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Extraction of vanadium from sulfuric acid leaching solution of stone coal by ion exchange

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The extraction of vanadium from the acid leaching solution contained high concentration of impurities from stone coal by ion exchange was studied. Experimental results showed that vanadium can be effectively separated and extracted from the solution containing 2.68 g/L V, 3.82 g/L Fe, 18.63 g/L Al, 5.67 g/L Mg, 5.94 g/L K, 1.43 g/L P and 0.62 g/L Si by ion exchange and selective scrubbing and chemical precipitation. The proper pH range for ion exchange was 1.8-2.0. It was found that 98.5% of vanadium with 9.5% of iron and 7.41% phosphorus and 8.89% silicon were adsorbed by the resin D201 from the feed solution. Loaded iron can be selectively scrubbed by 0.5 mol/L HCl. 99.68% of vanadium with the same proportion of phosphorus and silicon was eluted by 2 mol/L NaOH. The removal of P and Si from the eluted solution was performed by adding 2 times stoichiometry of $MgSO_4$ at pH 8.0 and 80 °C for 1 h. After precipitation of metavanadate and calcination, high purity of V_2O_5 was obtained.

Keywords: Stone coal, vanadium extraction, ion exchange

INTRODUCTION

Vanadium-bearing stone coal is an important vanadium resource in China, hence, vanadium extraction from stone coal is paid more attention to in this country. At present, acid leaching with H_2SO_4 have been widely adopted for vanadium leaching from stone coal due to the merits of high vanadium recovery and low pollution [1, 2]. In order to improve the vanadium leaching rate, the high H_2SO_4 concentration is needed in acid leaching process commonly. Therefore, many impurities, such as Al, Mg and Fe ions are also leached along with vanadium from stone coal, which results in the complex vanadium-bearing leaching solution with high concentrations of impurities elements and low pH value. These impurities are detrimental to the recovery of vanadium from the acid leaching solution and need further separation and purification [3].

In order to find an effective route for separating vanadium and iron, researchers have paid special attention to this subject in recent years. Solvent extraction [4, 5] and ion exchange [6, 7, 8] are widely used to recover vanadium from the leaching solution. The separation of vanadium from the acid leaching solution with the mixed reagent D2EHPA/TBP has been studied by many authors [9, 10]. Tavakoli and Dreisinger [11] studied the separation of vanadium from iron by solvent extraction using acidic and neutral organophosporus extractants and indicated that Cyanex 923 could selectively extract V(V) over Fe(III) and D2EHPA revealed a suitable separation for V(IV) over Fe(II). The separation of V(IV) and Fe(III) from the acid leach solution of stone coal by D2EHPA/TBP was studied by Ma [3]. However, separation of vanadium and iron is not complete in solvent extraction with the above extractants. Compared to solvent extraction, ion exchange has the advantage of simplely in operation and high purity of product. However, the study of extraction of vanadium by iron exchange mainly focus on low-acid solution with fewer impurities [6, 7, 8]. Moreover, little information has been found regarding the separation of vanadium from strong acid solution with high concentration of impurities by ion exchange. In our previous study, Al, Mg, Na and K almost have no effect on vanadium adsorption while it was difficult to separate V(V) from Fe(III) when weak base anion resin was selected [12]. Recently, by accident, it was found that the separation of vanadium and other ions from the acid leaching solution can be directly carried out with a strong base anion exchange resin D201. In this study, the loading behavior of D201 for vanadium at the optimum loading condition was determined. The recovery process of vanadium from the sulfuric acid leaching solution is reported.

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Table 1. Composition of the solution (g/L).

Elements	V	Fe	Al	Mg	K	P	Si
Acid leaching solution	2.68	3.82	18.63	5.67	5.94	1.49	0.49
Filtrate at pH 2.0	2.56	2.24	18.51	5.65	5.72	1.25	0.45
Effluent	0.04	2.02	18.49	5.65	5.71	1.16	0.33
Eluted solution	15.36	0.012	0.011	0.002	0.003	0.18	0.037
Purified solution	15.29	0.002	0.001	0.001	0.002	0.009	0.006

EXPERIMENTAL

Anion-exchange resin

The strong base anion exchange resin D201 with function group of [-N(CH_3)$_3$] and structure of crosslinking acrylate was obtained from Hangzhou Zhengguang Chemical Company of China. The diameter of more than 95% resin beads is in the range of 0.45-1.00 mm. The resin was first soaked in distilled water for 24 h, and then alternately soaked in 2 mol/L NaOH and 2 mol/L HCl for 12 h, repeated three times as this way, at last activated with 2 mol/L HCl and rinsed with distilled water before use. After adsorption, the loaded resin was eluted by 2 mol/L NaOH and regenerated by 2 mol/L HCl.

