

Article

# Preparation of High Purity $V_2O_5$ from a Typical Low-Grade Refractory Stone Coal Using a Pyro-Hydrometallurgical Process

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**Abstract:** The recovery of vanadium from a typical low-grade refractory stone coal was investigated using a pyro-hydrometallurgical process specifically including blank roasting, acid leaching, solvent extraction, and chemical precipitation. The appropriate role of parameters in each process was analyzed in detail. Roasting temperature and roasting time during the roasting process showed a significant effect on leaching efficiency of vanadium. Using  $H_2SO_4$  as a leaching agent, vanadium leaching efficiency can achieve above 90% under the optimum leaching conditions of  $CaF_2$  dosage of 5%, sulfuric acid concentration of 4 mol/L, liquid to solid ratio of 2:1 mL/g, leaching time of 2 h, and leaching temperature of 95 °C. 99.10% of vanadium can be extracted from the leaching solution in three stages under the conditions of initial pH of 1.6, trioctylamine (TOA) extractant concentration of 20% (vol), phase ratio (A/O) of 2, and reaction time of 2 min. 1.0 mol/L NaOH was used to strip vanadium from the extracted solvent phase. After purification and precipitation, vanadium can be crystallized as ammonium metavanadate. The  $V_2O_5$  product with a purity of 99.75% is obtained after ammonium metavanadate thermal decomposition at 550 °C for 2 h. The total vanadium recovery in the whole process is above 88%. This process has advantages of short operation time, high vanadium extraction efficiency, and high purity of the product.

**Keywords:** stone coal; vanadium extraction; roasting; sulfuric acid leaching; solvent extraction; precipitation

## 1. Introduction

Vanadium plays an important role in many fields because of its special properties in hardness, high tensile strength, excellent corrosion resistance at low temperature, and specific physiological functions [1]. In China, stone coal is a special vanadium-bearing resource that contains enormous reserves of vanadium. Stone coal is a kind of carbonaceous shale which looks like coal but mostly consists of quartz and with a low calorific value [2]. Typically, vanadium in stone coal exists in the isomorphism-like form in which vanadium replaces trivalent aluminum in the mica structure [3]. The mica structure is stable, so the key step of extracting vanadium from vanadium-containing mica is to destroy the lattice structure of the mica. Roasting and acid leaching are the most effective ways to destroy the lattice structure of mica [4]. To recover vanadium from stone coal, it is usually treated through several procedures, such as roasting, leaching, purification, and precipitation [5,6]. A considerable amount of investigation has been made to recover vanadium from stone coal. Some extraction processes, such as modified sodium salt roasting-dilute sulfuric acid leaching [7], oxidizing

roasting-alkaline leaching [8], calcium salt roasting-sulfuric acid leaching [9,10], and direct acid leaching [11,12] were developed. Among all of the above extraction processes, roasting with salt as an additive will result in serious air pollution and low vanadium recovery (less than 70%) [10], and oxidizing roasting-alkaline leaching or low acid leaching was only developed for vanadium in stone coal existing in the amorphous phase form [13]. As for calcium salt roasting-acid leaching processing, it usually suffered from high temperature and long roasting time, generally 900–1000 °C and 2–3 h [14,15], which results in high energy consumption. When the direct acid leaching method is adopted, high acid concentration (6 mol/L or higher) is usually needed [16] and other conditions, such as high temperature and high pressure, are also generally required [12]. Excessive acid consumption and the use of high pressure equipment make the entire process uneconomical. However, acid leaching can get higher vanadium leaching efficiency compared to water leaching and alkaline leaching. Therefore, the main task for vanadium leaching improvement is to reduce the acid consumption.

Apart from leaching, the purification of the acid leaching solution is another difficulty because this is the key step for vanadium precipitation. Commonly, there are massive impurities, such as Fe, Al, Mg, K, Na, Ca, P, and Si in the acid leaching solution, along with V. The methods for vanadium-containing solution purification include chemical precipitation [17], ion exchange [18,19], and solvent extraction [20–24]. However, chemical precipitation showed a poor performance of selectivity of vanadium over impurities and will result in vanadium loss together with impurity precipitation and ion exchange of vanadium only works in a low acidity solution, or a high acidity solution with fewer impurities. Compared to the other two methods, solvent extraction shows better selectivity and has the advantages of being sturdy in operation and being economically favorable [25]. Solvent extraction of vanadium from acid leach solutions have been studied and developed by many researchers [22–24]. According to the literature [26,27], D2EHPA (di-(2-ethylhexyl) phosphoric acid) is the most widely used extractant for its excellent performance in acidic solutions and ease in stripping. Unfortunately, this kind of extractant presents poor selectivity of V(IV) over Fe(III). To reduce the interference of Fe(III) on V(IV) extraction, Fe(III) is usually reduced to Fe(II) with a reductant. The reduction process is complex and Fe(II) will be re-oxidized to Fe(III) by air during the extraction. Amine-based extractants are found to be promising extractants to extract vanadium from solutions varying in acidity. It shows good performance on vanadium selectively over Mo, Co, Ni, Ca, and Fe [28]. However, there are few literatures focused on vanadium extraction from the acid leaching solution of stone coal characterized by high concentrations of impurities like Fe, Al, Mg, K, Na, Ca, P, and Si. Therefore, it is worth studying the extraction performance of amine extractant on vanadium separation from the acid leaching solution of stone coal.

It is well known that the higher the purity of the  $V_2O_5$  product, the more valuable it will be. However, limited attention was focused on the product. Ning [29] reported that vanadium precipitated as ammonium polyvanadate in acidic conditions in most plants of China and the purity of  $V_2O_5$  was lower than 98.5%, resulting in the lower value and the lower price of the product. Hence, it is necessary to improve the quality of the product.

