applied sciences

MDPI

Article

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

Hao Peng *, Liu Yang, Ya Chen and Jing Guo

Chongqing Key Laboratory of Inorganic Special Functional Materials, College of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, China; yznuyl@126.com (L.Y.); yznucy@126.com (Y.C.); cquguojing@126.com (J.G.)
* Correspondence: penghao@yznu.edu.cn; Tel.: +86-15123031643

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_2O_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 wascalculated as 19.93 $kJ{\cdot}mol^{-1}$ and 21.26 $kJ{\cdot}mol^{-1}$, 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_2SO_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_2O_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, MnO_2 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, MnO_2 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 $\lambda = 0.15418$ nm, 40 kV, and 40 mA at 10° to 90°, and the results are displayed in Figure 1.

Table 1. Composition of the vanadium–chromium reducing residue (wt.%).

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		

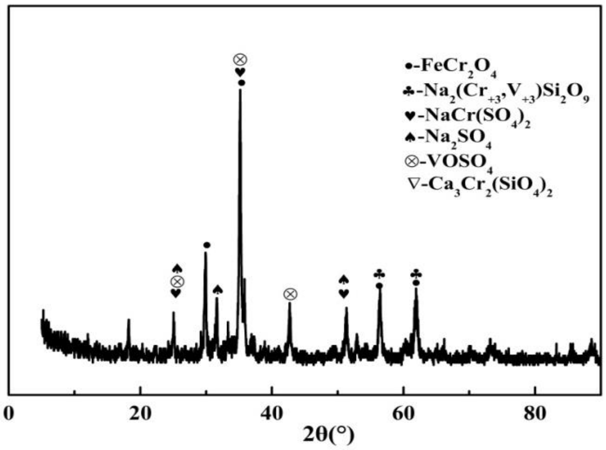


Figure 1. The XRD pattern of the original residue.

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.

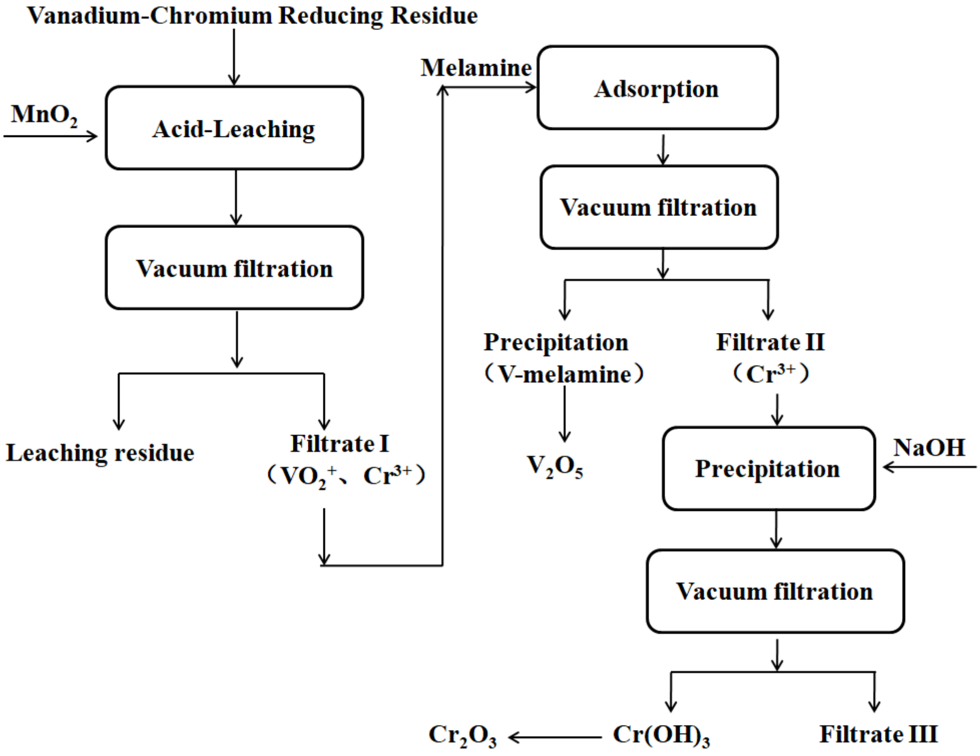


Figure 2. A flow sheet for the experimental procedure.

