Study of Vanadium Removal from Caustic Solutions

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Abstract

In the process of alumina production, vanadium is co-extracted in the caustic solution and can have detrimental effects on the extraction of target ions, such as aluminium and gallium. Removal of vanadium is an important process, accounting for about 50 % of the production cost in the gallium extraction. However, the species of vanadium ion in the caustic solution vary and no clear explanation of its binding mechanism has yet been proposed. At present, precipitation, extraction and ion exchange have been applied for removal of vanadium from caustic solution. The present paper summarizes the findings of recent studies for vanadium removal, discussing the interaction mechanisms from batch experiments, spectroscopy analysis and theoretical calculations. The advantages and disadvantages of the three proposed ways to remove V and prospects for the development of an optimum V removal method are presented.

Keywords: Vanadium, Removal, Interaction mechanism, Analytical chemistry, Caustic solutions.

1. Introduction

Vanadium is an important strategic material, with a high melting point and easy deformation processing characteristics. It is mainly used in the steel industry, national defense advanced technology, chemical industry and textile industry, and other fields. However, vanadium is a scarce resource, as there are no rich vanadium ore deposits in nature. vanadium only exists in low-grade ores alongside other minerals. Currently, 70 % of vanadium resources in China come from vanadium-containing steel residue, stone coal and waste catalysts, most of which have low grades and complex compositions [1].

Bauxite contains 0.038–0.14 wt.% V_2O_5. During the Bayer process treatment of bauxite, approximately 30 % of the vanadium enters spent liquor along with aluminium, due to the action of caustic soda in the dissolution process [2]. It is estimated [3] that the quantities of vanadium brought into alumina process are about 10–50 kt/y that is an important vanadium resource. The vanadium in alumina process is progressively enriched, and beyond a certain concentration limit, it will act as a poison in the growth of the hydrated alumina seeds and adversely influence the efficiency of precipitation process. Moreover, if vanadium is carried over to the final aluminium metal, it will bring down the electrical conductivity significantly. Therefore, vanadium must be precipitated in the form of silt through slow cooling or air clearing. This sludge typically contains 6–20 wt.% V_2O_5, making a potential raw material or vanadium production. The vanadium-containing sludge was dissolved and filtered with water to obtain a vanadium-containing solution, from which vanadium can be recovered through the precipitation of iron vanadate or calcium vanadate.

Currently, for the recovery or removal of vanadium in solution, there are various methods available, including precipitation, extraction, ion exchange and others. Among these, the ion

exchange method is particularly important due to its high efficiency, simple operation and easy regeneration. Resin is commonly used in the ion exchange methods, because it offers easy operation, low chemical consumption, good flexibility and versatility as an adsorbent.

However, the form of vanadium in aqueous solution is quite complex. Depending on factors such as coordination ion, valence state, concentration and pH value, vanadium ions can interact with each other. The toxicity of vanadium increases with its valence and solubility [4]. Vanadium pentavalent (V) and vanadium tetravalent (IV) are the most stable forms of vanadium compounds. Vanadium(IV) has low toxicity and is less toxic and insoluble at near neutral pH value. Therefore, vanadium valence can be altered under appropriate conditions for removal [5].

The various types of leach solutions and pretreatment process, as result in different forms and valence states of vanadium. To selectively and effectively recover or remove vanadium from solution, it is essential to have a deep understanding of the state of vanadium ions in solution and to clarify the important of valence state and form on vanadium recovery or removal.

Therefore, this paper mainly discusses the action mechanism of vanadium from the aspects of experiment, spectral analysis and theoretical calculation. It reviews the adsorption rules of precipitation, extraction and ion exchange methods on vanadium of different valence states. Additionally, the adsorption mechanism through Fourier transform infrared spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy were studied. The theoretical calculation provides a reference basis for the recovery or removal of vanadium in different valence states.

2. Vanadium Removal Method

2.1 Precipitation Method

Bauxite often contains a small amount of vanadium. During the Bayer process, approximately 30% of the vanadium present in the bauxite is transferred to the spent liquor along with aluminium, due to the present of caustic soda in the dissolution process. When the aluminium hydroxide is precipitated from the sodium aluminate solution, the vanadium remains in the Bayer liquor and reintroduced into the bauxite leaching process.