In conclusion, there are several disadvantages in the current research of vanadium extraction such as long operation time, low vanadium recovery, high cost, and low purity of the product. In the bibliography, researchers usually focus on one of the above-mentioned factors and ignore others. It is necessary to comprehensively consider every factor. In this study an extraction process to recover vanadium from a low-grade stone coal with the characteristics of shorter process and lower acid consumption, as well as higher purity of product was developed.  $V_2O_5$  can be prepared from stone coal by means of several procedures including roasting, acid leaching, solvent extraction, and precipitation. Effects of roasting and leaching parameters on vanadium leaching efficiency, and extraction parameter changes on vanadium extraction efficiency, were investigated in detail.

## 2. Experimental

### 2.1. Materials and Apparatus

In this work stone coal was supplied by Teng-da Mining and Metallurgy Co. Ltd., Xianning, China. The ore samples were crushed and ground to less than 74  $\mu\text{m}$  account for 70%. Various chemical reagents, including  $\text{H}_2\text{SO}_4$ ,  $\text{CaF}_2$ ,  $\text{Ca}(\text{OH})_2$ , trioctylamine (TOA), tributyl phosphate (TBP), and sulfonated kerosene were used during the whole process.

Chemical compositions of stone coal were measured using X-ray fluorescence (XRF, Netherland PANalytical B.V., AXIOS, Almelo, The Netherlands). The mineralogical composition of the stone coal was identified by powder X-ray diffraction (D/MAX-RB, RIGAKU Corporation, Tokyo, Japan). The surface morphology of the raw stone coal and the corresponding EDS analysis were examined using a field emission scanning electron microscope (ULTRA PLUS-43-13, ZEISS, Oberkochen, Germany). The vanadium valence of raw stone coal and leaching solution were determined by the potentiometric titration method [30]. The ions' concentration in the aqueous solution were analyzed using inductively-coupled plasma optical emission spectroscopy (ICP-OES, Optima 4300DV, Perkin-Elmer, Waltham, MA, USA). The solution pH measurement was performed with a pH meter (Mettler Toledo S220, Greifensee, Switzerland).

### 2.2. Procedure

#### 2.2.1. Roasting of Stone Coal

A ceramic crucible containing 50 g of raw stone coal was placed in the muffle furnace and roasted for a certain period at a preset temperature. After roasting, the crucible was rapidly taken out of the furnace and cooled to room temperature with free access to air.

#### 2.2.2. Leaching of Vanadium

The leaching experiments were carried out in a magnetic stirrer equipped with water bath heating. In each leaching experiment, 20 g of the roasted samples and  $\text{H}_2\text{SO}_4$  solution (L/S = 2:1, except for L/S ratio experiments) were stirred (1000 rpm) in a 250 mL Florence flask immersed in a water bath for a selected time. After leaching, the leach slurry was filtered and washed for a selected duration.

#### 2.2.3. Solvent Extraction and Stripping of Vanadium

The leaching solution was adjusted to the desired pH value by 2 mol/L  $\text{H}_2\text{SO}_4$  and 200 g/L  $\text{Ca}(\text{OH})_2$  before the solvent extraction. After pH adjustment, the system was filtered and the feed solution for solvent extraction was obtained. TOA was acidified by 1 mol/L  $\text{H}_2\text{SO}_4$  (volume ratio = 1:1) before use. Tributyl phosphate (TBP) was used as a phase modifier at a fixed concentration of 5% (vol) and sulfonated kerosene as a diluent. Solvent extraction and stripping experiments were carried out by magnetic stirring (600 rpm) the organic and aqueous phases at selected phase ratios in 250 mL conical flasks at 25  $^\circ\text{C}$  for a certain time. After the phase disengagement, the organic and aqueous phases were separated using separating funnels. The concentration of ions remain in aqueous solutions (raffinate) were analyzed with ICP-OES and that in the organic phase were calculated by mass balance.

#### 2.2.4. Precipitation and Thermal Decomposition

The pH of the stripped solution was adjusted to 8.0 by  $\text{H}_2\text{SO}_4$  solution, then twice the theoretical amount of  $\text{NH}_4\text{Cl}$  was added and the solution was stirred for 10 h at ambient temperature. Vanadium in the solution was gradually precipitated as ammonium vanadate. After solid-liquid separation, the precipitate was washed by  $\text{NH}_4\text{Cl}$  solution and dried in an oven. Finally, the precipitate was roasted for 2 h at 550  $^\circ\text{C}$  in the furnace to prepare  $\text{V}_2\text{O}_5$ .

### 3. Results and Discussion

#### 3.1. Characterization of Raw Stone Coal

Chemical compositions of stone coal were shown in Table 1, the content of  $V_2O_5$  in the raw ore was 0.71%, indicating the raw ore is low-grade vanadium-bearing ore. The XRD (X-ray diffraction) pattern of raw ore (Figure 1) revealed that the main mineral compositions were quartz, pyrite, calcite, and muscovite. Figure 2 showed the SEM (scanning electron microscope) image of the raw stone coal and the corresponding EDS (energy-dispersive X-ray spectroscopy) analysis of the sample were listed in Table 2. As can be seen in Figure 2, the particles of the raw ore present as irregular in shape, and the EDS analysis indicated that the main minerals like quartz, pyrite, calcite and muscovite were intertextured together and vanadium mainly existed in the mica structure. The analysis of vanadium valence of the raw ore showed that the vanadium contents of V(III) and V(IV) were 62.5% and 37.5%, respectively, and V(V) was not found. Due to the similar characteristics of electronegativity and ionic radius, V(III) in stone coal can replace the Mg(II) or Al(III) in the alumina oxygen octahedral structure of mica to form vanadium-contained muscovite  $K(Al,V)_2[Si_3AlO_{10}](OH)_2$  [4]. Hence, the raw stone coal is typically a refractory ore where vanadium is difficult to extract.

