Article

Efficient Recovery of Vanadium from High-Chromium Vanadium Slag with Calcium-Roasting Acidic Leaching

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Abstract: High-chromium vanadium slag (HCVS) is an important by-product generated during the smelting process of high-chromium-vanadium-titanium-magnetite. Direct acid leaching and calcium-roasting acid leaching technology were applied to recover vanadium and chromium from HCVS. The effects of experimental parameters on the leaching process, including concentration of H_2SO_4, reaction temperature, reaction time, and liquid-to-solid ratio, were investigated. The XRD and UV-Vis DRS results showed that vanadium and chromium existed in low valence with a spinel structure in the HCVS. The Cr-spinel was too stable to leach out; no more than 8% of the chromium could be leached out both in the direct acid leaching process and calcium-roasting acid-leaching process. Most low valence vanadium could be oxidized to high valence with calcium-roasting technology, and the leaching efficiency could be increased from 33.89% to 89.12% at the selected reaction conditions: concentration of H_2SO_4 at 40 vt.%, reaction temperature of 90 °C, reaction time of 3 h, liquid-to-solid ratio of 4:1 mL/g, and stirring rate of 500 rpm. The kinetics analysis indicated that the leaching behavior of vanadium followed the shrinking core model well, and the leaching process was controlled by the surface chemical reaction, with an Ea of 58.95 kJ/mol and 62.98 kJ/mol for direct acid leaching and roasting acid leaching, respectively.

Keywords: vanadium; calcium roasting; leaching efficiency

1. Introduction

Vanadium and chromium are strategic transition elements that have been widely used in some fields such as steel-making, energy-storage, catalysts, the petrochemical industry, and green chemistry owing to their excellence hardness, high corrosion resistance, and other excellent physicochemical properties [1–5]. High-chromium vanadium slag (HCVS) is a by-product generated during the smelting process of high-chromium-vanadium-titanium-magnetite, and it is an important vanadium source in China [6–10]. During the smelting process, the vanadium and chromium are reduced into the molten enriched in the spinel, which is hard to destroy directly and restricted the large-scale utilization of HCVS [11]. Thus, some enhancement technologies were needed to recover vanadium and chromium efficiently.

To date, the basic recovery technology for vanadium has been sodium-roasting leaching technology, which was first proposed by Birck in 1912 and is widely used in the Chinese industries since the 1980s [12–14]. The vanadium-containing ores are mixed with the sodium salts (sodium carbonate (800–1000 °C), sodium sulfate (1200–1250 °C), sodium chloride (750–850 °C), and sodium hydroxide (400–800 °C)) at determined mole ratios and then roasted in a vertical kiln under a high temperature atmosphere with O_2 [13,15,16]. The structure of vanadium-containing ores is destroyed in the high temperature and low-valence vanadium is exposed and oxidized to a high valence. The high-valence vanadium

is formed as sodium vanadate and can be easily leached out with acid, alkaline, or water-leaching [17–20]. However, some environmental hazards (sulfur dioxide, chlorine, and hydrogen chloride) and large amount of wastewater have limited continuous large-scale industrial application with the high environmental standards of today. To overcome the above problems, a roasting technology called calcium-roasting technology was developed, in which the sodium salts are replaced by calcium salts [21–25]. The roasting process is similar to the sodium-roasting process; the vanadium-containing ores are mixed with lime, limestone, and calcium salts at fixed mole ratios and then roasted at high temperatures, which are higher than with sodium roasting. During the roasting process, the vanadium spinel is decomposed and reacted with calcium salts to form different kinds of calcium-vanadate, which are determined by the mole ratio of the vanadium to calcium salts [26–30]. Usually, some leaching enhancing processes or multiple roasting processes accompany this process to achieve high recovery [16,31–34].

In this paper, direct acid leaching and calcium-roasting acid leaching technology were applied to leach out chromium and vanadium. The effects of experimental parameters including reaction time, liquid-to-solid ratio, reaction temperature, and concentration of H_2SO_4 on the leaching process were investigated. The leaching kinetics were also investigated.

2. Materials and Methods

2.1. Materials

The HCVS was collected from Pangang Group Co. Ltd., Panzhihua City, Sichuan Province, China. It was dried and ground to below 75 µm for further experiments. The elemental composition of HCVS was measured by XRF. The results displayed in Table 1 indicate that the vanadium and chromium were about 5.43 wt.% and 6.84 wt.%, respectively.

Table 1. Elemental accounts of the HCVS (wt.%).

