

Article

An Environment-Friendly Process Featuring Calcified Roasting and Precipitation Purification to Prepare Vanadium Pentoxide from the Converter Vanadium Slag

Juhua Zhang^{1,2,3,*} , Wei Zhang^{1,2,3} and Zhengliang Xue^{1,2,3}

¹ The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China; wei_zhang@wust.edu.cn (W.Z.); xuezhengliang@wust.edu.cn (Z.X.)

² Key Laboratory for Ferrous Metallurgy and Resource Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan 430081, China

³ Hubei Provincial Key Laboratory for New Processes of Ironmaking and Steelmaking, Wuhan University of Science and Technology, Wuhan 430081, China

* Correspondence: Judyzjh@hotmail.com

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Abstract: Converter vanadium slag is a byproduct of the iron making process when the vanadium titanomagnetite is used as iron raw material. A cleaner process including calcified roasting, dilute acid leaching, precipitation purification, vanadium precipitation with ammonium salt, followed by thermal decomposition was proposed to extract vanadium resource from this slag. And then vanadium pentoxide with purity over 98% was prepared, which can be used as additives for high strength low alloy steel production. A total vanadium recovery beyond 80% was achieved in this whole process. Since no sodium and potassium salt was introduced, wastewater generated was closed-circulating after removing the enriched impurities of P, Si, Ti and Cr with adding powder CaO. The content of V₂O₅ in residues after vanadium extraction was lower than 1.2 wt.%, while other valuable metals like Fe, Mn, Cr and Ti were concentrated. With no alkaline metal salts added in this process, the metal resources of Fe, Mn, Cr and Ti in the residues were more feasible to be recovered with pyrometallurgy processes.

Keywords: converter vanadium slag; calcified roasting; dilute acid leaching; chemical precipitation purification; cleaner process

1. Introduction

As a very important material, vanadium is widely applied in the iron and steel industry, aviation and aerospace, chemical and pharmaceutical industry. About 85% of the total vanadium in the world was consumed for production of high-strength low alloy steel [1], and others were mainly used to produce alloy, catalyst and metallopharmaceuticals and so on [2,3]. Presently, the primary vanadium resources are converter vanadium slag, stone coal, steel slag and spent catalyst. The converter vanadium slag that is a by-product of vanadium titanomagnetite smelting process accounted for more than 50% of the world overall vanadium production and the content of V₂O₅ in this slag is usually 8–21 wt.%.

The conventional process of sodium salt roasting followed by water leaching for vanadium extraction from the vanadium slag is mature and operationally steady. However, it seriously pollutes the environment, and has difficulties in comprehensive utilization of the leaching residue and in the recycling of wastewater, which contains high concentration of sodium. Consequently, some novel

processes for cleaner vanadium extraction have been proposed, like roasting without adding salt [4], submolten salt extraction [5–7], alkali decomposition enhanced by electrochemistry [8], direct acid leaching [9–11], sulfating roasting [12] and calcified roasting followed by dilute acid leaching [13,14]. Vanadium extraction with calcium salt roasting is increasingly concerned these years due to its lower cost of roasting additive, no emission of polluttional gas, like HCl, Cl₂, SO₂ and SO₃, and no sodium contained in subsequent leaching residual and wastewater. Besides, the roasted vanadium slag with calcium is usually leached by dilute sulfuric acid with relatively higher selectivity for vanadium, and then a weakly acidic vanadium solution is obtained, which is beneficial to subsequent purification procedure [15]. The calcified roasting–dilute acid leaching process was first proposed and carried out by the Tula Vanadium Factory in 1974 [16]. Hereafter, Pangang Research Institute also made a lot of research on this process [17–21]. However, because the problem of purifying the acidic vanadium solution was still unsolved, the purity of vanadium pentoxide was only 93–94% and was inferior to the vanadium pentoxide prepared by the sodium roasting process. In this paper, a cleaner process including calcified roasting, dilute acid leaching, precipitation purification, vanadium precipitation with ammonium salt followed by thermal decomposition was proposed to extract vanadium resource from the converter vanadium slag, and this process was evaluated in respective of vanadium recovery, quality of the vanadium pentoxide product and its influence imposed on environment.

2. Materials

The chemicals used in this study (CaO, H₂SO₄, NH₄F, MnSO₄, (NH₄)₂S₂O₈ (NH₄)₂SO₄, H₂C₂O₄·2H₂O and ammonia water) were all of analytical grade (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China). Powder CaO was used as the additive for roasting vanadium slag and was dried in an oven at 120 °C for 24 h before use. Water used in experiments was deionized one time.

Vanadium slag was supplied by Sichuan Weiyuan Iron & Steel Co., Ltd., Chengdu, China (after magnetic separation). After screening, the slag with particle size within 48–75 μm was chosen for roasting experiments. Based on chemical composition analysis, it was found that this slag contained 14.3% V₂O₅, 14.3% SiO₂, 24.8% FeO, 2.3% metal iron, 9.9% CaO, 8.5% MnO, 7.4% TiO₂, 4.4% Cr₂O₃, 3.7% MgO, 2.1%Al₂O₃ and 0.22% P. The mass ratio of CaO to V₂O₅ is much larger than 0.22, indicating it belongs to grade 3 of FZ3 vanadium slag in China, and the vanadium recovery would be lower if it was treated by the conventional sodium roasting process due to the generation of undissolved calcium vanadate. Mineral phase composition of the slag was analyzed by X-ray diffraction (X'Pert Pro MPD, PANalytical B.V., Almelo, Netherlands) and it was found that the slag was mainly composed of vanadium spinel (Mn, Fe)(V, Cr)₂O₄, fayalite Fe₂SiO₄, augite Ca(Fe, Mg)Si₂O₆ and a small amount of magnesium titanium oxide Mg₂TiO₄. The SEM graph of this slag sample and the corresponding EDS microanalysis data for different areas (SSX-550, Shimadzu Corporation, Kyoto, Japan) were shown in Figure 1.

