Oxidative Leaching Kinetics of Vanadium from the Vanadium-Chromium-Reducing Residue with K₂Cr₂O₇

Hao Peng,* Qian Shang, Ronghua Chen, Yumeng Leng, Jing Guo, Zuohua Liu, and Changyuan Tao*

ABSTRACT: Oxidative-alkaline leaching of vanadium from vanadium-chromium-reducing residue with K₂Cr₂O₇ was investigated in this paper. The effects of processing parameters including dosage of NaOH, dosage of K₂Cr₂O₇, reaction time, and reaction temperature on the leaching efficiency of vanadium were studied. The results simulated by response surface methodology indicated that vanadium leaching was affected significantly by the dosage of K₂Cr₂O₇ and NaOH, and the processing parameters that affected the leaching efficiency of vanadium followed the order m(NaOH)/m(residue) > m(K₂Cr₂O₇)/m(residue) > reaction temperature > reaction time. The leaching efficiency of vanadium was up to 99.92% under optimal conditions: reaction temperature of 90 °C, reaction time of 60 min, liquid-to-solid ratio of 5:1 mL g⁻¹, m(K₂Cr₂O₇)/m(residue) = 0.10, and m(NaOH)/m(residue) = 0.30. The kinetics analysis indicated that diffusion through the product layer was the controlling step and the apparent activation energy for vanadium leaching was calculated to be 8.275 kJ·mol⁻¹.

1. INTRODUCTION

Vanadium and its compounds are widely used in many fields due to their excellent properties.¹⁻¹² After recovery of vanadium from a vanadium-producing plant, a large amount of toxic wastewater containing vanadium (V) and chromium (VI) remains to be treated. Usually, some reductants are added followed by neutralization to form a vanadium-chromium-reducing residue (VCRR), which low-valence vanadium (IV) accounts for 3−10 wt % and low-valence chromium (III) accounts for about 10 to 20 wt %. In China, every year, more than 500,000 tons of the vanadium-chromium-reducing residue is produced.²⁻⁵ The inefficient treatment of the VCRR results in wastage of vanadium and chromium resources and environmental pollution.

In order to leach out low-valence vanadium and chromium, some oxidative leaching technologies were used. Oxidants like KClO₃, H₂O₂, and MnO₂ were applied to enhance the leaching process.⁹⁻¹¹ During the leaching process, the low-valence vanadium was brought into contact with an oxidant and was oxidized to high-valence vanadium in order to leach out. High-valence vanadium (99.80%) and 97.93% low-valence chromium were leached out during oxidative acid leaching with MnO₂, but they were very hard to filter due to the high content of Si. H₂O₂ alkaline leaching is a very environment-friendly technology for vanadium and chromium leaching except for its high cost. Submolten technology is used to recover vanadium with high alkalinity and energy consumption.¹²⁻¹³ Meanwhile, some supplementary methods have attracted more attention.

Electro-oxidation technology was applied to enhance the leaching process both in acidic and alkaline media,¹⁴⁻¹⁵ which offered selectivity for vanadium leaching, although it was hard to industrialize. Roasting technology was the most common technology, including sodium-roasting, calcium-roasting, and blank-roasting; most vanadium and chromium were leached out, but some poisonous gases were emitted and the processes require high energy. Microwave-roasting and ultrasound-assisted leaching have also received more attention.¹⁶⁻¹¹ Ion-exchange technology²⁻²⁴ and solvent extraction technology²⁵⁻²⁶ were also investigated to further improve the recovery efficiency of vanadium. However, these processes were noneconomical and were only applied on a small scale.

This paper introduced a novel process for the recovery of vanadium from the vanadium-chromium-reducing residue. In this process, K₂Cr₂O₇, which has high oxidizability, was introduced as an efficient oxidant for oxidation leaching of vanadium in alkaline medium. The redox product (Cr(III)) retained in the leaching residue could be used as a chromium source for chromium production. The effect of experimental...
parameters including reaction time, reaction temperature, mass ratio of NaOH to residue, and mass ratio of K2Cr2O7 to residue was studied. The leaching kinetics and also the optimal conditions for vanadium leaching were also investigated.