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 MnO_2 and concentration of sulfuric acid (H_2SO_4) 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 (η_V) and chromium (η_{Cr}) were calculated using Equations (1) and (2), as shown below:

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

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

where C_V and C_{Cr} are the concentration of vanadium and chromium in the filtrate, g/L; Vis the volume of the filtrate, L; ω_V and ω_{Cr} 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 V_2O_5 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. Cr_2O_3 was then obtained by drying the refined material at 110 °C for 2 h [18,20]. The effect of various paraments 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_2SO_4Dosage

The effect of H_2SO_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_2SO_4 was set as 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, and 30 wt.%. The results are detailed in Figure 3.

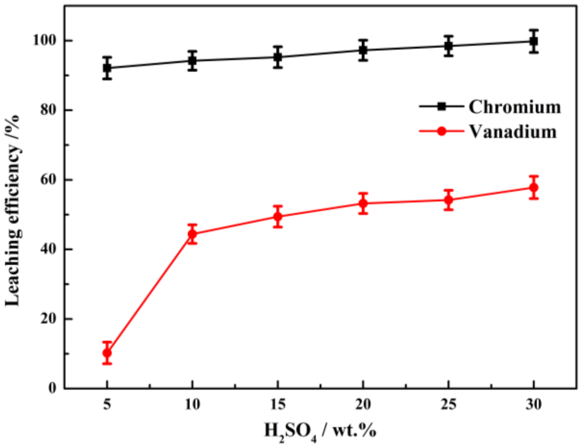


Figure 3. Effect of concentration of H_2SO_4 on the leaching efficiency of vanadium and chromium.

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_2SO_4. The leaching efficiency was 92.10% at 5 wt.% H_2SO_4 and up to 99.80% at 30 wt.% H_2SO_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.% $H_2SO_{4.}$ 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_2Dosage

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 $E^0{}_{MnO2/Mn2+}$ = 1.21 V and $E^0(VO_2{}^+/VO^{2+})$ = 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_2SO_4 at 30 wt.%. The results are detailed in Figure 5.

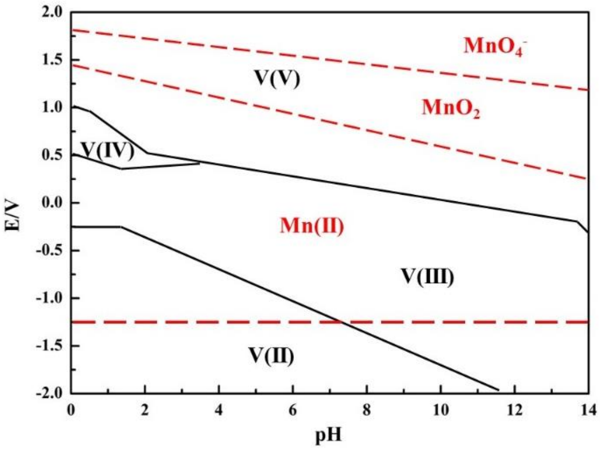


Figure 4. Potential-pH diagram of vanadium and manganese at 25 °C.

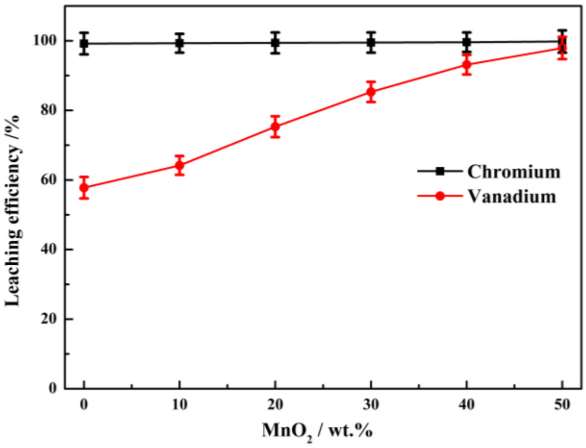


Figure 5. Effect of MnO_2 dosage on the leaching efficiency of vanadium and chromium.

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 MnO_2. The vanadium in low valences, like V(IV) and V(III), was oxidized to V(V) by MnO_2, and then dissolved in acidic medium and achieved high leaching efficiency. The results confirmed that MnO_2 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 MnO_2 at 50 wt.%, and concentration of H_2SO_4 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.