Zhao Zhuo [6] studied the industrial test of calcium oxide (CaO) deposition of vanadium. By adding CaO to the spent liquor, most of the V_2O_5 can be precipitated, resulting in a vanadium deposition rate of over 80%. There is still potential to optimize the experimental conditions further to improve the vanadium deposition rate. Additionally the V_2O_5 content in the obtained precipitated residue is greater than 0.4 % and can be increased to meet the grade requirements of the vanadium industry for raw materials. This is beneficial for the continued recovery of vanadium. Bai Wanquan [7] studied the precipitation process of vanadium in Bayer solution. By adding 10–30 g/L of CaO and reacting at 90–110 ℃ for 0.5–2 hours, 0.6–0.8 % V_2O_5 can be obtained in the filtered sludge. Therefore, the spent liquor is a suitable raw material for V_2O_5 recovery in the alumina production process.

2.2 Extraction Method

Zhao Zhao [8] conducted an extraction method to extract vanadium from a sodium aluminate solution. Extraction experiment were carried out on vanadium from the spent liquor using N235 (Extractant: Trialkyl tertiary amine, $C_nH_{2n+1}N$, n=8–10, Abbreviated as R_3N), P204 (Extractant: 2-2-ethylhexyl phosphoric acid, $(RO)_2POOH$, $R=C_4H_9CH(C_2H_5)CH_2$) and N263 (Extractant: Methyltrialkyl amine chloride, $CH_3(CH_2)_{7\sim11}NCl$, Abbreviated as R_3CH_3NCl) , respectively. The results revealed that the extraction efficiency of these three systems on vanadium from the spent liquor was very poor, with N235 and P204 systems showing almost no extraction effect. The

extraction rate of N263 was only 4.76 %. This poor result maybe be attributed to the excessive alkalinity of the spent liquid, with a Na_2O_k content of 150 g/L, surpassing the pH range of the extraction systems mention about. Additionally, the low concentration of vanadium in the spent liquor could lead to a low extraction efficiency when using the extraction method. Moreover, due to the presence of various elements in bauxite, impurity ions in the spent liquor are complex and diverse. Some impurity ions share similar properties with vanadium anion, which can significantly impact the extraction process.

2.3 Ion Exchange Method

The process of gallium recovery by amidoxime resin is highly selective and does not adsorb aluminium. However, it does co-adsorb gallium and vanadium in solution. Gallium adsorbed on the resin can be washed with inorganic acid (hydrochloric acid, sulfuric acid, nitric acid) to obtain a gallium-rich solution. Unfortunately, the vanadium ion on the resin is difficult to desorb, leading to resin poisoning. This reduces the adsorption capacity of gallium during recycling and shortens the life of the resin. Therefore, achieving the step-by-step desorption of gallium and vanadium in the resin is crucial. This not only reduces the impact of vanadium on the resin during the enrichment process and improves the service life of the resin, but also increases the added value of vanadium-related products.

In order to the separate and recover gallium and vanadium, batch adsorption experiments was conducted [9] using the macroporous chelating resin to systematically explore adsorption properties of gallium and vanadium, the influence of co-existing ions on the resin's adsorption and separation of gallium was also analyzed. The results showed that the adsorption of vanadium on the resin was obviously inhibited at high alkalinity and low temperature. The optimum separation conditions were NaOH concentration 5–10 mol/L, equilibrium adsorption capacity of gallium and vanadium were 1.75–1.82 mg/g and 0.18–0.71 mg/g, respectively. These results provide data support for the separation of gallium and vanadium using the ion exchange method.

Li Jie [10] studied the adsorption of tetravalent and pentavalent vanadium by D201 anion exchange resin (quaternary ammonium group [-$N(CH_3)_3Cl$] on styrene-divinylbenzene copolymer) under different experimental conditions. The effect of pH, time, temperature and ion concentration on the adsorption of D201 resin was investigated. The experimental results of V(IV)、V(V) adsorption by D201 resin showed that 99 % of V(V) was adsorbed at pH values in the range of 3–10 and a solid liquid ratio of 100, and vanadium showed an anionic form with D201 for anion exchange. Unfortunately, the adsorption rate of vanadium decreases sharply to 22.25 % when pH adjusted over 11. It is evident that the adsorption rate of vanadium decreases as the alkalinity of the solution increase.