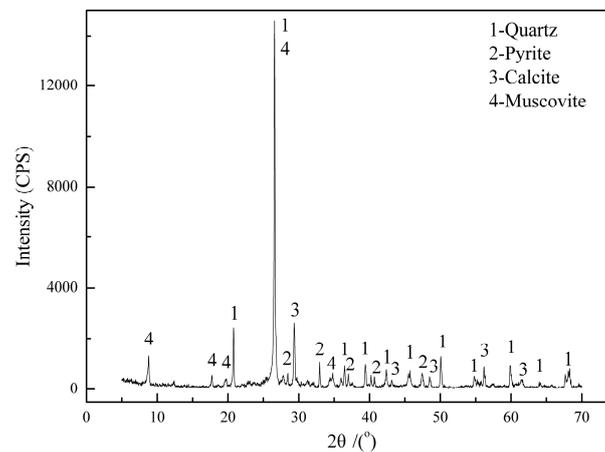


Figure 1. XRD (X-ray diffraction) patterns of raw stone coal.

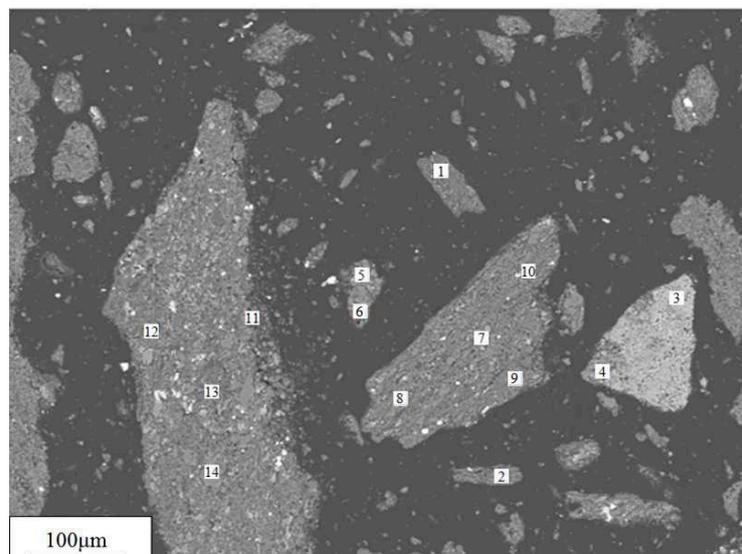


Figure 2. SEM image of raw stone coal.

**Table 1.** Chemical composition of raw stone coal wt %.

Composition	V <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	CaO	LOI
Content	0.71	4.99	49.28	8.91	2.18	3.02	0.38	4.35	6.26	17.82

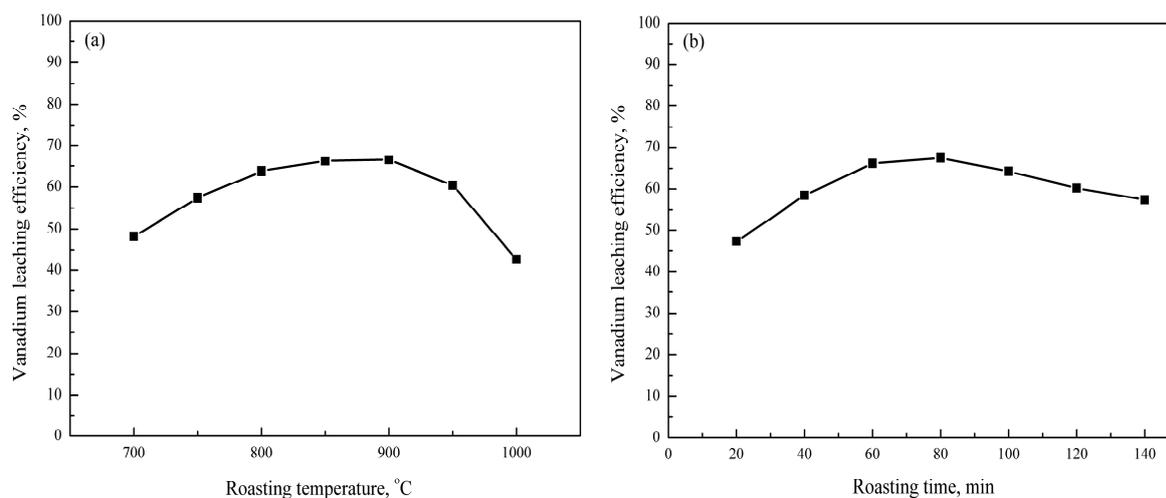
**Table 2.** EDS (energy-dispersive X-ray spectroscopy) analysis of the raw stone coal based on Figure 2 (wt %).

NO.	C	O	Mg	Al	Si	S	K	V	Fe	Ba	F	P	Ca
1	15.35	17.70	1.21	7.95	46.20	1.24	6.45	1.40	2.49				
2		27.76	0.47	8.53	51.28	0.53	8.55	0.62	0.95	1.30			
3	26.85	11.42			9.16	0.99					3.57	26.13	21.88
4	20.35	22.76		0.53	47.80	2.15	0.37		0.51			3.31	2.22
5	12.00	29.68	0.60	2.47	53.90	1.34							
6		13.68	1.30	7.67	55.78	8.66	5.64	1.48	0.81				
7		25.94	0.53	2.80	67.45	1.02	1.43		0.83				
8	9.45	8.91	1.47	2.58	18.36	23.27	1.16		34.81				
9		24.27		7.89	55.33	0.58	8.54			3.38			
10	11.43	23.22	0.91	4.18	56.16		2.89	0.49	0.71				
11	34.02	22.01	1.13	2.63	34.20	1.52	1.54	1.12	1.83				
12	6.60	15.67		7.89	34.13	14.39	8.23		9.02	4.07			
13		25.68	0.88	5.51	62.61	0.99	3.27		1.06				
14	8.96	34.29			56.75								