Element	V_2O_5	Cr_2O_3	FeO	CaO	MgO
Percentages (%)	9.7	10.2	24.7	2.8	13.8
Element	SiO_2	Al_2O_3	MnO	TiO_2	
Percentages (%)	25.7	10.3	1.6	2.7	

2.2. Experimental Procedure

The batch experiments were conducted in a 300 mL glass beaker placed in a thermostatic mixing water bath. Firstly, the water bath was heated to a determined temperature. Then, a predetermined concentration of H_2SO_4 solution and a predetermined amount of HCVS or roasting HCVS were added to the beaker. Then, the beaker was placed in the water bath. Finally, the filtrate was collected by vacuum filtration after the required reaction time.

2.3. Analytical Methods

The concentrations of chromium and vanadium in the filtrate were measured by inductively coupled plasma-optical mission spectrometry (ICP-OES, PerkinElmer Optima 6300DV, Kyoto, Japan.) and the leaching efficiency was calculated following Equations (1) and (2):

$$\eta_V = \frac{V \cdot C_V}{m \cdot \omega_V} \times 100\% \tag{1}$$

$$\eta_{Cr} = \frac{V \cdot C_{Cr}}{m \cdot \omega_{Cr}} \times 100\% \tag{2}$$

where C_V and C_{Cr}, are the concentration of chromium and vanadium in the filtrate in g/L; V, is the volume of the filtrate in liters; ω_V, and ω_{Cr}, are the percentages of chromium and vanadium in the HCVS; and m, is the mass of the HCVS used in the batch experiments in grams.
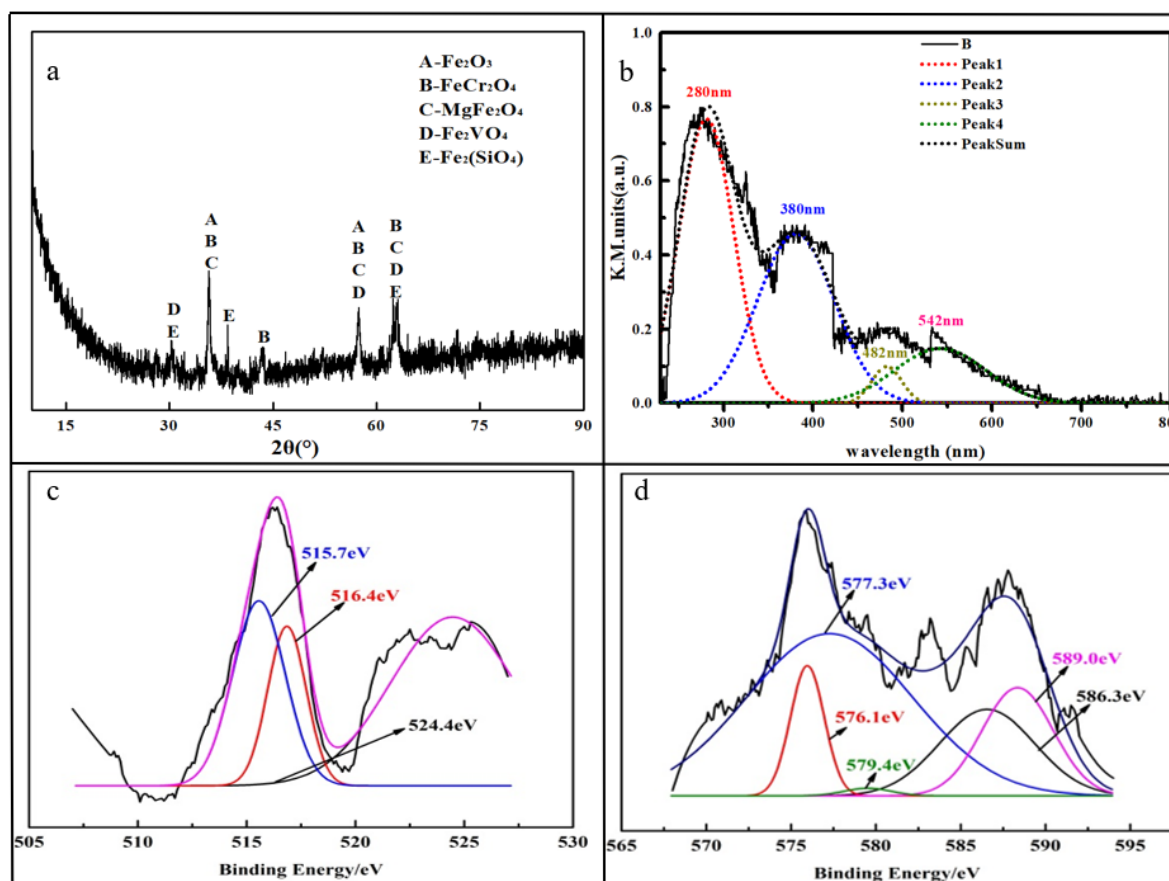
2.4. Characterization