Sample solution and analysis

The sulfuric acid leaching solution of stone coal was prepared by roasting the stone coal at 850 °C for 1 h followed by leaching with 15% (v/v) H_2SO_4 and 5% (wt) $NaClO_3$ (as oxidant) at 95 °C and for 6 h. Due to roasting and oxidative leaching, vanadium and iron in the leaching solution existed predominantly in the form of V(V) and Fe(III). The composition of this solution was listed in Table 1 and the pH value of the solution was 0.4. The adjustment of pH using CaO and H_2SO_4. After pH adjustment the solution was keep standing for 24 h and then the filtration was conducted. Vanadium concentration was titrated with ammonium ferrous sulphate [13]. The concentrations of other ions were determined by inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 4300DV, USA) after suitable dilution. The pH was determined with S220 SevenCompact^{TM} pH meter (Mettler Toledo, Switzerland), and the degree of accuracy is 0.001.

Batch adsorption experiments

The experiments were carried out in the conical flask (500 mL) on the constant temperature bath oscillator at 150 rpm, at room temperature (25±0.5 °C) for 24 h, the volumes of the solution and the wet resin were fixed in 200 mL and 10 mL respectively. After adsorption, the suspension was filtered, and the solution was analyzed for vanadium and other ions concentrations. Ion uptakes were obtained by determining the ion concentrations before and after contact with the resin.

Column experiments

Trials were carried out in a glass column Φ2.5×30 cm which operated with the leaching solution at the ambient temperature. Forty (40) mL of the pretreated resin, were wet-packed into the glass column. The operation was performed by downstream flow at a certain flow rate. Samples were collected periodically from the column eluate and analysed to determine ion content. The adsorption is stopped once the concentration of vanadium in the effluent reaches 0.05 g/L. 2 mol/L NaOH solution is then used to elute the loaded resin and the resin is then regenerated using 2 mol/L HCl.

Experiment fundamental

Fig.1 is the forms of vanadium (V) existing in sulfate solution under different pH and concentration [14]. As can be seen, vanadium (V) in the sulfate solution (log(V(V))=-1.28) is mainly in the forms of $VO_2SO_4^-$, $H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$ between pH 1 and 4. These anionic vanadium species with other anionic species such as PO_4^{3-}, SiO_3^{2-} in the feed solution can be adsorbed by anion resin while cations such as Al^{3+}, Mg^{2+}, K^+ and Na^+ remain in the solution. It has been reported that iron(III) has a tendency to combination with sulfate to form the complexes $Fe(SO_4)_2^-$ [15], which can also be adsorbed by anion resin. Loading reaction of vanadium and other ions can be represented as Eqs.(1) to (6) and RCl represents chloride form of D201.

$$RCl + VO_2SO_4^- = RVO_2SO_4 + Cl^-, \qquad (1)$$

$$4RCl + H_2V_{10}O_{28}^{4-} = R_4H_2V_{10}O_{28} + 4Cl^-, \qquad (2)$$

$$5RCl + HV_{10}O_{28}^{5-} = R_5HV_{10}O_{28} + 5Cl^-, \qquad (3)$$

$$3RCl + PO_4^{3-} = R_3PO_4 + 3Cl^-, \qquad (4)$$

$$2RCl + SiO_3^{2-} = R_2SiO_3 + 2Cl^-, \qquad (5)$$

$$RCl + Fe(SO_4)_2^- = RFe(SO_4)_2 + Cl^-, \qquad (6)$$

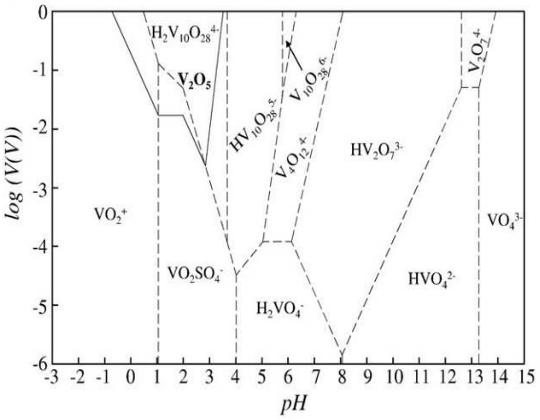

Fig. 1. Activity–pH diagram for vanadium(V)–water–sulfur–water system at 298.15 K [14].