2. RESULTS AND DISCUSSION
Vanadium exists as a low-valence element in the VCRR, and it is hard to leach out in alkaline medium directly.9 It is known that $E^{0}_{\text{Cr}^{2+}/\text{Cr}^{3+}} = 1.33 \text{ V}$ and $E^{0}_{\text{VO}_{2}^{+}/\text{VO}_{2}^{2+}} = 1.00 \text{ V}$; therefore, K2Cr2O7 was used to oxidize low-valence vanadium during the leaching process. The $\Delta G$ of the main reactions were calculated at 298 K.28,29 The results displayed in Figure 1 show that the $\Delta G$ was negative, indicating that the oxidative leaching of low-valence vanadium with K2Cr2O7 was feasible.

2.1. Oxidation Leaching of Vanadium in Alkaline Medium. 2.1.1. Effect of the Mass Ratio of K2Cr2O7 to the Residue. Based on the above analysis, the oxidation of low-valence vanadium with K2Cr2O7 was feasible thermodynamically. Thus, the dosage of K2Cr2O7 had a significant effect on the leaching efficiency of vanadium. Figure 2 shows the results of the effect of the mass ratio of K2Cr2O7 to residue ($m(\text{K}_2\text{Cr}_2\text{O}_7)/m(\text{residue})$) on the leaching efficiency of vanadium while other reaction conditions are kept constant: reaction time of 60 min, reaction temperature of 90 °C, liquid-
K2Cr2O7 was an effective oxidant for low-valence vanadium and chromium. The above results confirmed that K2Cr2O7 was an efficient oxidant for low-valence vanadium leaching, and m(K2Cr2O7)/m(residue) = 0.10 was chosen as the optimal condition for further experiments.

### Table 1. Levels for Parameters in Actual Values

| independent parameter | unit | level 1 | level 2 | level 3 |
|-----------------------|------|---------|---------|---------|
| A: m(K2Cr2O7)/m(residue) | mL/g(residue) | 1 | 0.05 | 0.1 |
| B: m(NaOH)/m(residue) | mL/g(residue) | 1 | 0.01 | 0.15 | 0.3 |
| C: reaction temperature | °C | 30 | 60 | 90 |
| D: reaction time | min | 10 | 30 | 60 |

### Table 2. Analysis of Variance

| source | S | Df | mean square | F value | p value | probability |
|--------|---|----|-------------|--------|---------|-------------|
| model  | 106.62 | 14 | 7.62 | 12.07 | <0.0001 | |
| residual | 8.84 | 14 | 0.63 | | | |
| lack-of-fit | 8.27 | 10 | 0.83 | 5.89 | 0.0511 | |
| pure error | 0.56 | 4 | 0.14 | | | |

Figure 6. Perturbation plot for the leaching efficiency of vanadium (A: m(K2Cr2O7)/m(residue); B: m(NaOH)/m(residue); C: reaction temperature; and D: reaction time).

to-solid ratio of 5:1 mL g⁻¹, and mass ratio of NaOH to residue (m(NaOH)/m(residue)) = 0.3.

The results shown in Figure 2 indicate that the leaching efficiency increased with the increase of the dosage of K2Cr2O7. Only a small amount of vanadium leached out in alkaline medium without oxidation. During the leaching process, the low-valence vanadium made contact with K2Cr2O7 and was oxidized to high-valence vanadium (VO4³⁻), which was easy to dissolve in alkaline medium and contributed to the high leaching efficiency of vanadium. Only 56.65% of the vanadium leached out without K2Cr2O7, and the leaching efficiency was up to 99.92% at m(K2Cr2O7)/m(residue) = 0.10. As the leaching solution had strong alkalinity, the Cr(III) in the VCRR and reduced K2Cr2O7 were retained in the leaching residue, and it acted as an efficient chromium source. Compared with oxidative leaching with H2O2,10,11,30 it offered selectivity for vanadium and separation of vanadium and chromium. The above results confirmed that K2Cr2O7 was an efficient oxidant for low-valence vanadium leaching, and m(K2Cr2O7)/m(residue) = 0.10 was chosen as the optimal condition for further experiments.