The element percentages of HCVS were measured by XRF (Shimadzu Lab Center XRF-1800, Kyoto, Japan) and the main phases were measured by XRD (Shimadzu Lab Center XRD-6000, Kyoto, Japan). The valences of the vanadium and chromium in the HCVS were detected by UV-Vis DRS (Shimadzu Lab Center, Kyoto, Japan) and XPS (ESCALAB-250Xi, Thermo Fisher Scientific, New York, NY, USA). The thermo-gravimetric analysis was conducted by TG-DSC (Shimadzu Lab Center DSC-60H, Kyoto, Japan) with a heating rate of 10 °C/min from 0 °C to 900 °C.

3. Results

3.1. Characterization of HCVS

The XRD pattern showed in Figure 1a shows that the main crystal structures in the HCVS were Fe_2O_3, $FeCr_2O_4$, $MgFe_2O_4$, Fe_2VO_4 and Fe_2SiO_4 [27,28,30]. The vanadium and chromium mainly existed as spinel structures ($FeCr_2O_4$ and Fe_2VO_4), which are hard to destroy. Therefore, the leaching efficiency of vanadium and chromium may not be high and some enhancing technologies are needed in the further experiments.
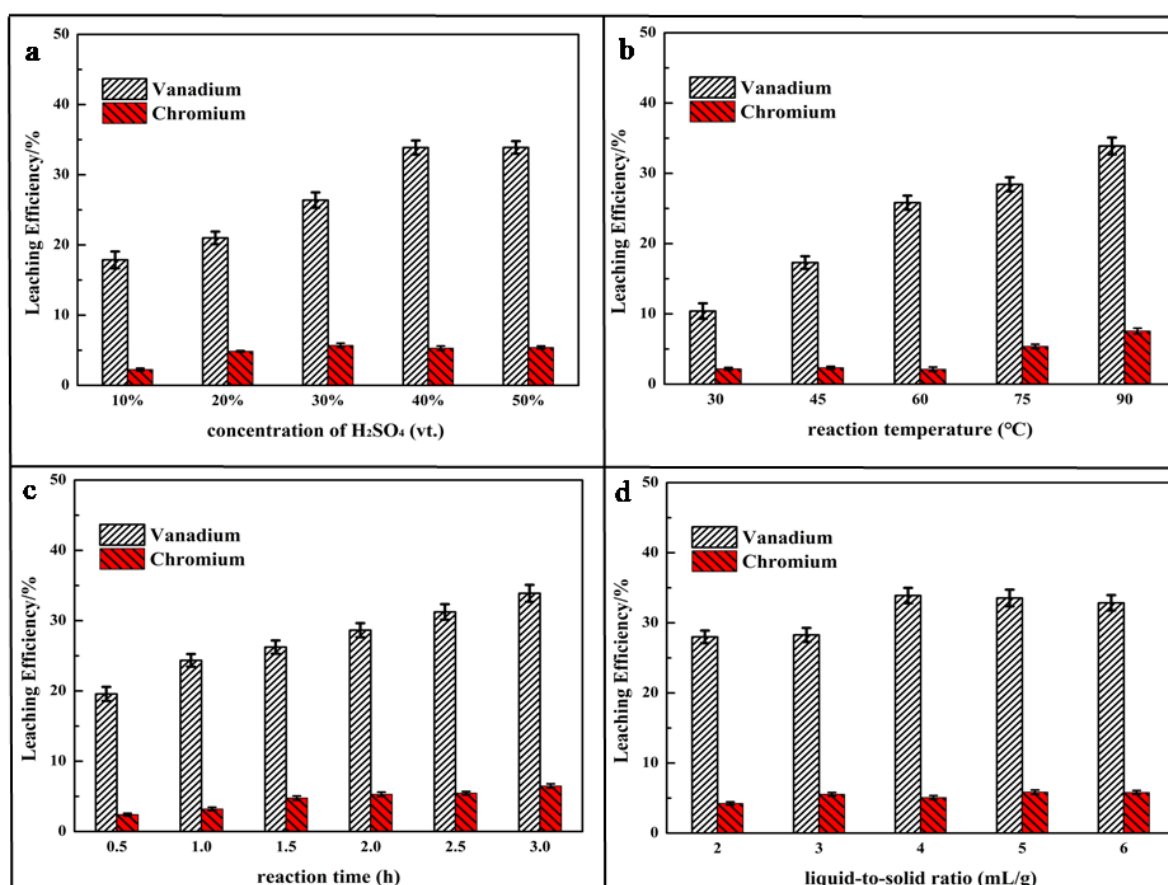

Figure 1. Characterization of HCVS. (**a**) XRD pattern of HCVS; (**b**) UV-Vis DRS of HCVS; (**c**) XPS of vanadium; (**d**) XPS of chromium.