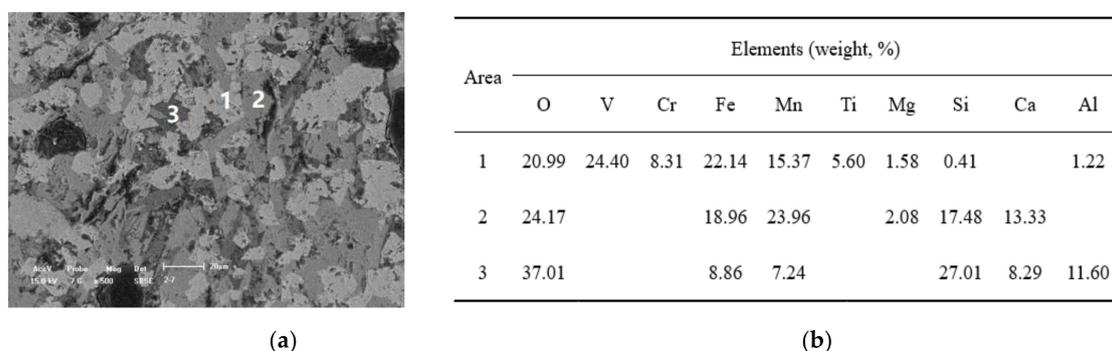


Figure 1. Scanning electron microscope and energy dispersive spectrometer (SEM-EDS) analysis for the converter vanadium slag (a) the scanning electron micrograph of the converter vanadium slag; (b) the energy dispersive spectrum analysis for different areas in Figure 1a.

Combining the chemical composition, phase composition with the scanning electron microscope and energy dispersive spectrometer (SEM-EDS) analysis of the raw vanadium slag, we knew that the main vanadium-bearing phase (white area in Figure 1) was vanadium spinel [(Mn, Fe) (V, Cr)₂O₄] which was wrapped by the matrix phases-fayalite (gray area) and augite (black area); the content of Si in augite was higher than that in fayalite; Fe was distributed as Fe²⁺ in spinel, fayalite and augite phases.

3. Experimental

The whole flow chart for treating the converter vanadium slag was displayed as Figure 2. Roasting experiments were carried out in a vertical tube furnace controlled by a Shinaden SR-53 temperature programmed instrument with molybdenum disilicide heating elements. Leaching, purification and vanadium precipitation were conducted in three-necked glass vessels centered in a thermostatic water bath (HH-4, China Changzhou Sino Instrument Co., LTD, Changzhou, China) and the pH values were measured by a pH-meter (Starter 3C). The operational parameters have been optimized in our previous studies [22–24].

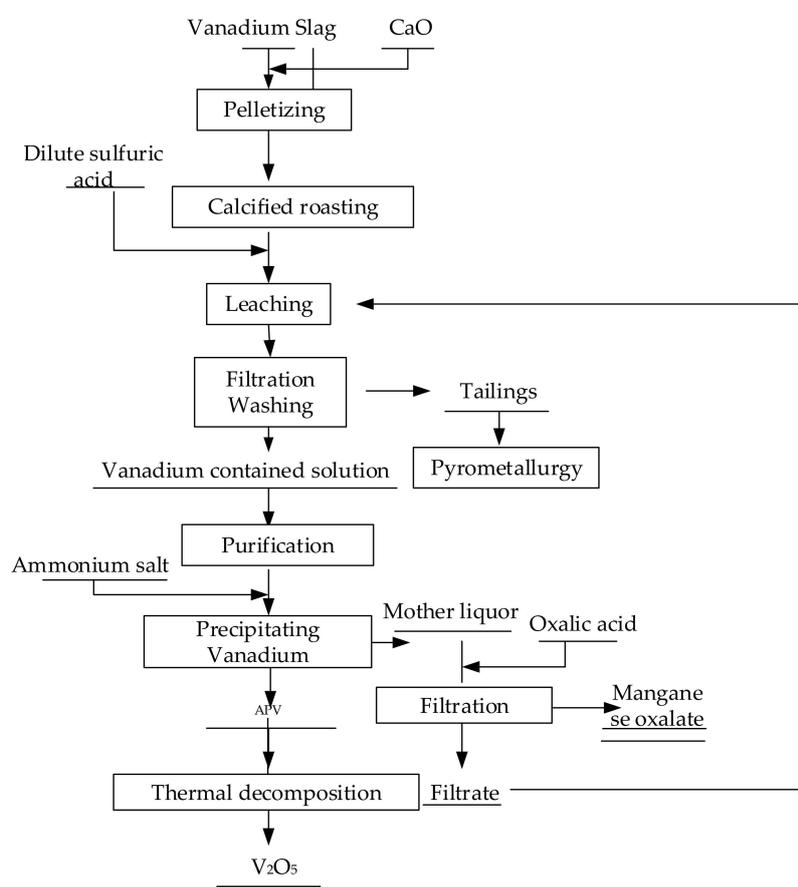


Figure 2. Flow chart for treating the converter vanadium slag.