3. Interaction Mechanism

3.1 Interaction Mechanism of Precipitation

The outermost electron arrangement of the vanadium element is $3d^3 4s^2$, and its existing forms in solution include V(II)~V(V). Generally speaking, the higher the valence state of vanadium, the more complex its existence form in solution, which largely depends on the soluble vanadium concentration and pH value in solution [11]. Therefore, in order to facilitate subsequent thermodynamic analysis, it is necessary to determine the types of vanadium compounds in each valence state and the chemical reactions between them.

The removal of vanadium from the alkaline sodium chromate solution with addition of lime was investigated based on the calculation of reaction Gibbs free energy and equilibrium solubility, and

the removal rule of vanadate [12], as well as the structure of vanadate, was also studied by experiments. The thermodynamic calculation indicates that VO^{3-}, CO_3^{2-}, SO_4^{2-}, VO_4^{3-} and CrO_4^{2-} can sequentially be precipitated by formation of compound containing calcium at 298−373 K. Meanwhile, the mutual transformation occurs between calcium salts. $CaCrO_4$ and $Ca_3(VO_4)_2$ can react with CO_3^{2-}, and $CaCrO_4$ can convert to $Ca_3(VO_4)_2$ in the presence of VO_4^{3-}. In addition, the formation of $CaCO_3$, $CaCrO_4$, $CaSO_4 \cdot nH_2O$ as well as $Ca_3(VO_4)_2$, $Ca_2V_2O_7$ may account for the excess lime in the removal of vanadium.

The results of residue phase analysis after vanadium deposition are shown in Figure 1. Adding calcium oxide to a pure sodium vanadate solution can produce calcium vanadate, as shown in Figure 1(b). Calcium carbonate and calcium chromate can be produced by adding calcium oxide to sodium chromate solution in the presence of CO_3^{2-}, as shown in Figure 1(a). Under the condition of excessive calcium oxide, the vanadium removal residue obtained from the solution of sodium chromate containing vanadium should be a mixed residue containing various calcium salts, as shown in Figure 1(c). According to the XRD pattern of vanadium removal residue, it can be determined that the vanadium removal residue is a mixture of calcium salts such as $CaCO_3$,$Ca(OH)_2$, $Ca_5(CrO_4)_3(OH)$, $Ca_{0.5}V_3O_5$, CaV_3O_7 and $Ca_2V_2O_7$ [12].

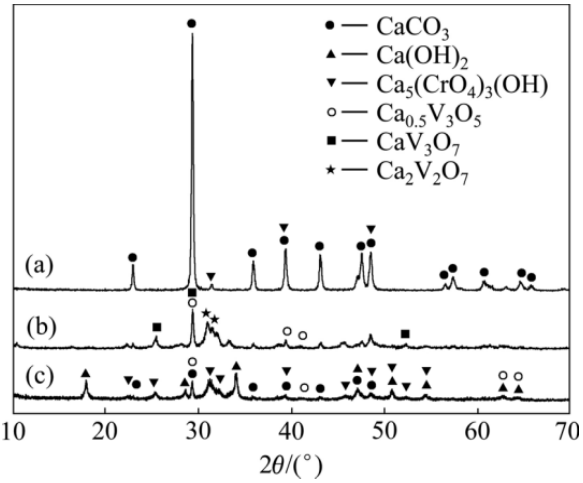

Figure 1. XRD patterns of solution reaction residue: (a) Sodium chromate solution ($Na_2Cr_2O_7$. $2H_2O$: 300 g/L, ρ(Na_2CO_3) ＜5 g/L); (b) Pure $NaVO_3$ solution (V_2O_5: 1 g/L); (c) Sodium chromate solution containing vanadium ($Na_2Cr_2O_7$. $2H_2O$: 300 g/L, V_2O_5: 1 g/L, Na_2CO_3: 1.41 g/L) [12].

However, it should be pointed out that the presence of CO_3^{2-} in solution is not conducive to vanadium removal. the addition of lime is helpful for separation and utilization of resource in vanadium residue. This action will significantly decrease the amount of residue and improve the vanadium content in the residue.

The solution chemical behaviour in the vanadium deposition process is relatively complex, with the vanadium concentration, solution pH value and REDOX potential all undergoing dynamic changes. Therefore, in-depth research on the thermodynamics of the reaction process is necessary to determine the influence of each condition on the trend, providing theoretical guidance for subsequent tests. Targeted precipitation is conducted to achieve the goal of separation and purification.