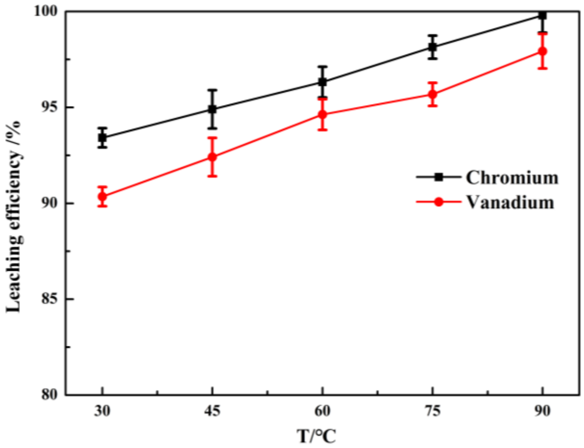


Figure 6. Effect of reaction temperature on the leaching efficiency of vanadium and chromium.

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 MnO_2 at 50 wt.%, and concentration of H_2SO_4 at 30 wt.%. Increasing of reaction time could promote the reaction between H_2SO_4 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.

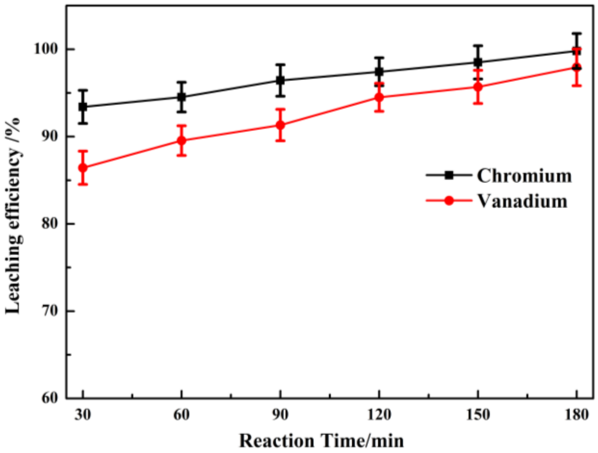


Figure 7. Effect of reaction time on the leaching efficiency of vanadium.

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 MnO_2 at 50 wt.%, and concentration of H_2SO_4 at 30 wt.%. The results are shown in Figure 8.

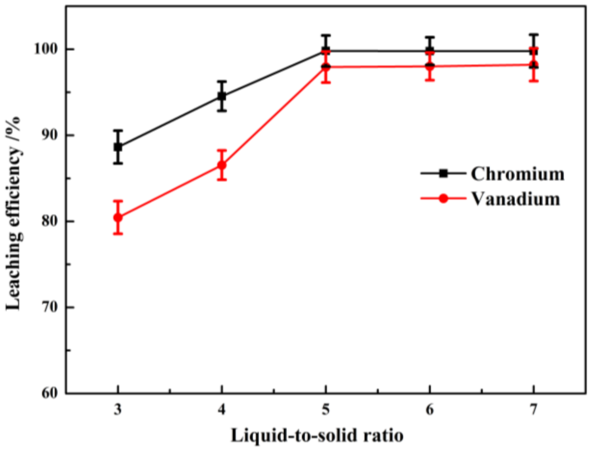


Figure 8. Effect of liquid-to-solid ratio on the leaching efficiency of vanadium.

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 MnO_2 at 50 wt.%, concentration of H_2SO_4 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

$$K_1 t = \eta \tag{3}$$

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

$$K_2 t = 1 - 2/3\eta - (1 - \eta)^{2/3} \tag{4}$$

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

$$K_3 t = 1 - (1 - \eta)^{1/3} \tag{5}$$

which, η 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.