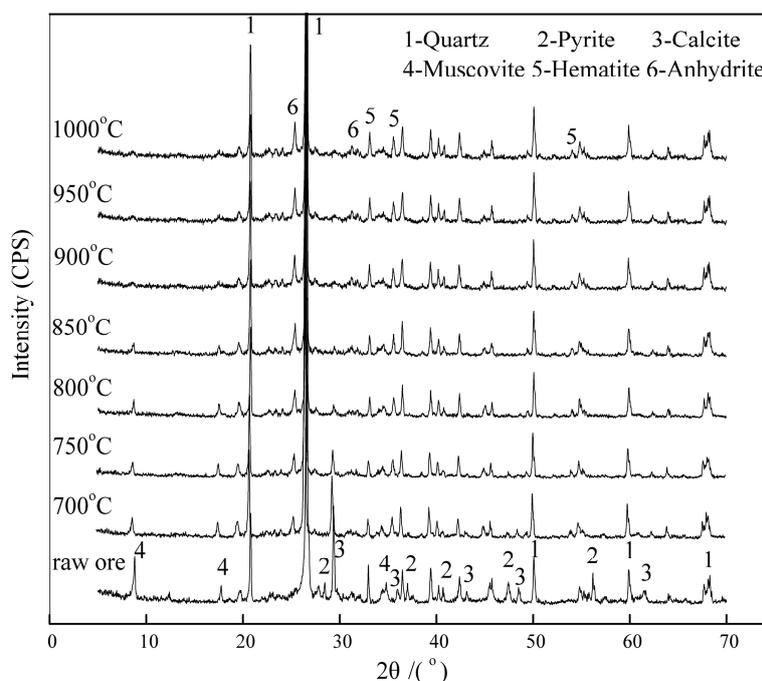
### 3.2. Effects of Roasting Conditions on Vanadium Leaching

In this study, vanadium in the ore is mainly fettered in the crystal structure of mica in the form of V(III) and, as the mica structure is very sturdy, it is difficult to extract vanadium by direct sulfuric acid leaching. Therefore, the purpose of roasting was to destroy the mica structure and remove carbonaceous and organic matter from the ore. In this process, the roasting efficiency was evaluated by leaching efficiency and the subsequent leaching experiments were performed under the following conditions: H<sub>2</sub>SO<sub>4</sub> concentration of 4 mol/L, liquid to solid ratio of 2:1 mL/g, leaching temperature of 95 °C, and leaching time of 6 h. With a roasting time of 60 min, the plot of leaching efficiency of vanadium vs. temperature is shown in Figure 3a. It was observed that the leaching efficiency of vanadium increased gradually with the increase of roasting temperature and reached a maximum value of 66.53% at 900 °C. However, with a further increase roasting temperature, the vanadium leaching efficiency began to decrease, which may be attributed to sintering of the sample and vanadium becoming enwrapped, according to the literature [4]. The comparison of XRD patterns of the raw ore and roasted samples are presented in Figure 4. It is clear from Figure 4 that, with the increase of roasting temperature, the mineral phase obviously changes, and the characteristic peaks of mica become weaker with the increase of roasting temperature. It is worth noting that the characteristic peaks of mica disappear at 900 °C, indicating a complete destruction of mica minerals.

To find the relation between vanadium leaching efficiency and roasting time, the reaction time was varied from 20 to 140 min, while keeping the roasting temperature of 900 °C. The experimental results are shown in Figure 3b. It is observed that vanadium leaching efficiency increases rapidly as the roasting time increased up to 60 min. A further increase in the roasting time would lead to a fall of vanadium leaching efficiency and this may also be attributable to sintering. Thus, the optimum roasting time was chosen as 60 min.