3.2 Interaction Mechanism of Extraction

Since the spent liquor is too alkaline and the Na_2O_k content reaches 150 g/L, which is beyond the application range of the pH value of the extraction system, the mechanism of the extraction method in alkaline sodium aluminate solution is not clear. The research on the mechanism after acid leaching is the main focus.

Guo Yun [13] proved the induced transformation mechanism of trioctylmethyl ammonium chloride (MTA) on vanadonic acid form, and based on this, established a microemulsion vanadium extraction method with high extraction capacity and efficiency. the microemulsion system of MTA / isoamyl alcohol/n-heptane /NaCl was established, with MTA as the surfactant to form microemulsion in n-heptane and isoamyl alcohol as the cosurfactant. The microemulsion extraction conditions for V were optimized. The highest extraction efficiency of vanadium reached was 99.90 % at pH 3 of feed solution with the extractant concentration of 73.35 mmol/L, phase ratio of 4, and extraction time of 2 min at 25 °C.

According to the optimized extraction conditions, the structure of polyoxovanadiums (POVs) before and after microemulsion loading was studied. Initially, the structural changes of $H_2V_{10}O_{28}^{4-}$ (abbreviated as POVs) were calculated using ab initio molecular dynamic (AIMD) theory. Subsequently, the calculated results were confirmed through various characterization methods, which were combined to explain the specific structural changes of POVs [13].

By utilizing AIMD quantum mechanics to calculate the structural evolution during the simulation process, we are able to determine the coordination mode of V after microemulsion loading depicted in Figure 2. The coordination mode was mainly primarily influenced by cations. Initially, the structure was $H_2V_{10}O_{28}^{4-}$, but following microemulsification, it transformed into $V_{10}O_{26}^{2-}$.

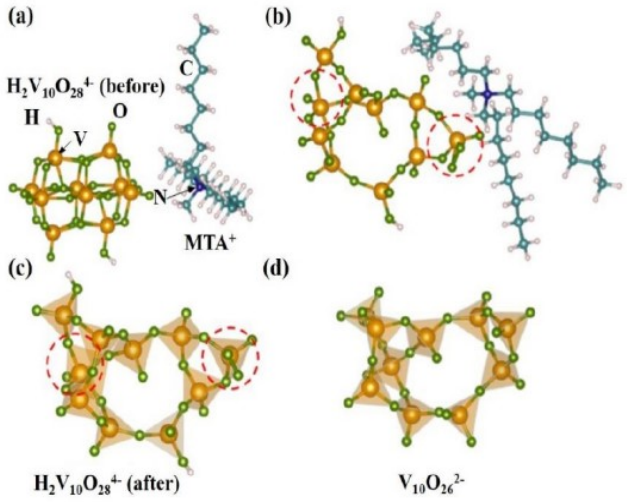

Figure 2. Transformation of POVs steered by cations. (a) Initial structure; (b) configuration after equilibration; (c) fully relaxed structure of POVs steered by MTA^+; (d) fully relaxed structure of $V_{10}O_{26}^{2-}$ [13].

To further verify the structural changes of POV, the changes of POVs before and after MTA^+ microemulsion loading were characterized by ^{51}V nuclear magnetic resonance (NMR) (Figure 3(a-b)). The results show that three widened resonance lines are observed at -419.27, -494.93 and -514.58 ppm in the loaded microemulsion. The transfer of all three resonances to the lower field indicates a decrease in the electron cloud density of all vanadium nuclei, which is related to a decrease in the coordination of oxygen from octahedral VO_6 to tetrahedral VO_4 (Figure 3(b)).