The vanadium slag (48–75 μm) was mixed with additive of CaO at a mass ratio (CaO)/(V₂O₅) of 0.42 and prepared into ϕ 8–10 mm pellets. The pellets were heated to 850 °C at rate of 2 °C/min from room temperature and then held for 150 min. When the holding time was completed, the roasted pellets were quenched to room temperature and ground to fine powder. Roasting efficiency was expressed by vanadium recovery upon leaching, and the leaching conditions were liquid to solid ratio of 3:1, temperature of 55 °C, time of 30 min, pH of 2.5 and stirring speed of 500 rpm.

Because the lower selectivity of dilute acid leaching, some impurities of Ca, Mg, Si, Al, and Mn transferred into vanadium solution accompanying with V, and which in turn affected vanadium

precipitation rate and quality of final product. According to analyses for occurrence of impurities and vanadium in leaching solution, neutralization separation could be adopted to remove Si and Al, during which the solution pH value was adjusted to 4.5 ± 0.05 . Taking into consideration of decreasing the vanadium loss, Ca, Mg, Al and Si were removed simultaneously through adding a composite reagent of MnNH_3F_3 to precipitate Ca, Mg and adjusting the solution pH to remove Al and Si. The purification conditions were set as stirring speed of 200 rpm, reagent adding amount of 1.6 (molar ratio of $2n(\text{F})/n(\text{Ca} + \text{Mg})$), temperature of 50°C and time of 30 min. Besides, flocculant polyacrylamide and diatomaceous earth (DA-1) were used to improve sedimentation and filtration respectively during the purification process.

Mn in solution was not removed before vanadium precipitation step and ammonium salt was added to precipitate vanadium since this method can alleviate the side effect of Mn on the quality of final product compared with hydrolysis precipitation. Vanadium precipitation step was conducted at $\text{pH } 2.00 \pm 0.05$ and temperature of 95°C , ammonium sulfate was added at molar ratio $(\text{NH}_3)/(\text{V})$ of 1.5, and the reaction time was controlled in 120 min. Some Vanadium precipitation was heated at 550°C for 2 h and then saffron yellow powder of vanadium pentoxide was obtained. The vanadium precipitation and vanadium pentoxide were characterized by XRD (X'Pert Pro MPD, PANalytical B.V., Almelo, Netherlands), SEM-EDS (SSX-550, Shimadzu Corporation, Kyoto, Japan) and laser particle size analyzer (Mastersizer 2000, Malvern Panalytical, Malvern, UK).

4. Results

4.1. Roasting and Leaching

The XRD and SEM graphs for the roasted slag were shown in Figures 3 and 4. After roasting the fayalite and vanadium spinel phases were destroyed. V^{3+} and Fe^{2+} contained in the converter vanadium slag were oxidized into V^{5+} and Fe^{3+} . The mechanism of vanadium slag roasting with powder CaO has been reported in our previous studies [13,22]. Calcium vanadate and Fe_2O_3 were generated as illustrated by the light gray area (area 1) and white area (area 4) in Figure 3 respectively. Besides that, new silicate phases (area 2 and area 3) formed.

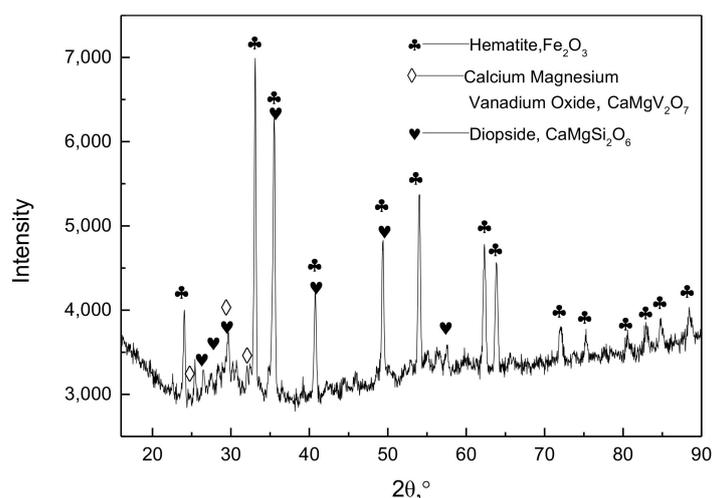


Figure 3. X-ray diffraction pattern for vanadium slag roasted at 850°C for 150 min.

The roasted slag was ground into a certain size range and screened for the subsequent leaching experiments. Compared with the conventional water leaching or alkaline leaching in the sodium roasting process, dilute acid leaching used in the calcified roasting process performs lower selectivity over the target element of vanadium. The effect of pH of leaching solution on leaching rate of V, Ca, Al, Mg, Si, P, Fe and Mn were shown in Figures 5 and 6.

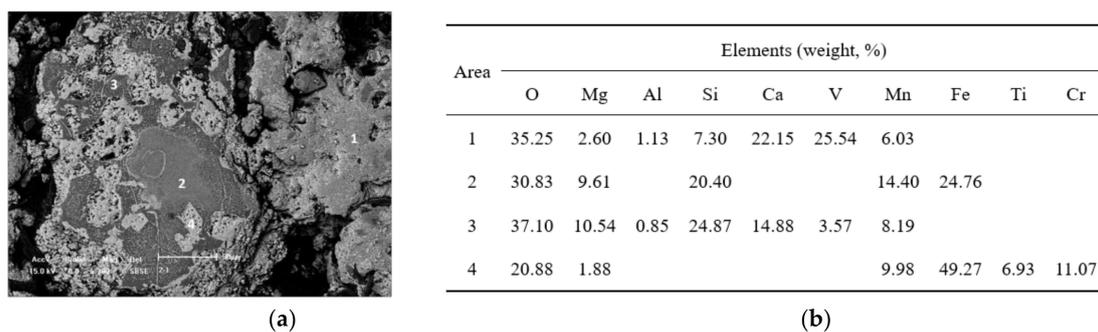


Figure 4. SEM-EDS analysis for the sample roasted at 850 °C for 150 min (a) the scanning electron micrograph of the roasted slag; (b) the energy dispersive spectrum analysis for different areas in Figure 4a.