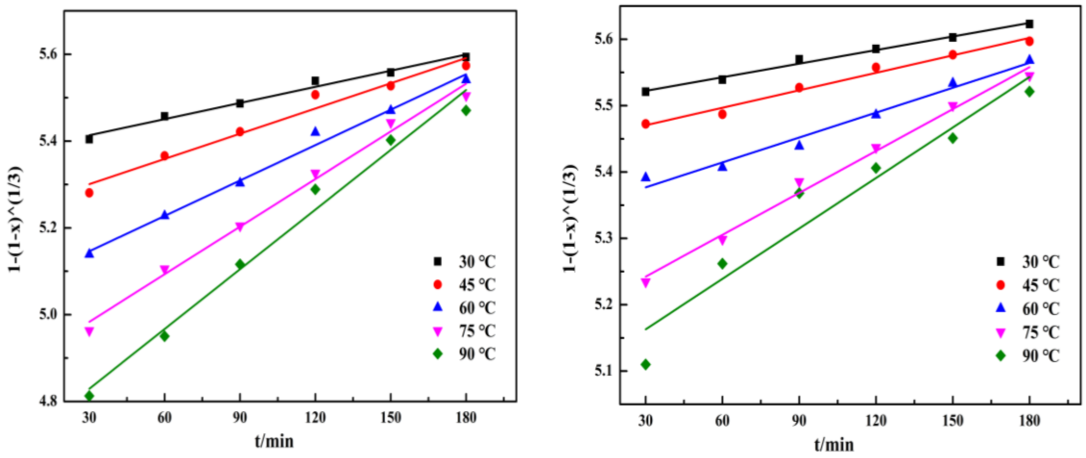
Table 2. Apparent rate constants K_1, K_2, and K_3 for the kinetic models and correlation coefficients.

Parameter	Diffusion through the Liquid Film		Diffusion through the Product Layer		Surface Chemical Reaction	
	η		$1 - 2/3\eta - (1 - \eta)^{2/3}$		$1 - (1 - \eta)^{1/3}$	
	K_1(min^{-1})	R^2	K_2 (min^{-1})	R^2	K_3(min^{-1})	R^2
Chromium						
30 °C	0.0004279	0.9596	0.000675	0.9350	0.000682	0.9887
45 °C	0.0005409	0.9699	0.000605	0.9251	0.000877	0.9897
60 °C	0.0007514	0.9428	0.000635	0.9316	0.001250	0.9951
75 °C	0.0012200	0.9524	0.000800	0.9199	0.002100	0.9991
90 °C	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
45 °C	0.001140	0.9681	0.000868	0.9152	0.00194	0.9826
60 °C	0.001500	0.9608	0.000901	0.9263	0.00272	0.9982
75 °C	0.001900	0.9735	0.00948	0.9369	0.00366	0.9988
90 °C	0.002380	0.9863	0.000965	0.9200	0.00459	0.9894

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_3isthe 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.

$$\ln K = \ln A - Ea/(RT) \tag{6}$$

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



(**a**) vanadium (**b**) chromium

Figure 9. Plot of leaching kinetics of vanadium at various reaction temperatures in different leaching processes.

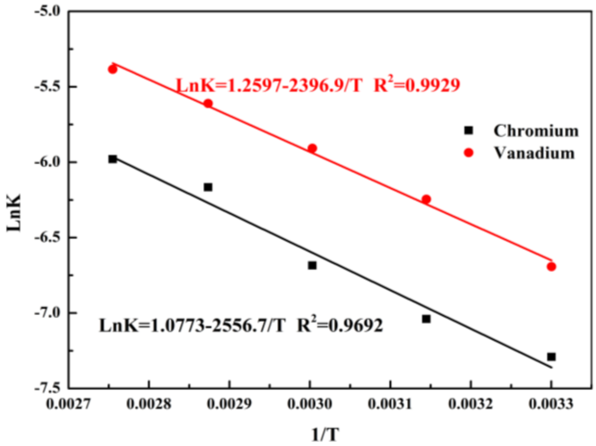


Figure 10. Natural logarithm of reaction rate constant versus reciprocal temperature for leaching process.

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_2SO_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 $V_2O_5$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_2O_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.