RESULTS AND DISCUSSION

Batch experiments

Effect of solution pH

In order to investigate the effect of solution pH on the loading of vanadium and other metal ions from sulfuric acid leaching solution, experiments were carried out in the solution pH range from 0.5 to 2.4. Fig. 2 shows that pH value is an important condition for the vanadium adsorption in the solution and the adsorption efficiency of the resin for the vanadium increases with the pH from 0.5 to 2.4. The loading behavior of vanadium with the acidity of the solution can be explained using the activity–pH diagram of vanadium shown in Fig. 1. From Fig. 1 it can be observed that with pH increasing, the predominant form of vanadium changed from VO_2^+ to $VO_2SO_4^-$, $H_2V_{10}O_{28}^{4-}$ and $HV_{10}O_{28}^{5-}$. It is well known that the higher the charge of ion the better adsorption performance of it, thereby the adsorption rate of vanadium increases with pH. Iron adsorption increases slowly with pH increase and the total adsorption is below 20%. However, both phosphorus and silicon adsorption decrease with pH increase. Since the charge of $H_2V_{10}O_{28}^{4-}$ and $HV_{10}O_{28}^{5-}$ is higher than PO_4^{3-}, SiO_3^{2-} and $Fe(SO_4)_2^-$, the adsorption performance of vanadium is much better than that of phosphorus, silicon and iron. The adsorption percentage of Al, Mg, K was negligible in our experimental range which indicates that vanadium can be separated from Al, Mg, K.

Although higher pH value is beneficial for vanadium adsorption, it was found that when pH is over 1.6, iron, phosphorus, silicon and vanadium gradually precipitated, which made the loss of vanadium. As showed in Fig. 3, the precipitation of the above ions increases with pH increases. Moreover, the loss of vanadium increases slowly with pH increased from 1.6 to 2.0 and increases rapidly with pH increased from 2.0 to 2.4. Hence, to maximise vanadium adsorption and minimise vanadium loss, accordingly, the solution pH was strictly controlled between 1.8-2.0.

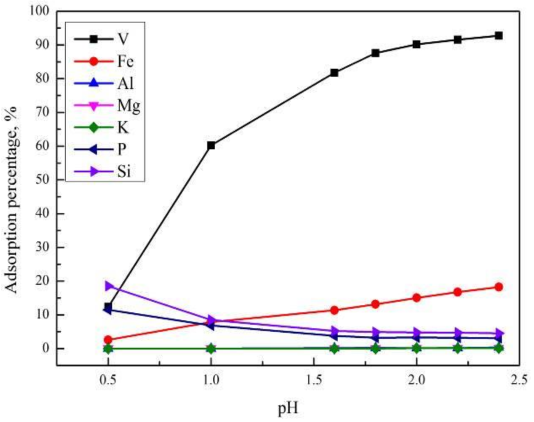

Fig. 2. Influence of pH value on vanadium and other metal ions adsorption.

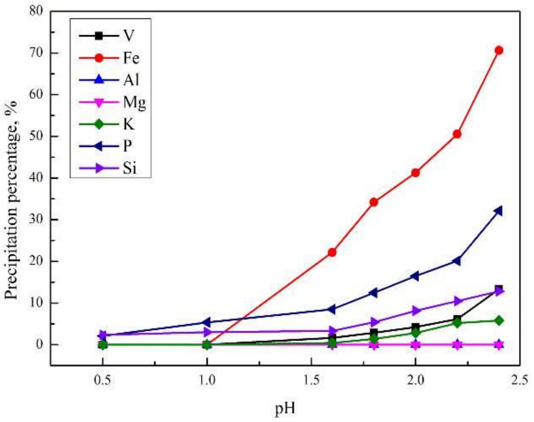

Fig. 3. Ions precipitation with pH.