### 2.1.3. Effect of Reaction Temperature

Higher reaction temperature often increases the activity of reagents, decreases the medium viscosity, and enhances the reaction intensity. Figure 4 shows the effect of reaction temperature on the leaching efficiency of vanadium. The leaching efficiency increased from 24.39 to 99.92% as the reaction temperature increased from 30 to 90 °C. Therefore, 90 °C was selected for further experiments.

### 2.1.4. Effect of Reaction Time

Figure 5 shows the leaching efficiency of vanadium by varying the reaction time ranging from 10 to 60 min under selected conditions: reaction temperature of 90 °C, liquid-to-solid ratio of 5:1 mL g⁻¹, m(K2Cr2O7)/m(residue) = 0.10, and m(NaOH)/m(residue) = 0.30. Further increasing the reaction time could increase the chances of contact of the VCRR with NaOH and K2Cr2O7, giving the low-valence vanadium in the VCRR enough time to be oxidized. Almost all of the vanadium was leached out within 60 min, and the leaching efficiency of vanadium increased from 48.64 to 99.92% as the reaction time increased from 10 to 60 min. Therefore, 60 min was sufficient to leach out vanadium.

Above all, K2Cr2O7 was an efficient oxidant for low-valence vanadium leaching from the VCRR in an alkaline medium, and the leaching efficiency of vanadium was up to 99.92% under the optimal conditions: reaction temperature of 90 °C, reaction time of 60 min, liquid-to-solid ratio of 5:1 mL g⁻¹, m(K2Cr2O7)/m(residue) = 0.10, and m(NaOH)/m(residue) = 0.30.

### 2.2. Response Surface Analysis

A single factor experiment was not enough to investigate the optimal reactions as it ignored the effects of the interactions between different factors. An effective method called response surface methodology was used to study the effects of interactions between different factors. In this study, response surface methodology simulated in Design-Expert software was used to optimize the reaction conditions. The operating parameters were set as: A: m(K2Cr2O7)/m(residue); B: m(NaOH)/m(residue); C: reaction temperature; D: reaction time, and the leaching efficiency of vanadium was set as a response. The actual values for each factor are detailed in Table 1.

The square root was used to express the simulated results for the leaching efficiency of vanadium after insignificant terms and it is presented in eq 1:
The analysis of variance results are detailed in Table 2. The F value and p value for the model 1 were 12.07 and <0.0001.

Figure 7. Response surface plots for factors.

Table 3. Kinetics Models and Equations

| controlling step                     | equations                                                      |
|--------------------------------------|----------------------------------------------------------------|
| diffusion through a liquid film      | \( K_f \) = \eta \) (2)                                       |
| diffusion through a product layer    | \( K_f = 1 - 2/3 \eta - (1 - \eta)^{2/3} \) (3)               |
| surface chemical reaction            | \( K_f = 1 - (1 - \eta)^{1/3} \) (4)                         |

\( \eta \) is the leaching efficiency, \( K_f, K_s, \) and \( K_d \), are the apparent rate constants for three different models, \( \text{min}^{-1} \), and \( t \) is the reaction time, \( \text{min} \).

\[
\text{Sqrt (Leaching efficiency)} = 6.76 + 0.60 \times A + 2.51 \times B + 0.53 \times C + 1.333 \times 10^{-4} \times D + 0.29 \times A \times B - 1.10 \times A \times C - 0.20 \times A \times D + 0.46 \times B \times C - 0.057 \times B \times D - 0.43 \times A^2 - 0.66 \times B^2 - 1.08 \times C^2 - 0.12 \times D^2
\]

(1)
The recovery of vanadium from the leaching solution was conducted by selective adsorption with melamine; almost all of the vanadium was adsorbed. The detailed adsorption conditions could be obtained from refs 50 and 51. Lastly, $V_2O_5$ was obtained by roasting the adsorption precipitate at 550 °C for 150 min in a muffle furnace.