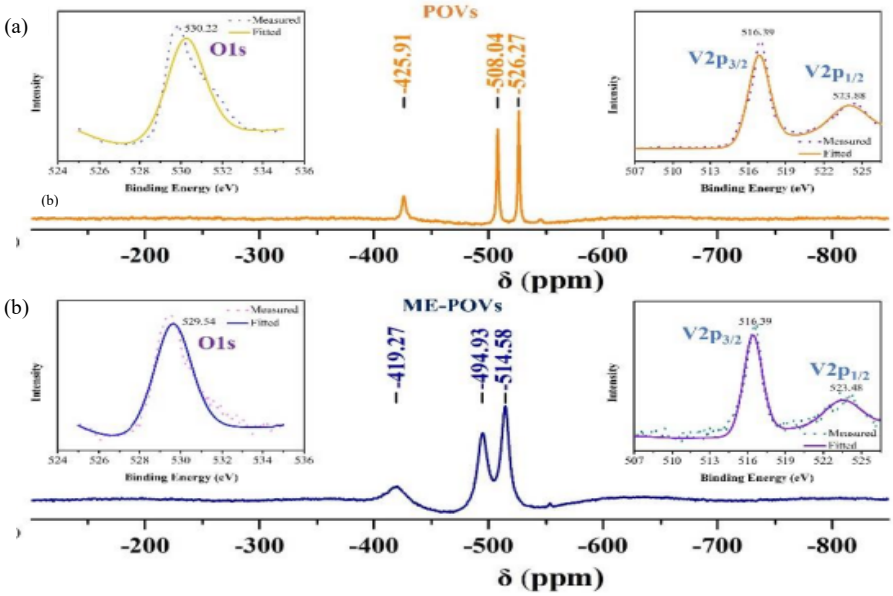

Figure 3. Characterization of the transformation of POVs. ^{51}V NMR spectrum of POVs before (a) and after (b) being loaded into microemulsion; insets: the XPS signals of O 1s and V 2p electrons of POVs [13].

The X-ray photoelectron spectroscopy (XPS) results showed a decrease in the number of oxygen atoms in coordinating with vanadium atoms. The V 2p1/2 (-0.40 eV) and O 1s (-0.68 eV) peaks exhibited very small shifts, indicating a decrease in the density of electron clouds around vanadium and oxygen atoms. This confirmed that the number of oxygen atoms coordinating with vanadium atoms had decreased.

Raman spectroscopy (Figure 4) results confirm the findings of XPS. The Raman spectra of loaded microemulsion phase are attributed to V-O-V tensile vibrations in POVs. This indicates a reduction in the number of oxygen atoms coordinating with vanadium atoms compared to the bands at 323, 404, and 452 cm^{-1} in the POVs solid Raman spectra.

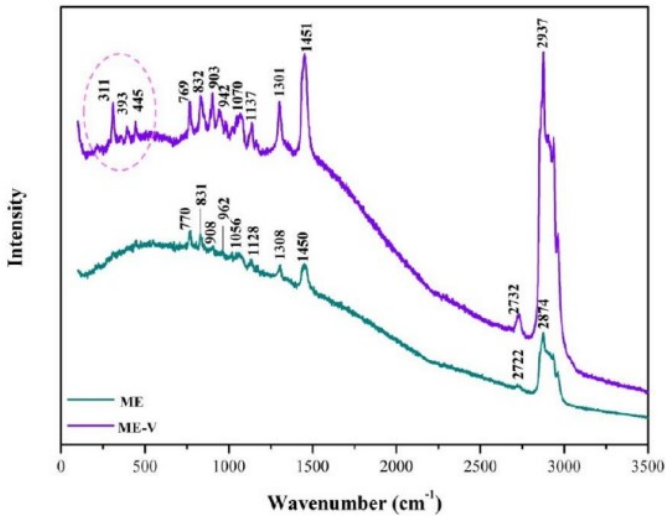

Figure 4. Raman spectra of the microemulsion phase before and after being loaded with POVs [13].

By combination of AIMD simulations and experimental characterization methods, it is revealed that the V-O octahedral coordinated $H_2V_{10}O_{28}^{4-}$ ion can transform into V-O tetrahedral coordinated $V_{10}O_{26}^{2-}$ ion with the inducing of MTA^+ cation, which indicates the high affinity and selectivity of MTA^+ for $H_2V_{10}O_{28}^{4-}$ ion.

3.3 Interaction Mechanism of Ion Exchange

According to the REDOX equation, the ionic form of vanadium in solution can be determined through thermodynamic analysis of the vanadium-aqueous pH diagram [14]. Generally, the occurrence states of vanadium anion change with different pH and vanadate concentrations, which has been proved by study [16], and the distribution areas of vanadium anion occurrence states are shown as Figure 5, in which [V]total represents the molar concentration [15].