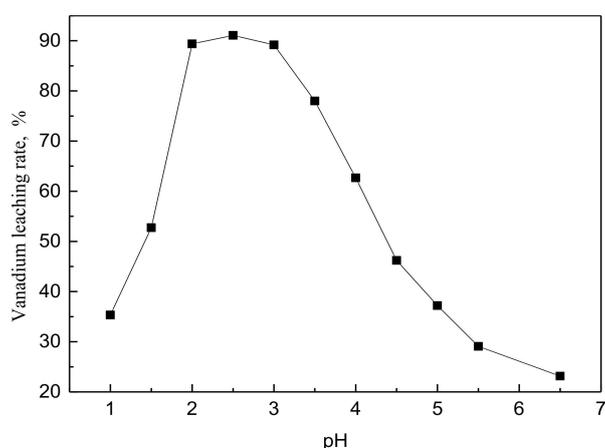


Figure 5. Effect of pH on the vanadium leaching rate (particle size of 75–96 μm , time of 60 min, $T = 65\text{ }^{\circ}\text{C}$, $L/S = 4$, stirring speed of 500 rpm).

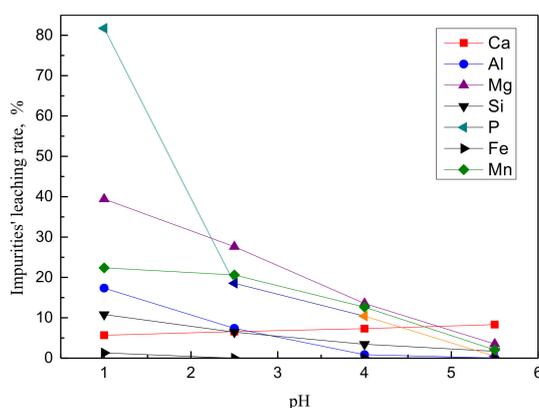


Figure 6. Effect of pH on the leaching rate of impurities (particle size of 75–96 μm , time of 60 min, $T = 65\text{ }^{\circ}\text{C}$, $L/S = 4$, stirring speed of 500 rpm).

It can be seen from the Figure 5 that the pH of leaching solution notably influences the recovery of vanadium. Increasing the acidity of the solution is beneficial to dissolution of calcium vanadate, but meanwhile, the concentration of SO_4^{2-} is increased as well, leading to more generation of insoluble calcium sulfate that will wrap the unreacted particle of roasted slag. Additionally, when the pH is lower than 2.0, vanadium in the solution is converted into insoluble vanadium oxides V_2O_5 [23]. Within the pH range of 2 to 3, a satisfactory vanadium recovery of 90% is achieved. From the Figure 6 we know that except Ca other impurities of Fe, Mn, Mg, Al, Si, P all transfer into the solution more as the pH decreases. The reason for the decrease of calcium leaching rate lies in the increase of SO_4^{2-}

as the acidity is improved. Since the leaching rate of Fe is lower over the whole pH range (pH 1–6) and its concentration is below $0.001 \text{ g}\cdot\text{L}^{-1}$, so the effect of Fe on the subsequent procedures is ignored. Combining the Figures 5 and 6, we found that when the most vanadium was extracted from the roasted slag, the impurities of Fe, Mn, Mg, Al, Si and P inevitably went into the solution.

Under the stated roasting and leaching conditions in the experimental section, the vanadium leaching rate was beyond 91%, and meanwhile 10–30% impurities of Ca, Mn, Mg, Al, Si, P were dissolved into the solution.

4.2. Purification of Vanadium-Bearing Solution

After roasting and leaching under optimized conditions, the obtained vanadium-bearing solution contained vanadium around 20 g/L which meets the requirements for vanadium concentration in the subsequent vanadium precipitation step. However, since the impurities contained in the solution will bring side effects on vanadium precipitation rate and quality of vanadium pentoxide, they have to be removed. In this study, a composite fluoride was used to remove Ca, Mn, Al and Si at constant pH of 4.50 ± 0.05 . This composite reagent was prepared through reaction between $\text{MnSO}_4\cdot\text{H}_2\text{O}$ and NH_4F for 20 min at molar ratio of 1/7 and temperature of $70 \text{ }^\circ\text{C}$ followed by filtration and washing several times to remove the free NH_4^+ and SO_4^{2-} . The white precipitate was then dried at $80 \text{ }^\circ\text{C}$ for 120 min for chemical analysis and characterization with XRD. It was found the mass ratio of F to Mn contained in this white powder was close to 1.0 and its XRD pattern was shown in Figure 7. It can be seen that the produced powder is mainly composed of $\text{Mn}(\text{NH}_4)\text{F}_3$, which is called as a composite reagent, and this composite reagent is represented by $\text{Mn}(\text{NH}_4)\text{F}_3$ to facilitate the calculation of adding amount.