Scrubbing of impurities

As mentioned above, the impurities of iron, phosphorus and silicon were adsorbed along with vanadium, and the scrub of these impurities from the loaded resin is necessary. The loaded resin was scrubbed by 0.5 mol/L HCl at the HCl/resin volume ratio of 2 and the results were shown in Table 2.

Table 2. Scrubbing ions from loaded resin.

Ion	V	Fe	P	Si
Scrubbing efficiency, %	5.17	94.19	15.23	23.15

It was shown that 94.19% of loaded iron and 15.23% of phosphorus and 23.15% silicon can be scrubbed by 0.5 mol/L HCl while 5.17% of vanadium was scrubbed off given a further separation of vanadium and iron, phosphorus and silicon. After scrubbing, there was a very small amount of impurities which may not effect the elution of vanadium.

Elution of vanadium

In vanadium ion exchange process, NaOH is usually adopted as eluant and the pH of the eluate is higher than 13. It can be seen from Fig.1 that vanadium mainly exist in the form of VO_4^{3-} under the pH value is higher than 13. Thus, the elution reaction can be represented by Eqs.(7) to (9), where ROH represents the hydroxide form of D201.

$$RVO_2SO_4 + 5OH^- = ROH + VO_4^{3-} + SO_4^{2-} + 2H_2O, \quad (7)$$

$$R_4H_2V_{10}O_{28} + 30OH^- = 4ROH + 10VO_4^{3-} + 14H_2O, \quad (8)$$

$$R_5HV_{10}O_{28} + 30OH^- = 5ROH + 10VO_4^{3-} + 13H_2O, \quad (9)$$

In this study, batch elution experiments were carried out with different concentration of NaOH, and the results are presented in Fig.3. As is shown in Fig.3, the elution percentage of vanadium increased rapidly from 42% to 92% with the increase of NaOH concentration from 0.5 to 2 mol/L. Due to there was little difference in the elution performance of vanadium with NaOH concentration increasing from 2 mol/L to 4 mol/L, 2 mol/L NaOH solution was chosen for the elution of vanadium in further experiments.

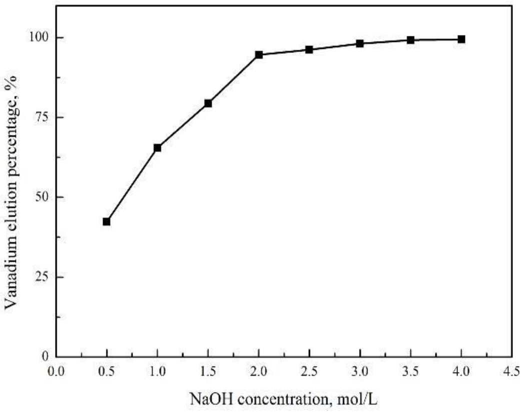

Fig. 4. Effect of NaOH concentration on the elution of vanadium.

Column experiment

Continuous column experiments were performed under pH of 2.0 and a constant flow rate of 100 mL/h. The adsorption results of vanadium and other ions are shown in Fig. 4. As can be seen in Fig. 5, the concentrations of iron, phosphorus and silicon increased rapidly in the effluent with the increasing of effluent/resin ratio. When effluent/resin volume ratio reached 18, in the effluent, iron concentration was the same as that of the feed solution, while vanadium concentration was close to 0.03 g/L at this time. It was interesting that the concentration of iron in the effluent was slightly higher than that in feed solution after the volume ratio was above 12, which indicated that iron was eluted when effluent/resin volume ratio was about 12, and the concentration of iron indicating that some iron adsorbed in the resin was replaced by vanadium, the same phenomenon was observed by Fan [16]. There was no further adsorption of phosphorus and silicon once the effluent/resin volume ratio increased to 14 and 16 respectively. The concentration of vanadium is not more than 0.03 g/L in the effluent until the volume ratio over 20. From Fig. 5 it can be seen that if the breakthrough point was 0.05 g/L vanadium, the volume ratio would be 30, and the average concentration of vanadium is less than 0.05 g/L in the collected effluent, suggesting that the vanadium can be removed effectively from the iron, phosphorus and silicon contained solution with the resin. The raffinate contained 0.04 g/L vanadium, 2.02 g/L iron, 1.16 g/L phosphorus and 0.41 g/L silicon, which equate to 98.44% vanadium extraction whilst about 9.83% of iron together with of 7.41% phosphorus and 8.89% silicon were extracted.