**Figure 3.** Effects of roasting conditions on vanadium leaching. (a) Roasting temperature; (b) roasting time.

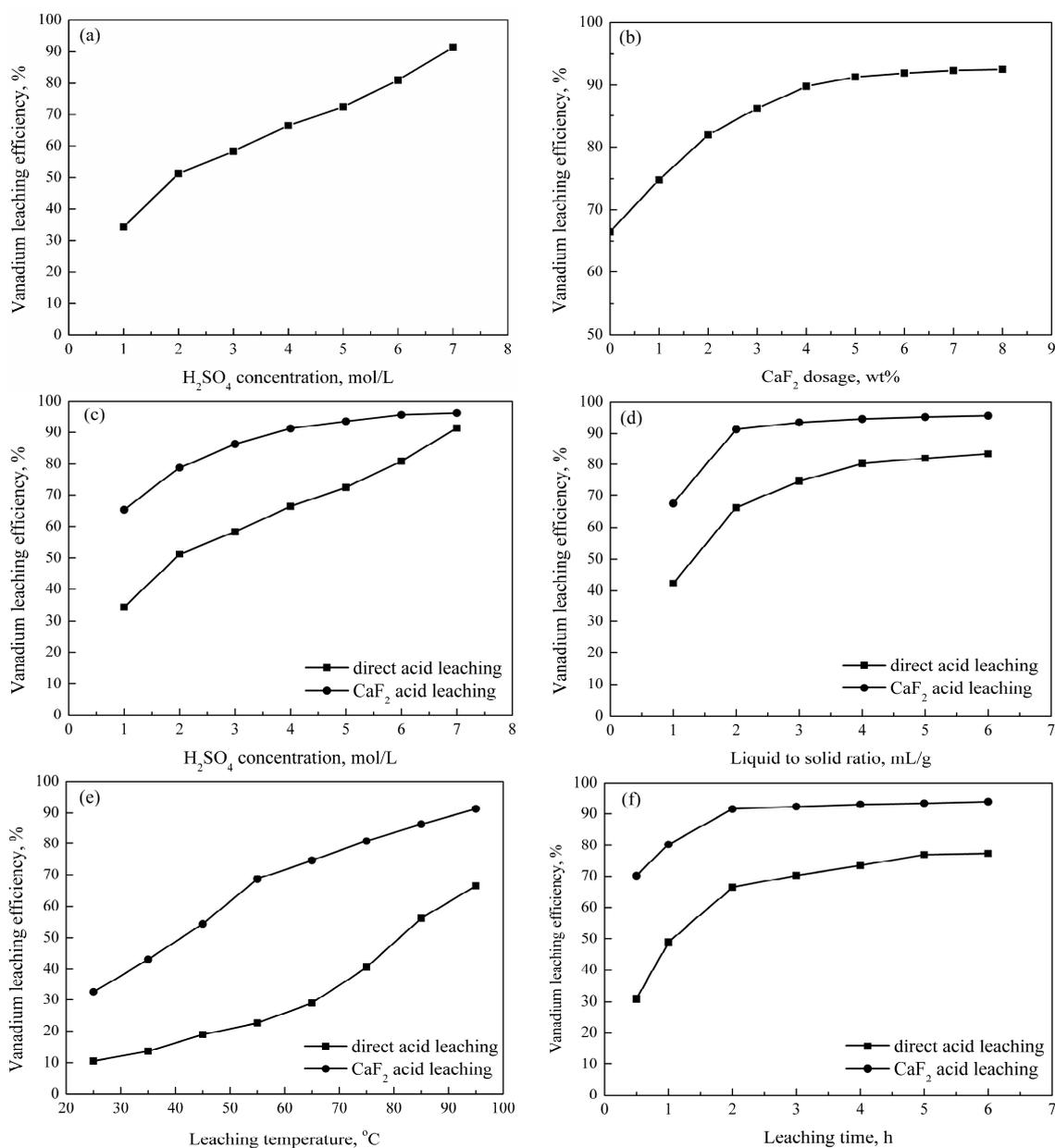


**Figure 4.** XRD patterns of raw ore and roasted samples under different roasting temperatures.

### 3.3. Sulfuric Acid Leaching of Roasted Stone Coal

Figure 5a shows the effects of  $\text{H}_2\text{SO}_4$  concentration on vanadium leaching at a liquid to solid ratio of 2 mL/g, leaching temperature of 95 °C, and leaching time of 2 h. Leaching efficiency is 34.5% at  $\text{H}_2\text{SO}_4$  concentration of 1 mol/L, while it is 90.19% at an  $\text{H}_2\text{SO}_4$  concentration of 7 mol/L. It can be noticed that leaching efficiency was relatively low under a low  $\text{H}_2\text{SO}_4$  concentration. For example, the leaching efficiency was only 66.53% when the  $\text{H}_2\text{SO}_4$  concentration was 4 mol/L. Thus, it is necessary to add leaching additives during the leaching process. Among all of the additives used in the literature, fluoric additives revealed better performance because fluoric additives could react with sulfuric acid and generate HF which could react with silicon and destroy the aluminosilicate minerals' crystal structure [31]. Concerning the lower causticity and toxicity, as well as lower price and commercial production,  $\text{CaF}_2$  was added as a leaching additive to the leaching system. The influence of  $\text{CaF}_2$

dosage on vanadium leaching efficiency is shown in Figure 5b. From Figure 5b, it is observed that the leaching efficiency of vanadium increased greatly with the increase of  $\text{CaF}_2$  dosage. When the dosage of  $\text{CaF}_2$  increased to 5%, vanadium leaching efficiency significantly increased to 91.23%.



**Figure 5.** Effect of leaching parameters on vanadium leaching efficiency. (a) Effect of sulfuric acid concentration on vanadium leaching efficiency without  $\text{CaF}_2$  addition; (b) effect of  $\text{CaF}_2$  dosage on vanadium leaching efficiency; (c) effect of sulfuric acid concentration on vanadium leaching efficiency with and without  $\text{CaF}_2$  addition; (d) effect of liquid to solid ratio on vanadium leaching efficiency with and without  $\text{CaF}_2$  addition; (e) effect of leaching temperature on vanadium leaching efficiency with and without  $\text{CaF}_2$  addition; (f) effect of leaching time on vanadium leaching efficiency with and without  $\text{CaF}_2$  addition.

Figure 5c compared the leaching results between direct acid leaching and  $\text{CaF}_2$  acid leaching under different  $\text{H}_2\text{SO}_4$  concentrations. From Figure 5c, we can see that vanadium leaching efficiency increases with the initial concentration of sulfuric acid. When 5% of  $\text{CaF}_2$  was added, vanadium

leaching efficiency increased significantly under the same initial concentration of sulfuric acid, and the lower the initial concentration of sulfuric acid, the more obvious was the increase. Figure 5d summarizes the changes in leaching efficiency with the change of liquid to solid ratio at H<sub>2</sub>SO<sub>4</sub> concentration of 4 mol/L, leaching temperature of 95 °C, and leaching time of 2 h. In both leaching processes, vanadium leaching efficiency increases with a lower liquid to solid ratio, and the increase in the liquid to solid ratio shows little effect on vanadium leaching. It can be concluded that, under the premise of better leaching efficiency, CaF<sub>2</sub> cannot only decrease the necessary ratio of liquid to solid, but also increases the concentration of vanadium in the leaching solution. Effects of leaching temperature on leaching efficiency are shown in Figure 5e. Leaching temperature has a significant effect on the vanadium leaching result. Under lower temperature (25–55 °C), the leaching efficiency of vanadium has a slow growth with the increase of temperature in both leaching processes. When the temperature is higher than 55 °C, vanadium leaching efficiency increases rapidly with the increase of leaching temperature. Figure 5f shows the effect of leaching time on leaching efficiency. Leaching efficiency increases significantly with prolonged leaching time, and this growth gradually becomes smooth. Furthermore, the leaching equilibrium time shortened from 4 to 2 h after the addition of CaF<sub>2</sub>.