References

1. Wei, Z.; Liu, D.; Hsm, C.; Liu, F. All-vanadium redox photoelectrochemical cell: An approach to store solar energy. *Electrochem. Commun.* **2014**, *45*, 79–82. [CrossRef]
2. Smirnov, M.B.; Kazimirov, V.Y.; Baddour-Hadjean, R.; Smirnov, K.S.; Pereira-Ramos, J.-P. Atomistic mechanism of phase transition in vanadium pentoxide. *J. Phys. Chem. Solids* **2014**, *75*, 115–122. [CrossRef]

3. Zadorozhnyy, V.Y.; Klyamkin, S.N.; Zadorozhnyy, M.Y.; Bermesheva, O.V.; Kaloshkin, S.D. Mechanical alloying of nanocrystalline intermetallic compound TiFe doped by aluminum and chromium. *J. Alloys Compd.* **2014**, *586*, S56–S60. [CrossRef]
4. Mechthild, L.; Ning, D.; Powell, M.J.; Brett, D.J.L.; Shearing, P.R.; Liu, Z.; Darr, J.A. VO_2 nano-sheet negative electrodes for lithium-ion batteries. *Electrochem. Commun.* **2016**, *64*, 56–60.
5. Yang, K.; Zhang, X.; Tian, X.; Yang, Y.; Chen, Y. Leaching of vanadium from chromium residue. *Hydrometallurgy* **2010**, *103*, 7–11. [CrossRef]
6. Peng, H.; Liu, Z.; Tao, C. Selective leaching of vanadium from chromium residue intensified by electric field. *J. Environ. Chem. Eng.* **2015**, *3*, 1252–1257. [CrossRef]
7. Liu, Z.; Ayinuer, N.; Chen, M.; Du, J.; Fan, X.; Tao, C. Hydrometallurgical leaching process intensified by an electric field for converter vanadium slag. *Hydrometallurgy* **2015**, *155*, 56–60. [CrossRef]
8. Peng, H.; Liu, Z.; Tao, C. A green method to leach vanadium and chromium from residue using NaOH-H_2O_2. *Sci. Rep.* **2018**, *8*, 426. [CrossRef] [PubMed]
9. Peng, H.; Wang, F.; Li, G.; Guo, J.; Li, B. Highly Efficient Recovery of Vanadium and Chromium: Optimized by Response Surface Methodology. *ACS Omega* **2019**, *4*, 904–910. [CrossRef] [PubMed]
10. Peng, H.; Guo, J.; Li, G.; Cheng, Q.; Zhou, Y.; Liu, Z.; Tao, C. Highly efficient oxidation of chromium (III) with hydrogen peroxide in alkaline medium. *Water Sci. Technol.* **2019**, *79*, 366–374. [CrossRef]
11. Yang, H.; Mao, L.; Xue, X. Separation and recovery of chromium and vanadium from reduced vanadium-chromium precipitate by calcinations-alkaline leaching. *J. Chem. Ind. Eng.* **2014**, *65*, 948–953.
12. Zhu, X.; Li, W.; Tang, S.; Zeng, M.; Bai, P.; Chen, L. Selective recovery of vanadium and scandium by ion exchange with D201 and solvent extraction using P507 from hydrochloric acid leaching solution of red mud. *Chemosphere* **2017**, *175*, 365–372. [CrossRef] [PubMed]
13. Fan, Y.; Wang, X.; Wang, M. Separation and recovery of chromium and vanadium from vanadium-containing chromate solution by ion exchange. *Hydrometallurgy* **2013**, *136*, 31–35. [CrossRef]
14. Li, Z.; Li, Q.; Xiao, L.; Zhang, Q. A study of the vanadium species in an acid leach solution of stone coal using ion exchange resin. *Hydrometallurgy* **2010**, *105*, 176–178.
15. Ye, G.; Hu, Y.; Tong, X.; Lu, L. Extraction of vanadium from direct acid leaching solution of clay vanadium ore using solvent extraction with N235. *Hydrometallurgy* **2018**, *177*, 27–33. [CrossRef]
16. Yang, X.; Zhang, Y.; Bao, S.; Shen, C. Separation and recovery of vanadium from a sulfuric-acid leaching solution of stone coal by solvent extraction using trialkylamine. *Sep. Purif. Technol.* **2016**, *164*, 49–55. [CrossRef]
17. Tavakoli, M.R.; Dreisinger, D.B. Separation of vanadium from iron by solvent extraction using acidic and neutral organophosporus extractants. *Hydrometallurgy* **2014**, *141*, 17–23. [CrossRef]
18. Wang, X.; Gao, D.; Chen, B.; Meng, Y.; Fu, Z.; Wang, M. A clean metallurgical process for separation and recovery of vanadium and chromium from V-Cr-bearing reducing slag. *Hydrometallurgy* **2018**, *181*, 1–6. [CrossRef]
19. Wang, M.; Chen, B.; Huang, S.; Wang, X.; Liu, B.; Ge, Q.; Xie, S. A novel technology for vanadium and chromium recovery from V-Cr-bearing reducing slag. *Hydrometallurgy* **2017**, *171*, 116–122. [CrossRef]
20. Chen, B.; Huang, S.; Liu, B.; Ge, Q.; Wang, M.; Wang, X. Separation and recovery of vanadium and chromium from acidic leach solution of V-Cr-bearing reducing slag. *J. Environ. Chem. Eng.* **2017**, *5*, 4702–4706. [CrossRef]
21. Peng, H.; Guo, J.; Zheng, X.; Liu, Z.; Tao, C. Leaching Kinetics of Vanadium from Calcification Roasting Converter Vanadium Slag in Acidic Medium. . *J. Environ. Chem. Eng.* **2018**, *6*, 5119–5224. [CrossRef]
22. Peng, H.; Liu, Z.; Tao, C. Leaching Kinetics of Vanadium with Electro-oxidation and H_2O_2 in Alkaline Medium. *Energy Fuels* **2016**, *30*, 7802–7807. [CrossRef]
23. Peng, H.; Liu, Z.; Tao, C. Adsorption Process of Vanadium (V) with Melamine. *Water Air Soil Pollut.* **2017**, *228*, 272. [CrossRef]
24. Peng, H.; Liu, Z.; Tao, C. Adsorption kinetics and isotherm of vanadium with melamine. *Water Sci. Technol.* **2017**, *75*, 2316–2321. [CrossRef] [PubMed]
25. Chen, X.; Lan, X.; Zhang, Q.; Ma, H.; Zhou, J. Leaching vanadium by high concentration sulfuric acid from stone coal. *Trans. Nonferrous Met. Soc. China* **2010**, *20*, 123–126. [CrossRef]