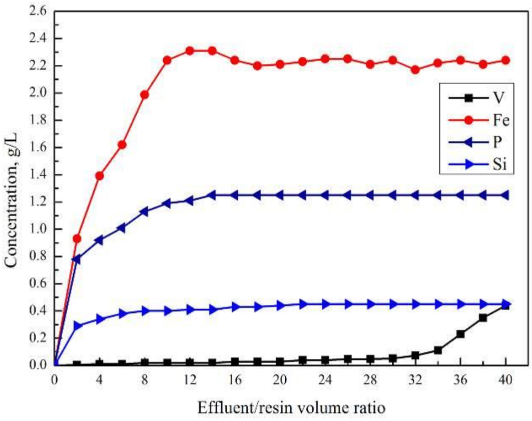

Fig. 5. Adsorption curves of the resin for irons.

Loaded resin was scrubbed by 0.5 mol/L HCl, the scrubbing curves were represented in Fig. 6. The results showed that iron can be effectively scrubbed from the loaded resin while only a small amount of loaded vanadium was scrubbed off. The scrubbing efficiency of phosphorus and silicon was in the range of 7%~20%. The differences of the scrubbing behavior of vanadium, iron, phosphorus and silicon indicating that vanadium and iron can be completely separated in the scrubbing process while the completely separation of vanadium and phosphorus and silicon need further operation. The scrubbing of iron was increased from 50.86% to 92.46% when the HCl to resin volume ratio was increased from 0.5 to 2. No significant difference was observed in the results obtained within the HCl to resin volume ratio range from 2 to 3. Therefore, HCl to resin volume ratio of 2 was selected for further investigations.

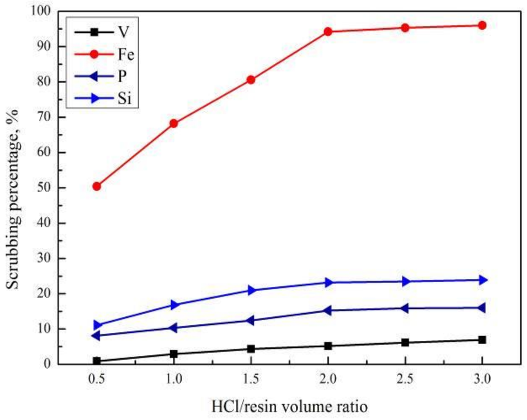

Fig. 6. Scrubbing of ions from the loaded resin using 0.5 mol/L HCl.

The scrubbed resin was eluted using 2 mol/L NaOH under the constant flow rate of 50 mL/h at room temperature, and the results were shown in Fig. 7.

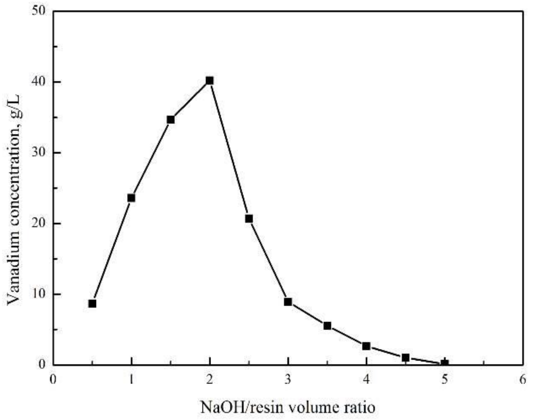

Fig. 7. Desorption curves of the loaded resin.

