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 °C 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

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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6. References

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