The UV-Vis DRS of HCVS was conducted to help understanding the composition of HCVS; the result is displayed in Figure 1b. The original spectrum signal was analyzed and the peaks were fitted to four main peaks: 280 nm, 380 nm, 482 nm, and 542 nm. The peak at 280 nm was assigned to Fe (III) and confirmed the existence of Fe_2O_3 and $MgFe_2O_4$ [35,36]. The peak at 380 nm was assigned to Cr (III) [37], which corresponds to the $FeCr_2O_4$ phase. The peak at 482 nm was assigned to V=O stretching, which confirmed the existence of V (IV) and V (V) [38,39].

The XPS results showed that most vanadium existed as V(III) and V(IV) (515.7 eV and 516.4 eV), and the Cr (III) accounted for about 82.84% of the HCVS (576.1 eV, 577.3 eV and 586.3 eV), while there were no V (III) and V (V) phases in the XRD pattern. According to our previous study, V(III), V(IV), and V(V) co-exist in HCVS, which means that some V(III) and V(V) compounds in the HCVS exist amorphously and could not detected by XRD [28].

3.2. Direct-Acid-Leaching Process

The direct acid leaching process was conducted to leach out vanadium and chromium from the HCVS. Figure 2 summarizes the effects of the liquid-to-solid ratio, reaction time, concentration of H_2SO_4, and reaction temperature on the leaching process. The leaching efficiencies of vanadium and chromium were relatively low (<35% for vanadium and 8% for chromium), which is consistent with the results of XRD.

Figure 2. Effect of parameters on leaching efficiency of vanadium and chromium: (**a**) concentration of H_2SO_4; (**b**) reaction temperature; (**c**) reaction time; (**d**) liquid-to-solid ratio.

Figure 2a shows that the leaching efficiency of vanadium increased with the increase of the concentration of H_2SO_4. During the leaching process, the H^+ attacks the spinel and destroys the spinel structure to release vanadium and chromium. With an increasing of concentration of H_2SO_4, the corrosion process of the spinel by the highly concentrated H^+ was intensified and the leaching efficiency of vanadium was increased from 17.87% to 33.90%, as the concentration of H_2SO_4 increased from 10 vt.% to 50 vt.%. As the chromium spinel was more stable than the vanadium spinel, the chromium was harder to leach out, with a leaching efficiency below 8%. Otherwise, the leaching efficiency showed no obvious increase when the concentration of H_2SO_4 increased from 40 vt.% to 50 vt.%, and high concentrations bring high impurities [40]; thus, the concentration of 40 vt.% was selected as optimal for further experiments.

The results showed in Figure 2b indicate that only 10.40% vanadium and 2.18% chromium can be leached out at 30 °C. Higher temperatures enhances the activity of vanadium and chromium ions and further favors the reaction intensity [41]. The leaching efficiency increased to 33.89% for vanadium and 7.56% for chromium at 90 °C. In other words, high reaction temperature was beneficial to the leaching process.

Usually, in order to produce more products, long reaction times are utilized. Figure 2c shows that the leaching efficiency of vanadium and chromium increased with the reaction time, but the increase amplitude was slow. Longer reaction times may not make any contribution to the leaching process; thus, the reaction time of 3 h was selected in the following experiments.