It was shown that the peak value of vanadium concentration in the effluent appeared when effluent/resin volume ratio was near 2, then the concentration of vanadium in the effluent was less than 0.1 g/L when the effluent/resin volume ratio was above 5, which can be regarded as the terminal point of the elution, and the desorption of vanadium reached 99.68% at this time. Phosphorus and silicon were eluted along with vanadium in the same proportion and need further purification. Then the resin was regenerated by 2 mol/L HCl and reused in adsorption. The concentrations of vanadium and other ions in the eluted solution were shown in Table 1. From Table 1, it can be seen that phosphorus and silicon were eluted along with vanadium and need further purification. To remove phosphorus and silicon, the chemical precipitation method was usually adopted. The pH of eluted solution was adjusted to 8.0-9.0, then 2 times of stoichiometry $MgSO_4$ solution was added at 80 °C under stirring for 1 h to precipitate phosphorus and silicon as $Mg_3(PO_4)_2$ and $MgSiO_3$ [8]. After purification, the impurities concentrations are all below 0.01 g/L indicating that the purified solution is qualified feed solution for vanadium precipitation.

Preparation of V_2O_5

The purified solution was mixed with 2 times of stoichiometry $(NH_4)_2SO_4$ to precipitate metavanadate for 4 hour at 60 °C. Precipitation was obtained after filtration, scrubbing with water and calcination at 550 °C for 2 h. The product of V_2O_5 with purity of 99.52% was achieved, indicating that the product was of high quality.

Process for the separation and extraction of vanadium from sulfuric acid leaching solution

According to the previously mentioned test results, a process flowsheet of separation of vanadium and iron from acid leaching solution is shown in Fig. 8.

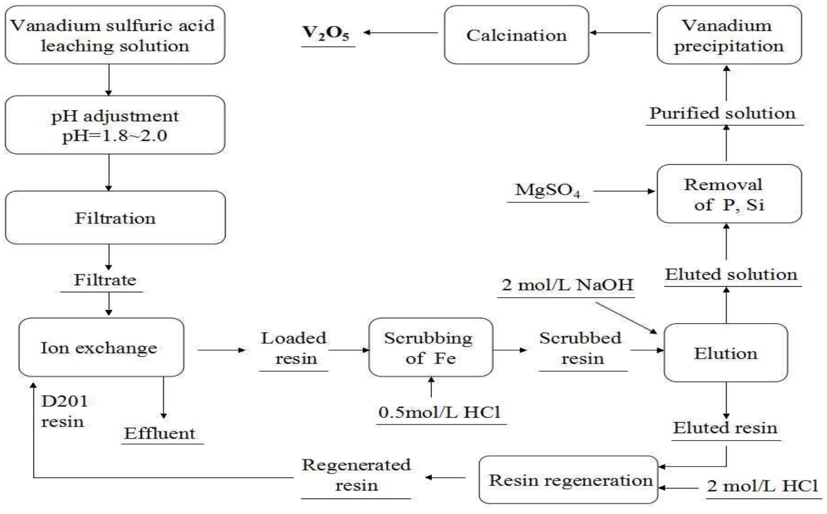

Fig. 8. Flowsheet of recovery of vanadium from sulfuric acid leaching solution of stone coal.

First, the solution pH was adjusted between 1.8~2.0 and then filtration was taken. Then the filtrate was contacted with the D201 resin and above 98% of vanadium and a small amount of iron, phosphorus and silicon was adsorbed by the resin. Loaded resin was scrubbed by 0.5 mol/L HCl and almost all the loaded iron can be scrubbed. Then the resin was eluted by 2 mol/L NaOH solution for vanadium desorption and then the resin was regenerated by 2 mol/L HCl. The eluted solution was purified by $MgSO_4$ to remove phosphorus and silicon. After precipitation and calcination, high purity of V_2O_5 can be obtained.

CONCLUSION

Batch adsorption experiments and column experiments have been carried out to verify the applicability of ion exchange for the separation of vanadium from the acid leaching solution of stone coal. The separation and recovery of vanadium from sulfuric acid leaching solution of stone coal in the presence of Fe, Al, Mg, K, P and Si were investigated using anion resin D201. The optimum pH value for the separation of vanadium with the resin was in the range of 1.8-2.0. Most of the vanadium together with a small amount of iron, phosphorus and silicon were selectively loaded by the resin at pH 2.0 but the loaded iron was separated from vanadium during scrubbing with 0.5 mol/L HCl solution. The loaded vanadium was successfully eluted by using 2 mol/L NaOH solution. The impurities of phosphorus and silicon in the eluted solution were removed by $MgSO_4$. After metavanadate precipitation and calcination, V_2O_5 with purity of 99.52% can be obtained.

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