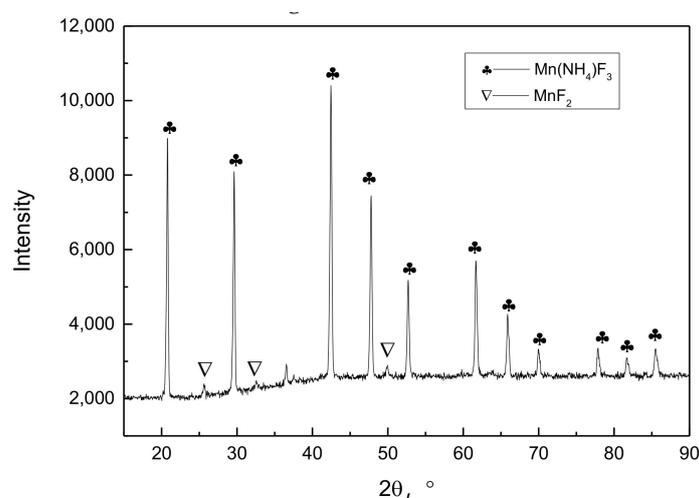


Figure 7. X-ray diffraction (XRD) pattern of the composite reagent for removing impurities.

Because F^- is feasible to react with Ca^{2+} and Mg^{2+} under weakly acidic conditions, producing CaF_2 and MgF_2 with smaller solubility product constants, Ca^{2+} and Mg^{2+} can be separated from the vanadium-bearing solution with the composite reagent. At the same time, as the solution pH value goes up after the composite reagent is added, impurities of Al^{3+} and Si^{4+} can be removed simultaneously due to hydrolysis. The composite reagent is slightly water-soluble, and the excess amount will be separated along with precipitation of Ca, Mg, Al and Si through filtration. With adding the composite fluoride of $\text{Mn}(\text{NH}_4)\text{F}_3$ the removal efficiencies for Ca, Mg and Al were all over 95% and for Si was 55%. In purification process some polyacrylamide and diatomite were also added to improve settleability and filtering quality of slurry. The loss of vanadium was lower than 5% during the whole purification. The concentrations of V and main impurities contained in vanadium-bearing solution before and after purification were given in Table 1.

Table 1. Concentrations of V and main impurities contained in the of vanadium-bearing solution ($\text{g}\cdot\text{L}^{-1}$).

Elements	V	Mn	Si	Al	Ca	Fe	Mg	Cr	Ti	P
Before Purification	21.4	5.99	1.49	0.20	1.02	0.010	1.59	0.010	0.0057	0.12
After Purification	19.8	10.1	0.88	0.009	0.033	0.009	0.079	0.010	0.004	0.089

4.3. Vanadium Precipitation with Ammonium Salt and Thermal Decomposition

After purification, the concentrations of Ca, Mg and Al decreased to 33, 79 and 9 $\text{mg}\cdot\text{L}^{-1}$ respectively, and only the concentration of Mn increased, which was caused by the reactions between $\text{Mn}(\text{NH}_4)\text{F}_3$ and Ca^{2+} , Mg^{2+} during the purification process. Vanadium was concentrated and precipitated with $(\text{NH}_4)_2\text{SO}_4$ from the purified solution at initial pH of 2.5, and precipitation efficiency was over 96%. Then the precipitation product was heated at 550 $^\circ\text{C}$ for 2 h, and saffron yellow vanadium pentoxide powder was produced. The XRD and SEM-EDS for product of vanadium precipitation were given in Figures 8 and 9, and the particle size distributions for the precipitation product and the vanadium pentoxide were shown in Figure 10. The chemical composition of the vanadium pentoxide product was presented in Table 2.

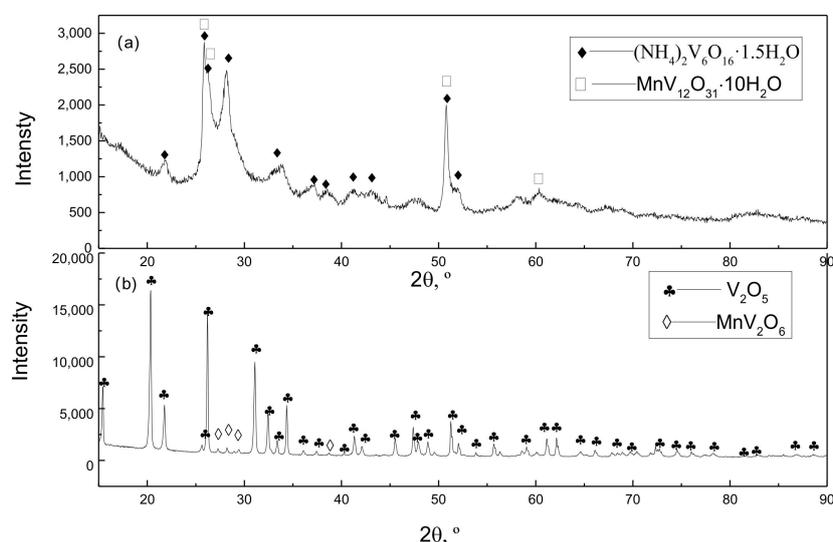


Figure 8. XRD pattern for products of vanadium precipitate (a) ammonium poly-vanadate; (b) vanadium pentoxide.

The precipitated product was hydrated hexamer of ammonium vanadate $(\text{NH}_4)_2\text{V}_6\text{O}_{16}\cdot 1.5\text{H}_2\text{O}$ existing in spherical and cylindrical structure with average particle diameter of 43.9 μm . The powder vanadium pentoxide was obtained after calcination of ammonium poly-vanadate $(\text{NH}_4)_2\text{V}_6\text{O}_{16}\cdot 1.5\text{H}_2\text{O}$ and it was present in cylindrical shape with average grain size of 1.25 μm . The main impurity in the product was manganese in occurrence of metavanadate (MnV_2O_6). According to chemical composition analysis, it was found that the obtained product met the national standard of 98 grade vanadium pentoxide (Chinese GB3283-87), which requires the impurities of Si, Fe, P, S, As and sum of Na_2O and K_2O are lower than 0.25%, 0.30%, 0.05%, 0.03%, 0.02%, 1.5% respectively.