The above results clearly demonstrate that H<sub>2</sub>SO<sub>4</sub> concentration, liquid to solid ratio, leaching temperature, and leaching time significantly affect the leaching efficiency of vanadium in the leaching procedure. CaF<sub>2</sub> not only improves vanadium leaching efficiency significantly, but also greatly reduces the consumption of sulfuric acid, reaction time and, eventually, reduces the energy consumption. Hence, the optimum leaching parameters was chosen as: CaF<sub>2</sub> dosage of 5%, H<sub>2</sub>SO<sub>4</sub> concentration of 4 mol/L, liquid-to-solid ratio of 2 mL/g, leaching temperature of 95 °C, and leaching time of 2 h.

#### 3.4. Solvent Extraction of Vanadium from Acid Leaching Solution

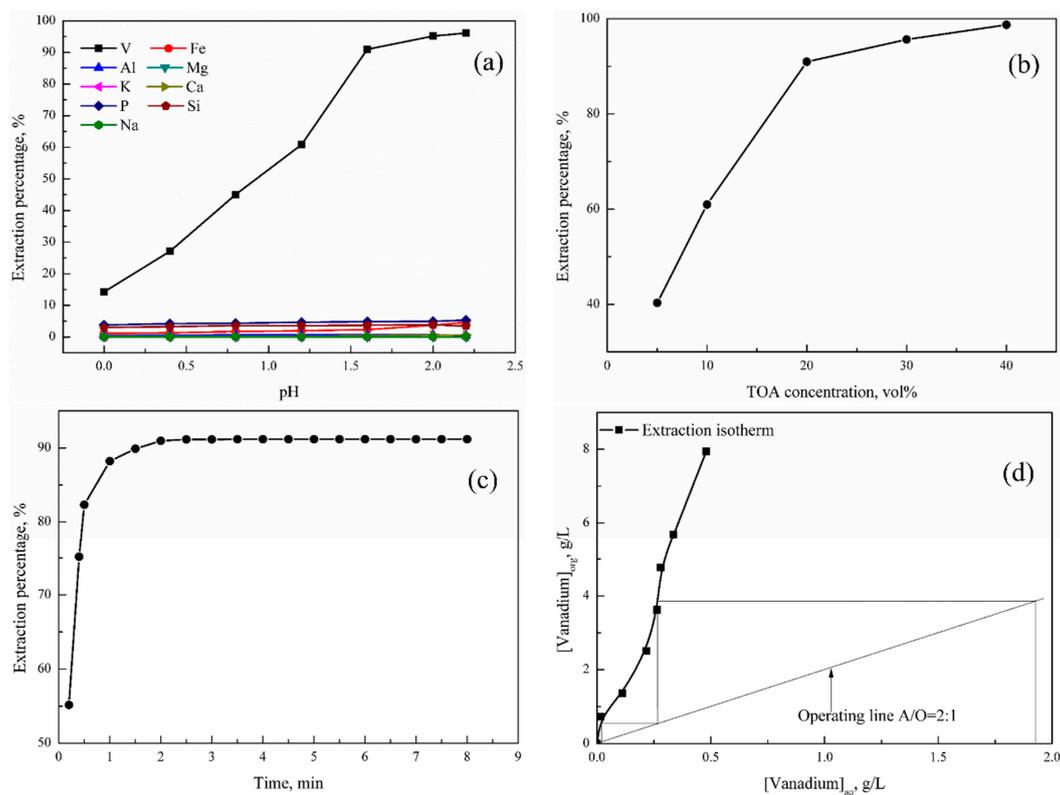
After leaching under the above-mentioned optimum leaching conditions, the leaching solution was obtained and the main composition was listed in Table 3. It can be seen from Table 3 that there was a high concentration of impurity ions in solution due to the poor selectivity of acid leaching. It is necessary to separate vanadium and impurities from the leaching solution before vanadium precipitation.

**Table 3.** Composition of the leaching solution (g/L).

Items	V	Fe	Al	Mg	K	Ca	P	Si
Concentration (g/L)	1.89	3.88	12.74	3.46	3.08	0.65	1.07	0.38

The analysis of vanadium valence showed 63% of V(IV) and 37% of V(V) in the leaching solution. V(IV) in the leaching solution was firstly oxidized to V(V) by NaClO<sub>3</sub> at twice the theoretical amount because the amine extractant is favorable to extracting V(V) than V(IV). A series of experiments were performed to determine the optimum extraction conditions and the influences of operating parameters on extraction efficiency are presented in Figure 6.

The effect of the initial solution pH on the extraction of vanadium is shown in Figure 6a with an organic phase composition of 20% (vol) TOA and 5% (vol) TBP, A/O phase ratio of 2, and extraction time of 2 min. The results showed that pH had a great effect on vanadium extraction as the extraction efficiency increased from 16% to 93% when the pH increased from 0.0 to 1.6. On the other hand, impurity ions showed an extremely low extraction ratio. The extraction ratio of Fe, P and Si varied from 3% to 5% with the pH changed while the extraction of Al, Mg, K, Ca and Na was null. This results demonstrated the chosed extractant TOA had good selectivity of vanadium over impurities. Nevertheless, when the initial pH was higher than 2.0, emulsifying phenomenon appeared and would influence the operation of the extraction process greatly. Hence, the optimal solution pH was determined to be 1.6.