During the leaching process, the HCVS particles was ground fine enough for good contact with the concentrated H_2SO_4 solution. The leaching process was most controlled by parameters such as the reaction temperature and concentration of H_2SO_4, but less by the liquid-to-solid ratio, as the liquid-to-solid ratio had no obvious effect on the leaching efficiency (seen in Figure 2d).
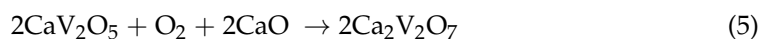
As the spinel structure was hard to destroy directly, the leaching efficiencies of vanadium and chromium were 33.89% and 7.56%, respectively, at the selected optimum conditions: reaction time of 3 h, liquid-to-solid ratio of 4: 1 mL/g, concentration of H_2SO_4 of 40 vt.%, reaction temperature of 90 °C, and stirring rate of 500 rpm.
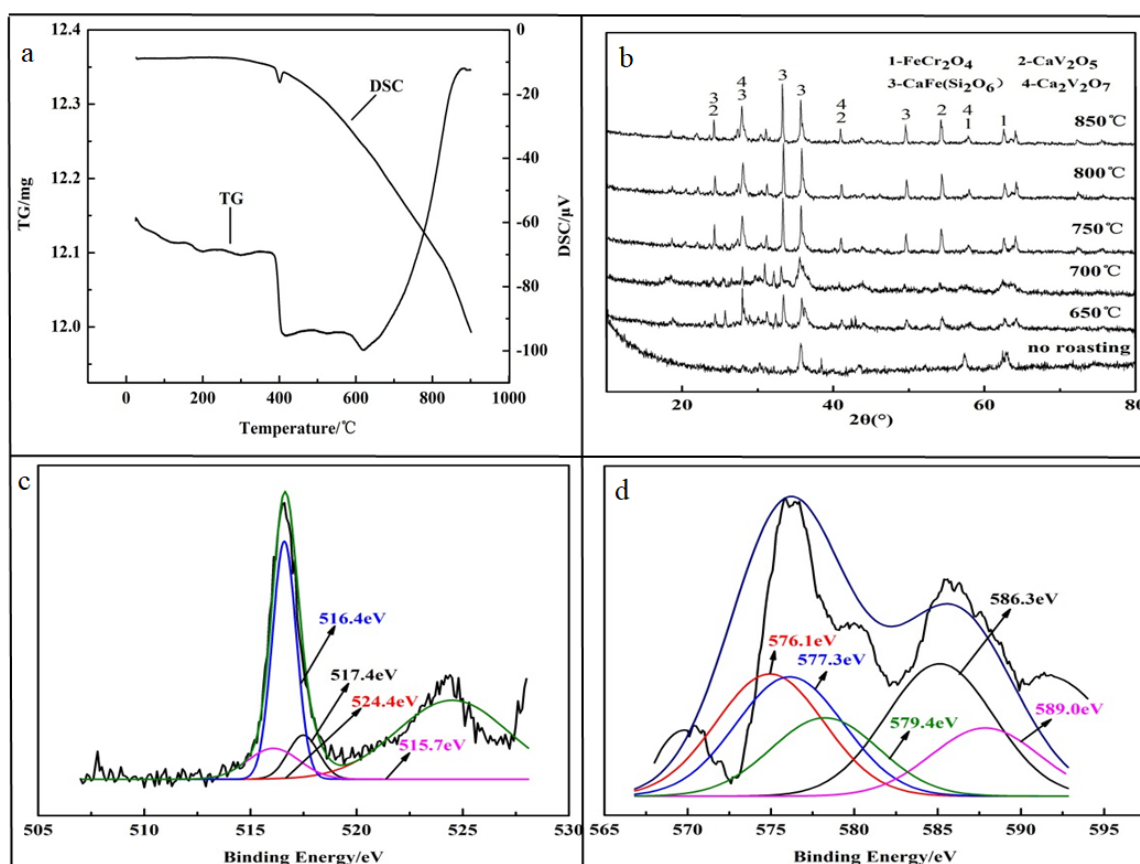
3.3. Characterization of Roasting HCVS

In order to achieve efficient leaching performance of HCVS, calcium-roasting technology was applied to oxidize the low valence compounds. The obtained TG-DSC curves shown in Figure 3a indicate that there was a dehydration step, with weight loss of 1.23% from 0 °C to 400 °C, and an obvious exothermic peak of the DSC curve at 400 °C was observed, which corresponds to the decomposition of the spinel structure. After the temperature increased to 620 °C, a dramatic mass gain of 6.46% was obtained due to the oxidative decomposition of the vanadium spinel phase. This means that the oxidative roasting of vanadium spinel should be conducted above 620 °C. Thus, the calcium-roasting process was conducted at 650–850 °C and the HCVS was mixed with CaO at a mole ratio of $n(CaO)/n(V_2O_5) = 1.1$

The XRD pattern was used to analyze the phase changes during the calcium-roasting process. The results showed in Figure 3b indicate that some new peaks appeared, corresponding to the new phases of $Ca_2V_2O_5$, $CaFe(Si_2O_6)$, and $Ca_2V_2O_7$. These three new phases appeared at 650 °C, and the crystal structures became more stable as the roasting temperature increased from 650 °C to 850 °C. During the calcium-roasting process, the Fe_2VO_4 decomposed (seen in Equation (3)) to form V_2O_4 at nearly 400 °C according to DG-TSC results, and then reacted with CaO to form $Ca_2V_2O_5$. With the increasing roasting temperature, partial $Ca_2V_2O_5$ was further oxidized to $Ca_2V_2O_7$, which means that in the calcium roasting of HCVS, the V(IV) and V(V) co-existed.