Table 2. Chemical composition of the vanadium pentoxide product (wt. %).

V_2O_5	Mn	S	Si	Fe	Al	P	Ca	Na_2O	K_2O
98.63	0.85	0.011	0.031	0.012	0.011	0.016	0.007	-	0.011

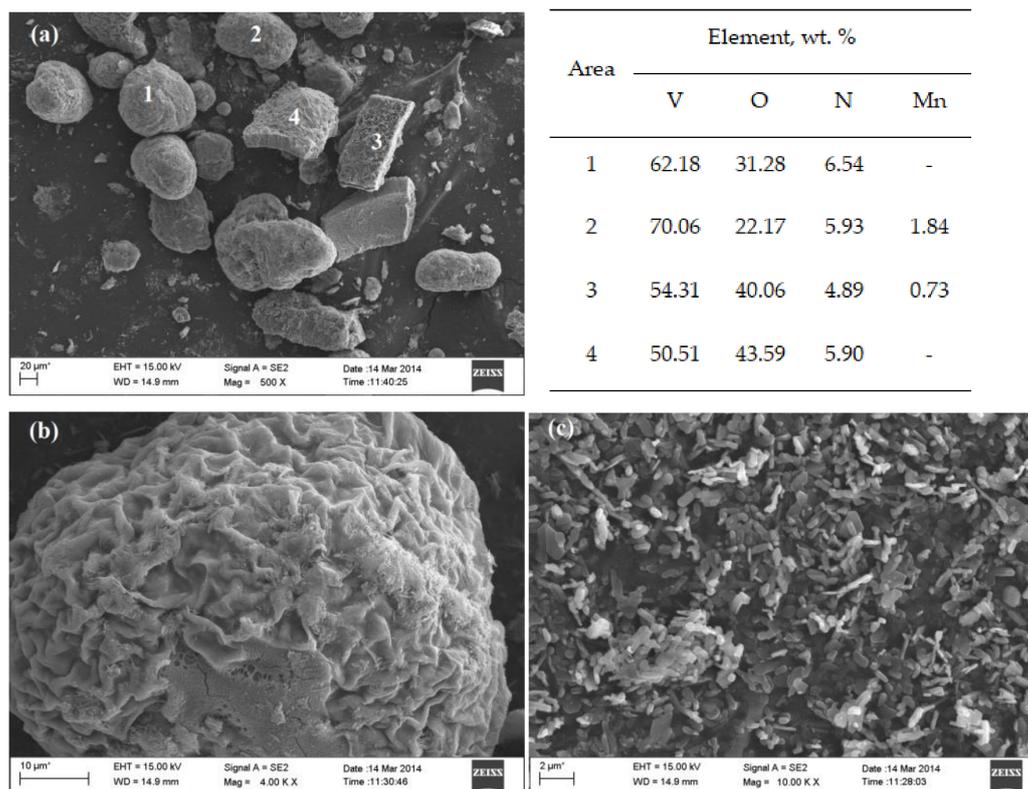


Figure 9. Scanning electron micrographs for ammonium poly-vanadate and vanadium pentoxide powder, (a) ammonium poly-vanadate $\times 500$; (b) ammonium poly-vanadate $\times 4,000$; (c) vanadium pentoxide powder $\times 10,000$.

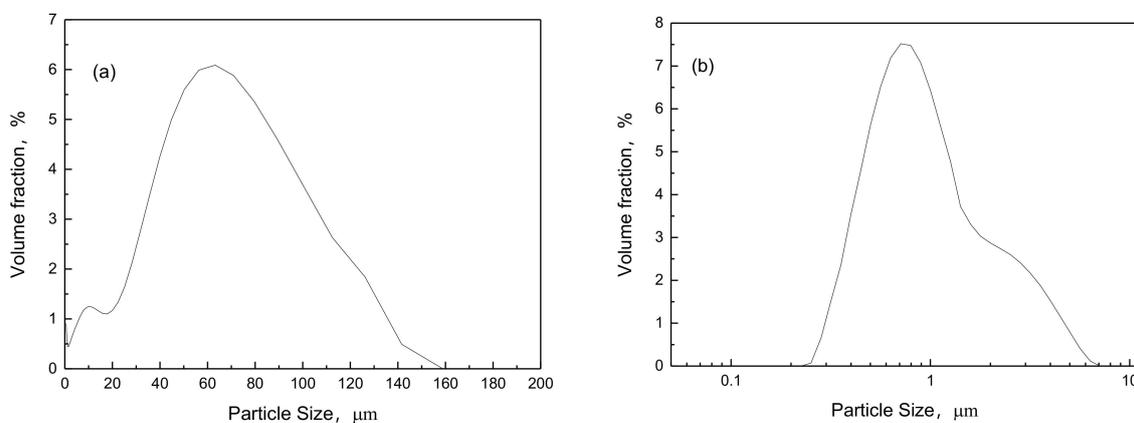


Figure 10. Particle size distribution for ammonium poly-vanadate and vanadium pentoxide (a) ammonium poly-vanadate; (b) vanadium pentoxide.

4.4. Wastewater and Tailings

In the purification procedure, Ca, Mg, Al and Si were removed but Mn was increased. After vanadium precipitation with ammonium sulfate salt, the main elements contained in the mother liquor were listed in Table 3.