26. Minakshi, M.; Singh, P.; Issa, T.B.; Thurgate, S.; de Marco, R. Lithium insertion into manganese dioxide electrode in MnO_2/Zn aqueous battery: Part III. Electrochemical behavior of γ-MnO_2 in aqueous lithium hydroxide electrolyte. *J. Power Sources* **2006**, *153*, 165–169. [CrossRef]
27. Biswal, A.; Tripathy, B.C.; Sanjay, K.; Subbaiah, T.; Minakshi, M. Electrolytic manganese dioxide (EMD): A perspective on worldwide production, reserves and its role in electrochemistry. *RSC Adv.* **2015**, *5*, 58255–58283. [CrossRef]
28. Levenspiel, O. *Chemical Reaction Engineering*; John Wiley and Sons: New York, NY, USA, 1962.
29. Liu, H.; Du, H.; Wang, D.; Wang, S.; Zheng, S.; Zhang, Y. Kinetics analysis of decomposition of vanadium slag by KOH sub-molten salt method. *Trans. Nonferrous Met. Soc. China* **2013**, *23*, 1489–1500. [CrossRef]
30. Qiu, S.; Wei, C.; Li, M.; Zhou, X.; Li, C.; Dong, Z. Dissolution kinetics of vanadium trioxide at high pressure in sodium hydroxide–oxygen systems. *Hydrometallurgy* **2011**, *105*, 350–354. [CrossRef]
31. Szymczycha-Madeja, A. Kinetics of Mo, Ni, V and Al leaching from a spent hydrodesulphurization catalyst in a solution containing oxalic acid and hydrogen peroxide. *J. Hazard. Mater.* **2011**, *186*, 2157–2161. [CrossRef]
32. Wen, C.Y. Noncatalytic heterogeneous solid fluid reaction model. *Ind. Eng. Chem. Res.* **1968**, *60*, 34–54. [CrossRef]
33. Demirkiran, N. A study on dissolution of ulexite in ammonium acetate solutions. *Chem. Eng. J.* **2008**, *141*, 180–186. [CrossRef]
34. Habbache, N.; Alane, N.; Djerad, S.; Tifouti, L. Leaching of copper oxide with different acid solutions. *Chem. Eng. J.* **2009**, *152*, 503–508. [CrossRef]