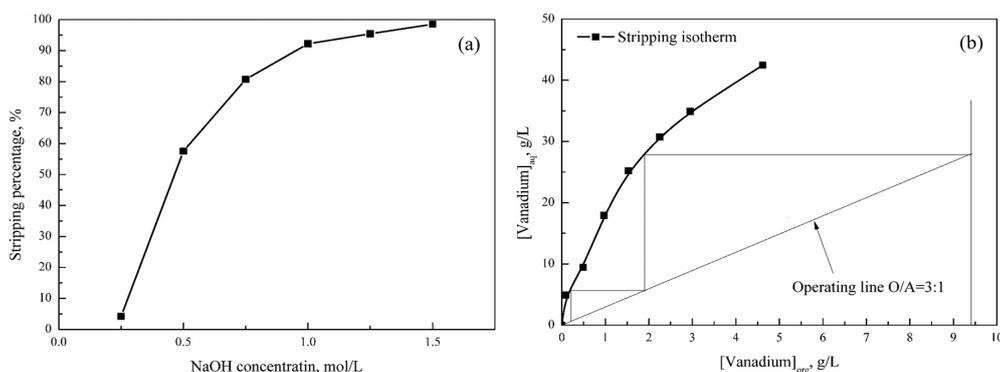
**Figure 6.** Effects of extraction conditions on the vanadium extraction percentage. (a) Effect of pH on vanadium and other ions extraction; (b) effect of TOA concentration on vanadium extraction; (c) effect of reaction time on vanadium extraction; (d) vanadium extraction distribution isotherms.

Under the conditions of a solution pH of 1.6, A/O phase ratio of 2, and extraction time of 2 min, the effect of TOA concentration on vanadium extraction was performed at different TOA concentrations (vol) from 5% to 40%. It can be observed from Figure 6b that the vanadium extraction efficiency increased from 41% to 92% as TOA concentration in the organic phase increased from 5% to 20%, which indicated that the concentration of TOA influenced vanadium extraction greatly. However, with a further increase of TOA concentration from 20% to 40%, the extraction of vanadium increased only 5%. Additionally, the viscosity of the organic phase increased when the TOA concentration increased from 20% to 40%. The higher viscosity of the organic phase made it more difficult for the organic phase to be mixed with aqueous solutions and more time-consuming to reach equilibrium. Therefore, the optimum concentration of TOA was chosen as 20%.

To determine the effect of extraction time on vanadium extraction, the experiments were performed under the conditions of initial pH of 1.6, A/O phase ratio of 2, and TOA concentration of 20%. It can be seen from Figure 6c that vanadium extraction increased from 55% to 92% as the extraction time increased from 10 s to 2 min. When the extraction time was longer than 2 min, vanadium extraction efficiency was almost constant with the extraction time increase.

For better understanding of the extraction process, the vanadium extraction experiments were performed at different phase ratios (A/O) and vanadium extraction distribution isotherms are shown in Figure 6d using phase variation data. It can be seen from Figure 6d that two stages are required, theoretically leaving approximately 0.03 g/L vanadium in the raffinate at an A/O ratio of 2. A three-stage countercurrent extraction was conducted, as an additional stage is usually needed in the actual operation. The vanadium concentration in raffinate was only 0.017 g/L, indicating vanadium extraction efficiency was 99.10%.

The vanadium-loaded organic phases were stripped using NaOH solution for its high stripping efficiency. The results (Figure 7a) show that stripping efficiency of vanadium increased from 3.75% to 98.75%, while the NaOH concentration increased from 0.25 to 1.5 mol/L under the conditions of stripping time of 2 min and O/A phase ratio of 2. However, free NaOH in the stripped solution is not desirable because more H<sub>2</sub>SO<sub>4</sub> will be consumed for the subsequent neutralization. For this study, 1.0 mol/L NaOH was chosen as optimum.



**Figure 7.** Effects of stripping conditions on vanadium stripping. (a) Effect of NaOH concentration on vanadium stripping; (b) vanadium stripping distribution isotherms.

To determine the stripping isotherms, the vanadium-loaded organic phases were stripped with different phase ratios (O/A) while keeping the total phase volume constant. The stripping isotherms plot (Figure 7b) shows that two theoretical stripping stages are needed for complete vanadium stripping at an O/A phase ratio of 3. After the three-stage countercurrent stripping, the stripped solution was collected and analyzed and the results are listed in Table 4. The stripped solution contained 25.64 g/L vanadium, indicating vanadium stripping efficiency achieved 98.66%.

**Table 4.** Composition of stripped solution.

Solution	V	Fe	Al	Mg	P	Si
Stripped solution (g/L)	25.64	0.011	0.008	0.006	0.087	0.032
Purified solution (g/L)	25.32	0.002	0.001	0.001	0.011	0.008