After roasting, some V(III) and V(IV) were oxidized to V(V). The XPS results indicate that only 9.55% V(III) was retained in the roasted HCVS, while Cr(III) still accounted for about 80.32%. As the Cr spinel was more stable than the V spinel [13], the Cr was not oxidized and still existed in $FeCr_2O_4$, according to the XRD results. It was concluded that the chromium was still hard to leach out.
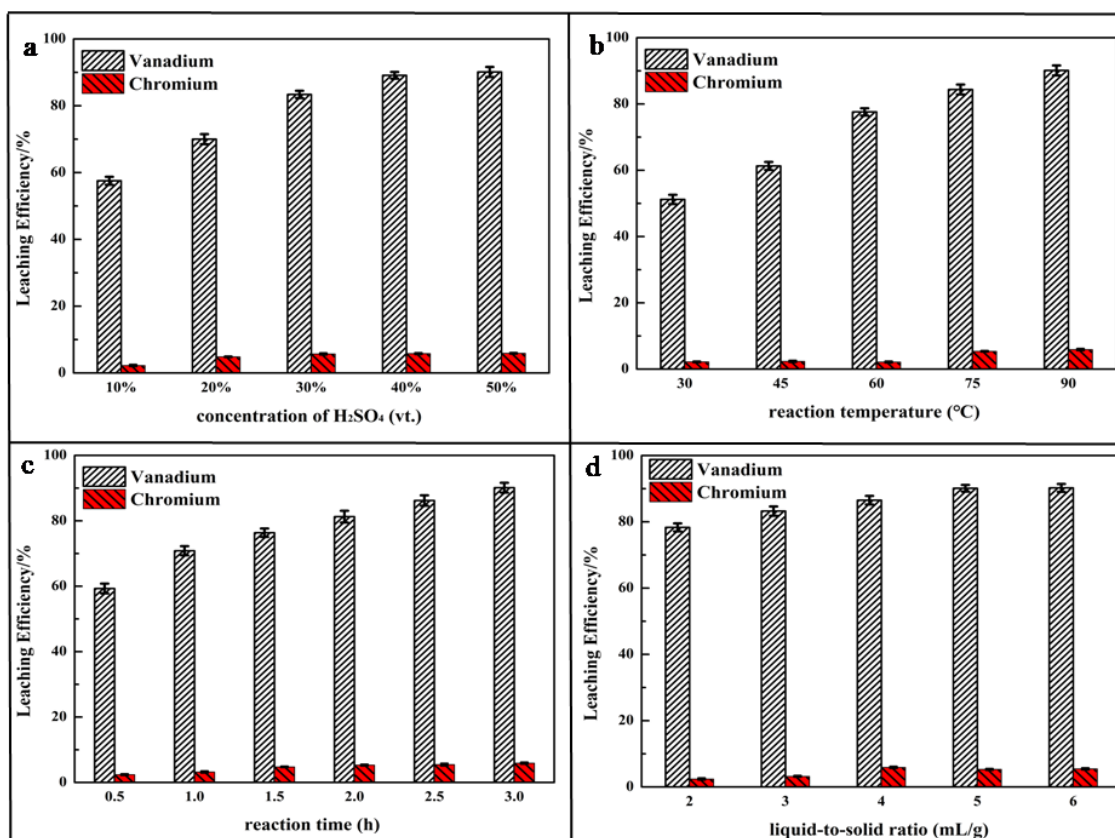
$$2Fe_2VO_4 \rightarrow 4FeO + V_2O_4 \tag{3}$$

$$V_2O_4 + CaO \rightarrow CaV_2O_5 \tag{4}$$

$$2CaV_2O_5 + O_2 + 2CaO \rightarrow 2Ca_2V_2O_7 \tag{5}$$

Figure 3. Characterization of roasting HCVS. (**a**) TG and DSC; (**b**) XRD pattern of roasted HCVS; (**c**) XPS of vanadium; (**d**) XPS of chromium.

3.4. Acid Leaching for Roasting HCVS

The acid-leaching experiments with calcium roasting of HCVS were conducted to investigate the effect of calcium roasting on the leaching process under the same reaction conditions as the direct acid leaching process described above. As the Cr spinel was still stable under the roasting temperature, the leaching efficiency of chromium showed no obvious increase compared with the direct acid leaching process; therefore, the leaching behavior of chromium is not discussed in this part.