It can be seen that the residual vanadium concentration is $0.69 \text{ g}\cdot\text{L}^{-1}$ and Mn is $9.82 \text{ g}\cdot\text{L}^{-1}$. If the mother liquor is circulated directly to the leaching step, the quality of vanadium pentoxide product will be lowered as the Mn is gradually enriched. Hence, Mn should be collected before recycle of the mother liquor. In this proposed process, Mn was recovered by oxalate precipitation method at pH of 4.0 and temperature of $55 \text{ }^\circ\text{C}$. When the oxalate was added at a molar ratio $(\text{H}_2\text{C}_2\text{O}_4)/(\text{Mn})$ of 1.5 and reaction

time was beyond 1 h, the recovery of Mn was over 94%. Based on the analysis of XRD and chemical composition, it was found that the precipitated manganese existed as MnC_2O_4 with purity of 98.6%.

Table 3. Concentrations of V and the main impurities contained in mother liquor after vanadium precipitation ($g \cdot L^{-1}$).

V	Mn	Ca	Mg	Al	Ti	Cr	P	Si
0.69	9.82	0.016	0.061	0.006	0.003	0.010	0.055	0.70

After the manganese was extracted, the mother liquor was reused to leach the roasted slag. In our study, the wastewater was recycled six times, and relationships between the number of recycle and the concentrations of impurities in the leaching solution were shown in Figure 11. Correspondingly, the effects of number of recycling mother liquor on the quality of vanadium pentoxide were shown in Table 4.

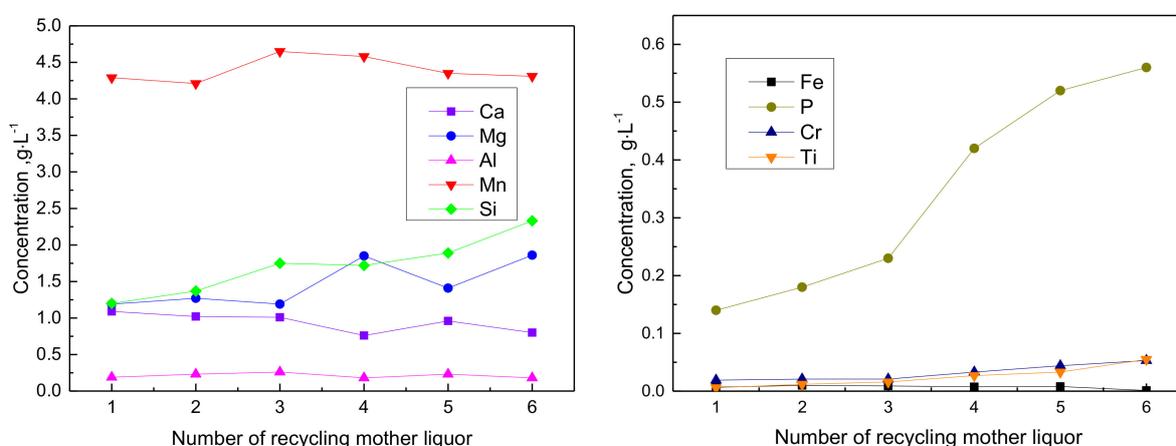


Figure 11. Relationships between concentrations of impurities and the number of recycling mother liquor (a) variation of the concentration of main impurities of Ca, Mg, Al, Mn and Si as the recycle increases; (b) variation of the concentration of the minor impurities of Fe, P, Cr and Ti as the recycle increases.

Table 4. Effect of the number of recycling mother liquor on the quality of final product (wt. %).

Number of Recycle	V_2O_5	Mn	Si	Cr	Ti	Fe	S	Al	P	Ca	Mg	K_2O
1	98.73	0.39	0.052	-	-	0.022	-	-	0.014	0.020	-	-
2	98.63	0.73	0.023	-	-	0.024	-	0.010	0.021	0.034	-	0.012
3	98.04	0.92	0.079	-	0.035	0.019	0.007	0.011	0.022	0.011	0.005	0.020
4	97.30	1.09	0.21	-	0.060	0.019	0.044	0.038	0.078	0.011	0.011	0.018
5	91.65	0.53	2.41	0.164	0.114	0.024	0.132	0.035	0.308	0.064	0.040	0.031
6	88.00	0.50	4.55	0.137	0.258	0.021	0.196	0.024	0.279	0.050	0.034	0.033

As shown in Figure 10, as the number of recycling mother liquor increases, the concentrations of main impurities, like Ca, Mg, Al and Mn, fluctuate slightly while Si increases gradually because only a portion of it is removed in purification operation every time. Meanwhile, the minority impurities such as Cr, Ti and P are enriched with an increase in circulations of mother liquor. The concentration of Fe is almost constant and lower than 0.010 g/L since the solubility of Fe is only related to the pH of leaching solution system. From Table 4, it was found the quality of vanadium pentoxide still meets the standard of grade 98 when the mother liquor is reused for three times. However, as the number of circulations is increased, the contents of Si and P in the product both go up. Meanwhile the minority impurities of Ti and Cr have little effect on the quality of vanadium pentoxide in the first two times of circulation, but as the mother liquor is circulated further, the increasing content of Ti and Cr also bring side effect to the grade of vanadium pentoxide. Hence, in order to realize closed recycle of the wastewater, the mother liquor has to be treated when the impurities is enriched to a certain extent. In this proposed process,

powder CaO was added to neutralize the solution and precipitate the enriched impurities like Si, P, Cr and Ti. When the pH was improved to 8.6, the stirring was stopped and then the solution was allowed to stand for 10 min. After analysis, it was found that the residual impurities were satisfactory, the concentration of Si lower than $75 \text{ mg}\cdot\text{L}^{-1}$ and P, Cr, Ti all lower than $3 \text{ mg}\cdot\text{L}^{-1}$, and this solution could be recycled to leach the roasted slag again.