### 3.5. Preparation of V<sub>2</sub>O<sub>5</sub>

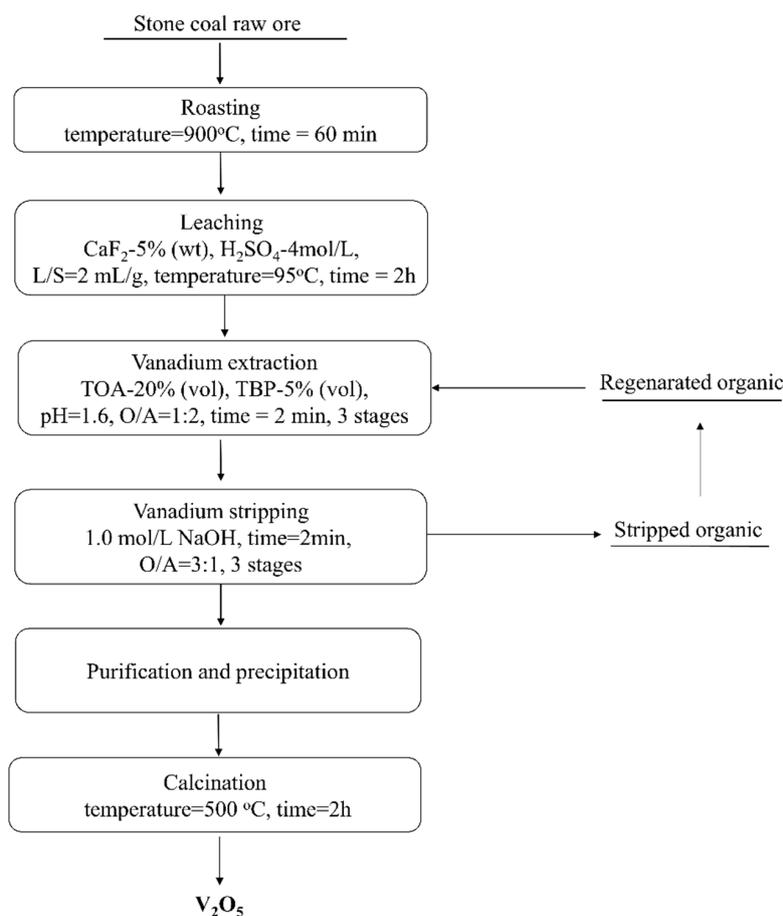
After enrichment, the average vanadium concentration in the stripped liquor reached approximately 25.64 g/L, which is shown in Table 4. From Table 4, it can be seen that impurities P and Si were extracted along with the vanadium and then followed into the stripped solution. It was reported that the concentration of P and Si should be below 20 mg/L to precipitate a high-purity product of vanadium [32]. In alkaline solution, P and Si mainly present as PO<sub>4</sub><sup>3-</sup> and SiO<sub>3</sub><sup>2-</sup> and could be precipitated with Mg<sup>2+</sup> as Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and MgSiO<sub>3</sub>, respectively. To remove the impurities, the pH of the stripped solution was adjusted to 9.0, then five times the theoretical MgCl<sub>2</sub> solution was added, as it usually requires an excess amount of Mg<sup>2+</sup> at 80 °C under stirring for 2 h to remove P and Si [33]. The purification results are listed in Table 4. Table 4 shows that the impurities were almost removed from the vanadium solution after purification. Twice the theoretical amount of NH<sub>4</sub>Cl was added into the purified solution to precipitate ammonium meta-vanadate at pH about 8.0 and at ambient temperature for 10 h. The precipitate was filtered and dried before being roasted in a muffle furnace at 500 °C for 2 h to obtain V<sub>2</sub>O<sub>5</sub>. The chemical composition of the V<sub>2</sub>O<sub>5</sub> product is shown in Table 5 and compared with related Chinese Industry Standards (YB/T5304-2011) [34]. The V<sub>2</sub>O<sub>5</sub> purity reached 99.75%, and the impurities were in trace amounts, meeting the standard specification.

**Table 5.** Chemical composition of vanadium pentoxide.

Component (%)	V <sub>2</sub> O <sub>5</sub>	Si	Fe	P	S	As	K <sub>2</sub> O + Na <sub>2</sub> O
V <sub>2</sub> O <sub>5</sub> Product in This Study	99.75	0.026	nill	0.009	0.006	nill	0.012
YB/T5304-2011 V <sub>2</sub> O <sub>5</sub> 99	≥99.0	≤0.20	≤0.20	≤0.03	≤0.01	≤0.01	≤1.0

### 3.6. Establishment of Process Flow Sheet for Vanadium Extraction

Based on the above study, a process flow sheet was established for extracting vanadium from stone coal (Figure 8). In this flow sheet, the vanadium product can be obtained by roasting-acid leaching-solvent extraction-purification and precipitation. After roasting at a temperature of 900 °C for 60 min and leaching under conditions of CaF<sub>2</sub> dosage of 5%, H<sub>2</sub>SO<sub>4</sub> concentration of 4 mol/L, liquid-to-solid ratio of 2 mL/g, leaching temperature of 95 °C, and leaching time of 2 h, 91.23% of vanadium can be leached. Through three stages of countercurrent extraction and three-stage countercurrent stripping, the vanadium concentration of the stripped solution could be raised to 25.64 g/L given an extraction and stripping yield of 99.10% and 98.66%, respectively. After adding MgCl<sub>2</sub> to the stripped solution at a pH of 9.0, P and Si can be removed and the solution was purified. Vanadium could be crystallized as ammonium metavanadate at ambient temperature and a pH of 8.0 with the addition of twice the theoretical amount of NH<sub>4</sub>Cl to the purified solution. The V<sub>2</sub>O<sub>5</sub> product with a purity of 99.75% is obtained after roasting at 550 °C for 2 h. The recovery of vanadium during the whole process was above 88%. This process has advantages of short operation time, high vanadium extraction efficiency, and a high purity of the product.

**Figure 8.** Vanadium recovery process flow sheet.

#### 4. Conclusions

It is feasible to recover vanadium from refractory stone coal with high recovery efficiency by an appropriate combination of pyrometallurgical and hydrometallurgical processes, including roasting, acid leaching, solvent extraction, purification, and precipitation. The optimum parameters established for roasting and vanadium leaching were: roasting temperature of 900 °C, roasting time of 60 min, CaF<sub>2</sub> dosage of 5%, H<sub>2</sub>SO<sub>4</sub> concentration of 4 mol/L, liquid-to-solid ratio of 2 mL/g, leaching temperature of 95 °C, and leaching time of 2 h. Under these conditions, more than 90% of vanadium in the raw ore can be leached out. Vanadium was selectively separated from the liquor using 20% TOA at pH 1.6 and stripped with 1 mol/L NaOH solution; the solvent extraction and stripping efficiencies are 99.10% and 98.66%, respectively. The product of vanadium pentoxide has a high purity 99.75%. This process has the advantages of shortening the process, simplifying operation, higher recovery efficiency of vanadium, and better adaptability to refractory raw ore.

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