Figure 4a shows that the calcium roasting made a great contribution to the leaching process. The leaching efficiency of vanadium was increased by nearly 40 percentage (up to 57.54%) after roasting, compared with the direct acidic leaching process (at the concentration of 10 vt.% H_2SO_4). During the roasting process, most V(III) and V(IV) were oxidized to V(V), making a contribution to the great leaching performance of roasting HCVS. The leaching efficiency increased quickly at the beginning and then smoothly with the increase of H_2SO_4 concentration. The highest leaching efficiency was up to 90.12% at a concentration of 50 vt.%, which showed nearly a 58% improvement compared to the direct acid leaching process. Compared to our previous study, the leaching efficiency might be increased more with some enhancing technologies, such as oxidative leaching and electro-oxidative leaching [28]. Otherwise, the formation of the by-product $CaSO_4$, which is a villous particle, might adsorb on the surface of leaching residue and have negative effects on the leaching process [40]; thus, a too high concentration of H_2SO_4 is not suitable for leaching while calcium roasting HCVS. Meanwhile, the leaching efficiency showed little increase as the concentration increased from 40 vt.% to 50 vt.%; thus, a concentration of H_2SO_4 of 40 vt.% was selected for further experiments.

Figure 4. Effect of parameters on leaching efficiency of vanadium and chromium: (**a**) concentration of H_2SO_4; (**b**) reaction temperature; (**c**) reaction time; (**d**) liquid-to-solid ratio.

The same phenomenon can also be observed in Figure 4b. The leaching process was greatly enhanced by calcium roasting; the leaching efficiency was increased from 10.4% to 89.12% as the reaction temperature increased from 30 °C to 90 °C. Usually, metal ions have high solubility at high temperatures, accompanied by high activity; thus, 90 °C was chose in further experiments.

The results displayed in Figure 4c,d indicate that the liquid-to-solid ratio and reaction time showed similar effects on the leaching process, and a suitable liquid-to-solid ratio and a long reaction time could achieve high leaching efficiency. As can be seen, the calcium-roasting process can oxidize low valence vanadium to high valence vanadium and enhance the leaching process to achieve high leaching efficiency of vanadium, but has no influence on the change trend of leaching efficiency affected by the experimental parameters.

To summarize, low valence vanadium in V spinel was decomposed and oxidized to V(V) during the calcium-roasting process, but Cr spinel was too stable to decompose. For vanadium, 89.12% was leached out under the optimal reaction conditions: reaction time of 3 h, reaction temperature of 90 °C, liquid-to-solid ratio at 4:1 mL/g, concentration of H_2SO_4 at 40 vt.%, and stirring rate at 500 rpm. Most chromium existing as $FeCr_2O_4$ was hard to leach out and was retained in the leaching residue.

3.5. Leaching Kinetics

In order to understand the reaction mechanism, the leaching kinetics of vanadium were analyzed (leaching out chromium was very difficult; thus, it is not analyzed here). Usually, the leaching kinetics followed the shrinking core model described in Equation (6), which was used to describe the liquid-solid reaction [40,42–45]:
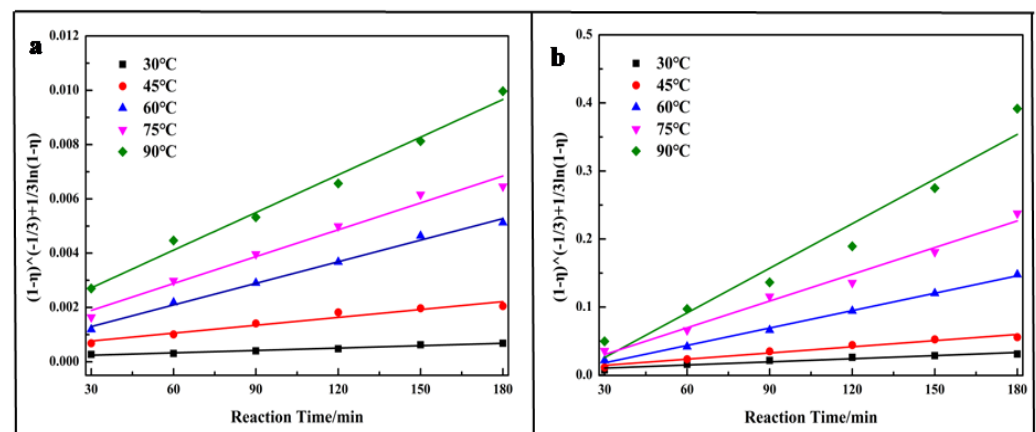
$$[(1-\eta)^{-1/3} - 1] + 1/3 \cdot Ln(1-\eta) = k \cdot t \tag{6}$$

