^\circ \text{C}, t = 120 \text{ min}, \) and \( r = 500 \text{ rpm} \). It could be seen that vanadium was almost leached out and only 0.15 wt % was retained in the residue, which was consistent with the experimental results mentioned above. Chromium was about 28.05 wt %, and the leaching residue could be used as a chromium resource for chromium recovery.

2.2. Leaching of Chromium. The results shown in Table 1 indicate that chromium was almost retained in the leaching residue. In the second leaching process, \( \text{H}_2\text{O}_2 \) was added to oxidize the low-valence chromium, according to refs 17, 18, 22.

2.2.1. Effect of Dosage of \( \text{H}_2\text{O}_2 \). \( \text{H}_2\text{O}_2 \) as a main oxidant played an important role during the leaching process. The effect of dosage of \( \text{H}_2\text{O}_2 \) \( (V(\text{H}_2\text{O}_2)/m(\text{residue})) \) on the leaching process was investigated under the following conditions: \( m(\text{NaOH})/m(\text{residue}) = 1.0:1.0 \text{ g/g}, L/S = 4.0 \text{ mL/g}, T = 90^\circ \text{C}, t = 120 \text{ min}, \) and \( r = 500 \text{ rpm} \). The results shown in Figure 9 indicate that the dosage of \( \text{H}_2\text{O}_2 \) had a significant positive effect on the leaching process, and the leaching efficiency of chromium increased linearly with the increase in the dosage of \( \text{H}_2\text{O}_2 \). With the addition of \( \text{H}_2\text{O}_2 \), the low-valence chromium was oxidized to water-soluble chromate \( (\text{CrO}_4^{2-}) \) in the alkaline medium. Also, the results indicated that vanadium that remained in the leaching residue was easily leached out.

2.2.2. Effect of Dosage of \( \text{NaOH} \). During the oxidation process, \( \text{NaOH} \) was not only an important reactant but also provided an alkaline medium. Figure 10 shows that the dosage of \( \text{NaOH} \) significantly affected the leaching process. The leaching efficiency increased from 55.13% at \( m(\text{NaOH})/m(\text{residue}) = 0.2:1.0 \text{ g/g} \) to 96.24% at \( m(\text{NaOH})/m(\text{residue}) = 1.0:1.0 \text{ g/g} \).

2.2.3. Effect of Reaction Temperature. A higher temperature could increase the activity of atoms and molecules, increase collisions, increase the reaction rate, etc. The effect of reaction temperature was studied under the standard conditions: \( m(\text{NaOH})/m(\text{residue}) = 1.0:1.0 \text{ g/g}, L/S = 4.0 \text{ mL/g}, t = 120 \text{ min}, \) and \( V(\text{H}_2\text{O}_2)/m(\text{residue}) = 1.0 \text{ mL/g} \) and \( r = 500 \text{ rpm} \). It was concluded from the results shown in Figure 11 that the reaction temperature also had a positive effect on the leaching process. The highest leaching efficiency was 96.24% at a reaction temperature of 90°C. Thus, 90°C was chosen as the optimal condition.

2.2.4. Effect of Reaction Time. As seen in Figure 12, the effect of reaction time was investigated as \( m(\text{NaOH})/m(\text{residue}) = 1.0:1.0 \text{ g/g}, L/S = 4.0 \text{ mL/g}, T = 90^\circ \text{C}, V(\text{H}_2\text{O}_2)/m(\text{residue}) = 1.0 \text{ mL/g} \) and \( r = 500 \text{ rpm} \), respectively. The results indicated that the leaching efficiency of chromium was increased from 30 to 120 min. The oxidation of chromium tended to balance at a reaction time from 30 to 120 min, and the leaching of chromium was up to 96.24% at 120 min and increased only 0.1% at 150 min. Thus, the reaction time of 120 min was chosen as the optimal condition.

2.3. Phase Analysis. X-ray diffraction (XRD) analysis of the residue after leaching stage II was conducted. The result shown in Figure 13 indicates that the main content phases of the original residue disappeared and only a peak of \( \text{SiO}_2 \) and \( \text{Fe}_2(\text{SO}_4)_3 \) remained after leaching. In other words, vanadium and chromium in the original residue leached out, which was consistent with the results discussed above.

3. CONCLUSIONS

An electric field and \( \text{H}_2\text{O}_2 \) as an efficient oxidant, were successfully applied in the two-step alkaline leaching process.

1. Low-valence vanadium could be oxidized to high-valence vanadium by applying an electric field. The addition of an electric field enhanced the leaching process of vanadium, while chromium was hardly leached out. The overall leaching efficiency of vanadium reached up to 95.32% under optimal conditions: mass ratio of \( \text{NaOH} \)-to-residue, 1.0:1.0 g/g; current density, 0.25 A/cm²; liquid-to-solid ratio, 4 mL/g; reaction temperature, 90°C; reaction time, 120 min; and stirring rate, 500 rpm.

2. Chromium was retained in the leaching residue after leaching stage I and it was easily oxidized to high valence \( (\text{CrO}_4^{2-}) \) with \( \text{H}_2\text{O}_2 \) in an alkaline medium in leaching stage II. Under optimal conditions, 96.24% chromium was leached out: mass ratio of \( \text{NaOH} \)-to-residue, 1.0:1.0 g/g; liquid-to-solid ratio, 4.0 mL/g; reaction temperature, 90°C; reaction time, 120 min; volume ratio of \( \text{H}_2\text{O}_2 \) to mass of residue, 1.0 mL/g; and stirring rate, 500 rpm.

4. MATERIALS AND METHODS

4.1. Materials. The vanadium—chromium reducing residue was collected from Pangang Group Co., Ltd. (Panzhihua, Sichuan Province, China). Before the experiment, the residue was dried and ground to suitable particles. The chemical composition of the residue, measured using an XRF (XRF-1800, Shimadzu, Japan), is listed in Table 2. The phase composition, measured by an X-ray diffractometer (XRD-6000, Shimadzu, Japan), is detailed in Figure 14.
mixing water bath pot.7,10,18,27,28 The detailed experimental procedure can be seen in refs 7, 10, 18, 27, 28 and also in Figure 3.

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Science and Technology Research Program of Chongqing Municipal Education Commission (No. KJQN20191403) and the Chongqing Science and Technology Commission (No. cstc2018jcyjAX0018).

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