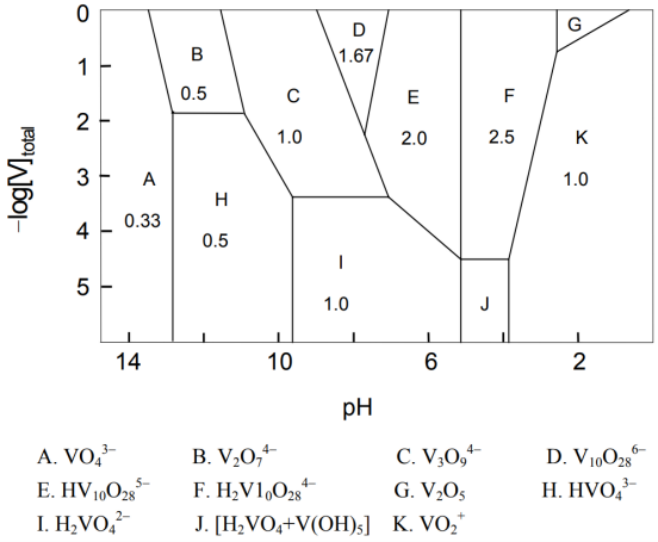

Figure 5. Occurrence states of vanadium in vanadium solution at different pH and total vanadium concentrations [15].

In general, the actual solution concentration of vanadium [V] is > 10^{-3} mol/L, that is, the concentration of V_2O_5 is > 0.091 mg/L, which is distributed in the upper part of the Figure 5, so resin exchange adsorption mainly occurs in the upper half of the Figure 5. When the resin is in contact with the vanadium solution, the vanadium-containing anion is exchanged with the anion in the resin, and the vanadium anion is adsorbed by the resin, and its reaction formula is shown in Table 1.

Table 1. Reaction equations for adsorption of vanadium by resin.

Exchange reaction equation theoretical adsorption capacity	(V/resin) / (mol·mol^{-1})	Main pH range
$VO4^{3-} + 3RCl = R_3VO_4 + 3Cl^-$	1:3 = 0.33	>13
$HVO_4^{2-} + 2RCl = R_2HVO_4 + 2Cl^-$	1:2 = 0.5	11–13
$V_4O_{12}^{4-} + 4RCl = R_4V_4O_{12} + 4Cl^-$	4:4 = 1	8–11
$V_{10}O_6^{28-} + 6RCl = R_6V_{10}O_{28} + 6Cl^-$	10:6 = 1.67	7.2–8.2
$HV_{10}O_5^{28-} + 5RCl = R_5HV_{10}O_{28} + 5Cl^-$	10:5 = 2	5.5–7.2
$H_2V_{10}O_4^{28-} + 4RCl = R_4H_2V_{10}O_{28} + 4Cl^-$	10:4 = 2.5	2.5–5.5

The Na_2O concentration is more than 150g/L in the spent liquor, the pH value is over 14, and the concentration of V_2O_5 contained in it is more than 0.1g/L, therefore, It can be seen from the Figure 5 that the occurrence state of vanadium anion in the spent liquor mainly exists in the form of VO_4^{3-}.

In order to desorb or separate a specific form of V, the binding mechanism of tetravalent vanadium V(IV) and pentavalent vanadium V(V) with carbamic oxalate resin was studied by Li Jie [10]. The Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) were conducted to characterize the resin before and after adsorption. This study revealed the adsorption mechanism of carbamic oxalate and sodium orthovanadate by carbamic oxalate chelating resin.

The results of infrared spectrum analysis are depicted in Figure 6. As shown in Figure 6a, a new V-O absorption peak appeared at 560 cm^{-1} after adsorption of vanadium oxalate. The widening and strengthening of the characteristic peaks of N-O originally located at 935 cm^{-1}could be due to the phenomenon of multiple peaks overlapping, as the absorption peak of V=O is also situated at 900–1000 cm^{-1} [16]. Additionally, the N-O and O-H peaks at 3000–3700 cm^{-1} broadened, suggesting that vanadium was bound to the amine oxime group in the resin. Simultaneously, the absorption peak of C=N became wider, potentially due to overlapping multiple peaks, as the absorption peak of C=O is near 1550 cm^{-1}. These changes in the peaks indicate that the binding of vanadium oxalate to the resin involves both the amino group and the oxime group.