The main chemical composition and XRD pattern for tailings produced in this process were shown in Table 5 and Figure 12.

Table 5. Chemical composition of tailings after vanadium extraction with calcified roasting-acid leaching (wt. %).

V ₂ O ₅	Fe ₂ O ₃	SiO ₂	CaO	MnO	TiO ₂	Cr ₂ O ₃	MgO	Al ₂ O ₃
1.20	33.24	10.97	15.91	6.45	7.08	4.70	2.33	1.54
P ₂ O ₅	SO ₃	Nb ₂ O ₅						
0.49	16.05	0.047						

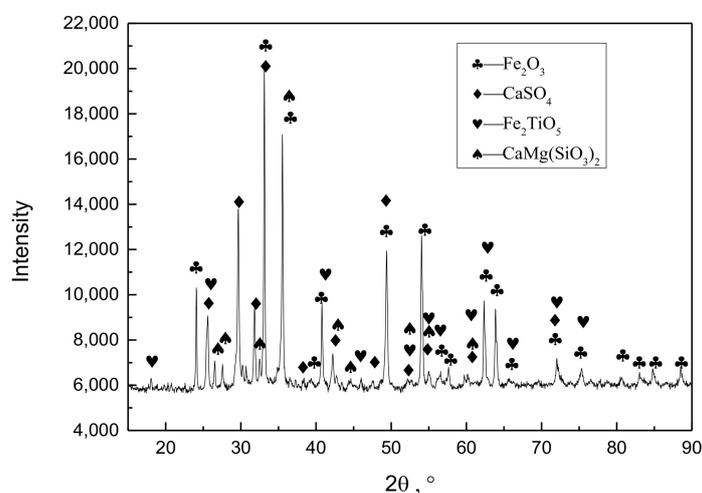


Figure 12. XRD pattern for tailings of vanadium extraction.

After vanadium extraction, the tailings contained 1.20% V₂O₅, which can also be recycled to roasting step at a certain ratio to lower the residual content of vanadium. As shown in Table 5 it was found that the tailings from this proposed process are rich in calcium and almost free of sodium, which is beneficial to recover other valuable metals like Fe, Cr, Mn and Ti with the traditional pyrometallurgical process since we know that high contents of sodium will bring serious damage to refractories.

5. Evaluation of the Proposed Process and Conclusions

The proposed process for vanadium pentoxide production in this paper mainly includes five operational steps of calcified roasting, dilute acid leaching, chemical precipitation purification, vanadium precipitation with ammonium salt, thermal decomposition and recycle of mother liquor.

Compared with the sodium roasting process widely used in vanadium pentoxide production industry, this process performs best in environmental protection and resource utilization. The traditional vanadium extraction process of sodium roasting followed by water leaching has strict requirements for calcium content in raw vanadium slag. If the content of CaO is increased by 1%, vanadium leaching rate will decrease by 4.7–9% due to the formation of water-insoluble vanadate during roasting. On the contrary, powder CaO is applied as additives in the calcified roasting, and high content of calcium in the raw vanadium slag can decrease the adding amount of additive of CaO. During roasting step, poisonous gases, such as Cl₂, HCl, SO₂ and SO₃ are discharged in the sodium

roasting process, which results from the decomposition of additives of NaCl and Na₂SO₄ at high temperature, while calcified roasting can avoid this problem. Furthermore, calcified roasting can alleviate the phenomenon of burden bonding roasting furnace, which usually happens due to the generation of the low melting-point phase of sodium salts during sodium roasting process.

Since no sodium and potassium salt is introduced in the process, wastewater can be closed-circulating after removing the enriched impurities of P, Si, Ti and Cr with adding powder CaO. In contrast, it is well known that the wastewater from the sodium process contains high concentration of sodium, which is difficult to remove from the aqueous solution, resulting in enrichments of Na₂SO₄ which makes the viscosity of mother liquor increased and let the mother liquor not suitable for recycling to leach the roasted slag. In addition, because lots of chromium transfers into the vanadium-bearing solution as Cr⁶⁺ during the sodium roasting-water leaching process, the residual chromium in the mother liquor has to be treated with reduction and precipitation. In this proposed process, the valuable metals like Fe, Cr, Ti, Mn in the tailings after vanadium extraction are more feasible to be comprehensively recovered through conventional pyrometallurgical processes since little Na is contained. The product of vanadium pentoxide contains little alkaline metals of Na and K, it will be better to be used in the iron and steel industry.

In the proposed process, a chemical precipitation method was used to purifying the acidic solution. Unlike the conventional method of solvent extraction for purification of acidic vanadium-bearing solution, adding the composite reagent of Mn(NH₄)F₃ to remove the impurities from the acidic vanadium-bearing solution is easy to operation and convenient to apply in industry, meanwhile, does not bring forth any serious secondary pollution.

In the whole process, from roasting to thermal decomposition, the total vanadium recovery is more than 83% (> 91% × 95% × 96%), which is higher than 75% of that for the conventional sodium roasting process. Manganese resources can be simultaneously recovered as MnC₂O₄ with purity of 98.5% during the proposed process.

In conclusion, the final product of vanadium pentoxide prepared with this proposed process meets the standards of Grade 98 and the total vanadium recovery is higher than 83%, which is a relatively satisfactory vanadium resource utilization rate. In addition, during the whole process, little poisonous gas is discharged, wastewater almost realizes closed recycle, and the tailing after vanadium extraction is rich in Ca and favor to be treated with pyrometallurgy to recover other valuable metal resources.

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