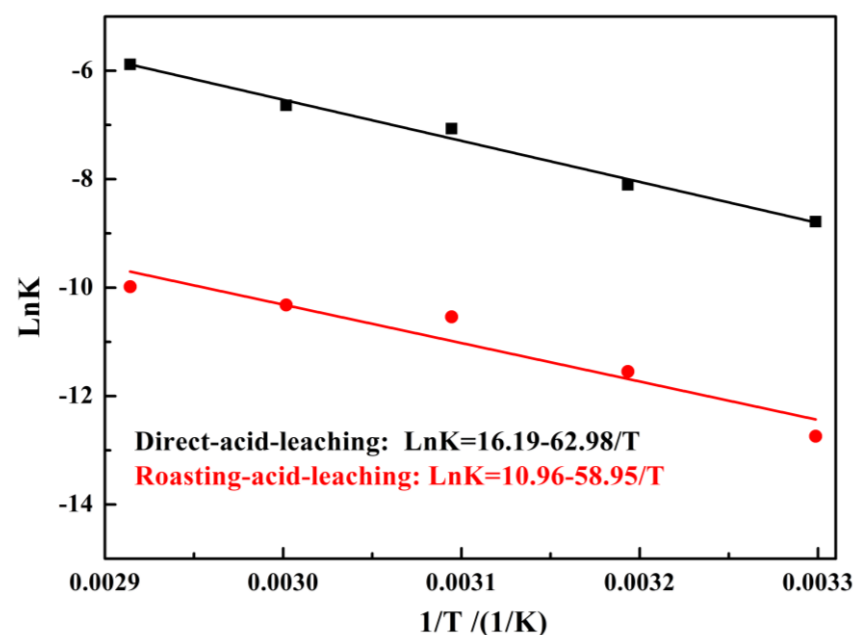where η is the leaching efficiency of vanadium, in percentage.

The experimental data was fitted to Equation (6) and the results are shown in Figure 5. Based on the fitting results, the Ea for vanadium leached out was calculated following the Arrhenius equations (Equation (7)). Figure 6 shows that the Ea for vanadium leached out was 58.95 kJ/mol for the direct acid leaching process and 62.98 kJ/mol for the calcium-roasting acid leaching process, which indicates that the controlling step for vanadium leaching is the surface chemical reaction [40,43–45]. Compared with the references [40,43,45,46], the Ea was much larger, indicating that the vanadium in the HCVS was hard to leach out by both direct acid leaching technology and calcium-roasting acid leaching technology. In order to improve the leaching efficiency and enhance the leaching process, some more efficient pre-treatment technologies are needed.

$$Lnk = LnA - Ea/(RT) \tag{7}$$

where Ea is the apparent activation energy, A is the pre-exponential factor, and R is the mole gas constant.

Figure 5. Plot of leaching kinetics of vanadium at various reaction temperatures. (**a**) direct acid leaching process; (**b**) calcium-roasting acid leaching process.

Figure 6. Natural logarithm of reaction rate constant versus reciprocal temperature of vanadium.

4. Conclusions

A direct acid leaching process and a calcium-roasting acid leaching process on HCVS were conducted. The following conclusions were obtained:

(1) The chromium and vanadium existed as spinel structure in the HCVS, which are too stable to destroy directly; only 33.89% of vanadium and 7.56% of chromium could be leached out at the selected conditions during the direct acid leaching process: reaction time of 3 h, liquid-to-solid ratio at 4:1 mL/g, concentration of H_2SO_4 at 40 vt.%, reaction temperature of 90 °C, and stirring rate at 500 rpm. The Ea of the vanadium leached out was 62.98 kJ/mol, which indicates that the vanadium was hard to leach out directly;

(2) Most low valence vanadium could be oxidized to high valence during the calcium-roasting process, and the leaching efficiency could achieve 89.12% under the optimal conditions: reaction time of 3 h, liquid-to-solid ratio at 4:1 mL/g, reaction temperature of 90 °C, concentration of H_2SO_4 at 40 vt.%, and stirring rate at 500 rpm. The leaching behavior followed the shrinking core model well, and the controlling step was the surface chemical reaction, with an Ea of 58.95 kJ/mol for the calcium-roasting acid leaching process.

(3) Chromium was hard to leach out both in the direct acid leaching process and the calcium-roasting acid leaching process; the leaching efficiency was below 8%. Higher roasting temperatures and new additive agents will be needed for efficient chromium recovery in our future works.

Author Contributions: Methodology, B.L.; supervision, W.S. and Z.L.; other contributions were made by H.P. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: Not applicable.

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