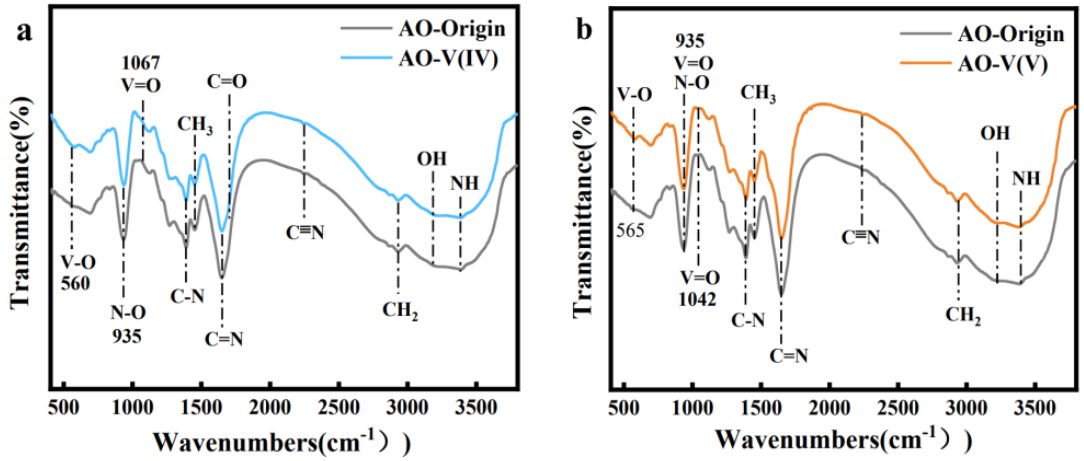

Figure 6. FT-IR of Amidoxime resin before and after adsorption.
Left: (a) of V(IV), Right: (b) of V(V) [10].

As shown in Figure 6b, the comparison between the amidoxime resin after adsorption of sodium vanadate and before adsorption reveals that a new V-O absorption peak appears at 580 cm^{-1} and a V=O absorption peak is evident at 1042 cm^{-1}. Additionally, the N-O and O-H peaks at 3000–3700 cm^{-1} have widened, indicating that vanadium was bound to the amine oxime group in the resin. The change in the peak value suggests that the binding of sodium vanadate and the resin involves both the amino group and the oxime group.

In order to further explore the adsorption mechanism of vanadium oxalate and sodium orthovanadate by amidoxime resin, as well as the valence state and structure of vanadium loaded on the resin, X-ray photoelectron spectroscopy (XPS) was used to characterize the resin before and after adsorption. The results are shown in Figure 7. As shown in Figure 7, absorption peaks of C 1s, N 1s and O 1s appeared both before and after adsorption, with binding energies of 284.8 eV, 400.75 eV and 530.9 eV, respectively. Absorption peaks of V 2s, V 2p, V 3s and V 3p

were present in the resin spectra after adsorption, indicating that vanadium ions form vanadium oxalate and sodium orthovanadate had bonded with amidoxime resin.

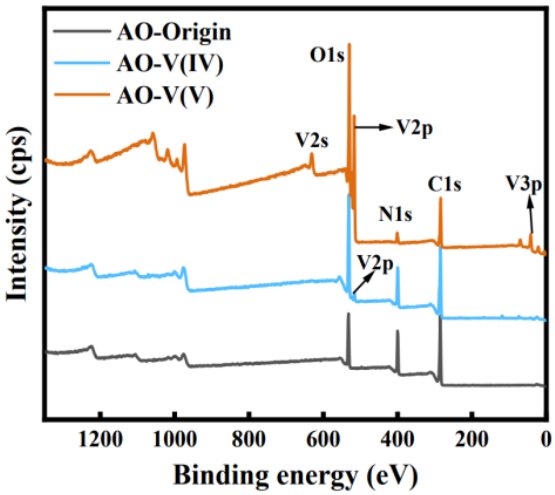

Figure 7. XPS diagram of AO-resin before and after adsorption [10].

Figure 8 shows the XPS spectra of O 1s (a) and V 2p (b). The difference between the adsorption of tetravalent vanadium and pentavalent vanadium observed in the energy spectrum of O 1s. It has been demonstrated that vanadium oxalate and amine oxime resin may be combined through the oxime group. The resin after adsorbing vanadium oxalate, exhibits an additional O^{2-} absorption peak and a C=O peak, indicating that vanadium may be adsorbed onto amine oxime resin in the form of a complex ion formed with oxalate.