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2.4. Kinetics Analysis. The shrink core model is widely used to describe the kinetics behavior of the leaching process between solid and liquid reagents. 14,47–50 The typical three kinetics models are represented in Table 3.

The experimental data were simulated with the above three equations and the apparent rate constant and correlation coefficients are provided in Table 4. The results indicated that the regression coefficient of diffusion through the product layer was maximum, and it meant that diffusion through the product layer was the rate-controlling step. Therefore, eq 4 was selected to describe the leaching kinetics behavior of vanadium from the VCRR. The results shown in Figure 8 indicate that the apparent activation energy for vanadium leaching was 58.275 kJ·mol$^{-1}$, which proposed that the leaching process was controlled mainly by diffusion of the solution through the surface layer, which was consistent with the results discussed above.

$$\ln K = \ln A - E_a/(RT)$$

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

3. CONCLUSIONS

This paper focused on the oxidative leaching of vanadium with $K_2Cr_2O_7$ from vanadium-chromium-reducing residues in alkaline medium. The conclusions are given as follows:

1. The optimal processing factors were obtained from response surface methodology, and the influence of processing parameters on the leaching efficiency of vanadium followed the order: $m(\text{NaOH})/m(\text{residue})$ (B) > $m(K_2Cr_2O_7)/m(\text{residue})$ (A) > reaction temperature (C) > reaction time (D). Under optimal conditions, leaching efficiency of vanadium was up to 99.92% (reaction temperature of 90 °C, reaction time of 60 min, liquid-to-solid ratio of 5:1 mL g$^{-1}$, $m(K_2Cr_2O_7)/m(\text{residue}) = 0.10$, and $m(\text{NaOH})/m(\text{residue}) = 0.30$).

2. The diffusion through the product layer was the rate-controlling step, and the leaching kinetics behaviors followed the shrink core model. The apparent activation energy for vanadium leaching was calculated to be 58.275 kJ·mol$^{-1}$.

4. MATERIALS AND METHODS

4.1. Materials. The VCRR was dried and ground to a suitable particle size before each experiment. The X-ray fluorescence (XRF) (XRF-1800, Shimadzu, Japan) and X-ray
Figure 9. Flow sheet of recovery of vanadium.

diffraction (XRD) (XRD-6000, Shimadzu, Japan) results indicated that the VCRR contained 18.80% Cr, 11.30% Si, and 3.11% V, and the main phases were FeCr₂O₄, NaCr(SO₄)₂, Na₂(Cr,V)Si₂O₉, and VOSO₄. All the reagents used in the experiments were of analytical grade, which were purchased from Kelong Co., Ltd., Chengdu, China, and used as received without purification.

4.2. Experimental Procedure. The experiments were performed according to the flow sheet as shown in Figure 9, which includes the procedures of oxidation leaching of vanadium and adsorption of vanadium. All experiments were performed in a glass beaker (250 mL) with a thermostatic mixing water bath pot. The detailed experimental procedure could be seen in references 10, 11, and 51.

■ AUTHOR INFORMATION

Corresponding Authors
Hao Peng — Chongqing Key Laboratory of Inorganic Special Functional Materials, College of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, P. R. China; orcid.org/0000-0001-6014-0249; Phone: +8615123031643; Email: cqupenghao@126.com

Changyuan Tao — College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 408100, P. R. China; Email: taocy@cqu.edu.cn

Authors
Qian Shang — Chongqing Key Laboratory of Inorganic Special Functional Materials, College of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, P. R. China

Ronghua Chen — Chongqing Key Laboratory of Inorganic Special Functional Materials, College of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, P. R. China

Yumeng Leng — Chongqing Key Laboratory of Inorganic Special Functional Materials, College of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, P. R. China

Jing Guo — Chongqing Key Laboratory of Inorganic Special Functional Materials, College of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, P. R. China

Zuohua Liu — College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 408100, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00339

Notes
The authors declare no competing financial interest.

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