The resin after adsorption of sodium orthovanadate, exhibits an additional O^{2-} absorption peak, indicating that vanadium may be adsorbed to amine oxime resin in the form of polyvanadate [17]. The decrease in OH in the oximide group (C=NOH) further confirms that sodium orthovanadate interacted with the oximide group (C=NOH) in the amine oxime resin, as supported by the N 1s energy spectrum. Both the amine group ($C\text{-}NH_2$) and oximide group (C=NOH) are involved in the binding process between sodium orthovanadate and the amine oxime resin [18].

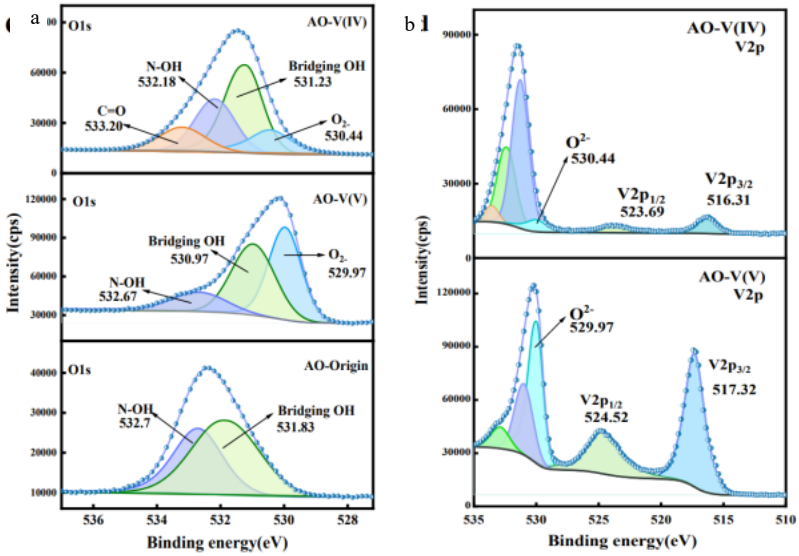

Figure 8. XPS spectra of AO-resin and V-loaded AO-resin.
Left: (a) O 1s, Right (b) V 2p, [10].

The V 2p energy spectrum shows that the binding energies of the absorption peaks for vanadium oxalate on aminoxime resin V 2p3/2 and V 2p1/2 are 516.31 eV and 523.69 eV, respectively. This indicates that vanadium maintains a +4 valence on the resin after adsorption of vanadium oxalate. After sodium vanadate adsorption, the binding energies of V 2p3/2 and V 2p1/2 absorption peaks are 517.32 eV and 524.52 eV, respectively. This suggests that vanadium maintains a +5 valence on the resin after sodium vanadate adsorption.

In the infrared spectrum and X-ray photoelectron spectroscopy, it is evident that vanadium ions in vanadium oxalate are adsorbed to the resin in the form of a complex anion with oxalic acid, while vanadium ions in sodium orthovanadate are adsorbed to the resin as vanadium oxanion.

4. Conclusions

In this paper, the research progress on the removal/recovery of vanadium by precipitation, extraction and ion exchange was reviewed. The aim was to discuss the selective removal/extraction of impurity vanadium from sodium aluminate solution under strong alkali conditions, and to reduce the influence of vanadium on the quality of alumina products. Understanding the mechanism of action of these three methods is crucial for effective vanadium remove or extraction. The paper elucidates, the mechanism of action at a molecular level using molecular dynamics or density functional theory through advanced spectral analysis. The advantageous control process based on the morphological change law of vanadium ions provides references for designing a reasonable extraction/removal path and achieving deep separation of vanadium from aluminium and gallium.

From the standpoint of vanadium removal, the precipitation method can prevent the influence of vanadium on the subsequent extraction of aluminium and gallium from the source. However, due to the pH of Bayer solution exceeding its application range, the extraction method cannot directly act on strong alkaline solution. The ion exchange method can selectively separate gallium and vanadium, but the selectivity of the resin needs further improvement. Through material innovation, the issue of vanadium being difficult to desorb from the resin can be resolved, extending the resin recycle.

In terms of vanadium extraction, a combination of the three methods is necessary. The raw material is obtained through precipitation, and the vanadium-containing aqueous solution is acquired through leaching. Vanadium is then enriched through extraction or ion exchange based on the different valence states of vanadium. Finally, the vanadium product is obtained through crystallization and roasting.

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