Implication of hydrolysis on vanadium precipitation with acidic ammonium salt from high concentration of alkaline vanadium solution

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Abstract−Vanadium precipitation with acidic ammonium salt is widely applied in industrial practice of vanadium pentoxide production. However, the ammonia wastewater produced in the precipitation process and resultant environmental issues have been paid increasing attention. With the intention of reducing wastewater and extra cost, an enhancement in the vanadium content of basic qualified solution is the most directly effective method. Unfortunately, high vanadium concentration brings about a low precipitation rate and a high Na content in ammonium polyvanadate, as a result of hydrolysis existence in the precipitation process. The effect of hydrolytic vanadium reaction on acidic ammonium salt precipitation has rarely been reported. Therefore, the whole precipitation process, including the effect of pH value, reaction temperature and vanadium concentration on precipitation result were clarified by analyzing the thermodynamic form of vanadate radicals in this work. Simultaneously, a study on technological parameters was inquired based on the theoretical analysis. The phase composition and crystal morphology of precipitates were also inspected using XRD and SEM-EDS. The results show the negative reaction of vanadium hydrolysis cannot be eliminated in the process of vanadium precipitation with acidic ammonia salt. When vanadium content is higher than 35 g/L, Na in APV is easy to exceed 0.6%. Na mainly precipitates in $V_2O_5 \cdot H_2O$ in the formation of amorphous body or chemical absorption. The results in this work provide a fundamental guide for the application of high concentration vanadium precipitation technology.

Keywords: Vanadium Precipitation, Alkaline Vanadium Solution, Hydrolysis Reaction, Ammonium Polyvanadate

INTRODUCTION

Vanadium extraction from vanadium slag is a mainstream refining process at home and abroad [1-4], whose capacity accounts for about 70% of the world's total vanadium products in terms of raw material types [5]. Among a multiple of industrial flowsheets, sodium roasting technology plays a dominant role in the production of vanadium oxide [1,6,7]. Throughout the extraction procedure, alkaline vanadium solution is first acquired from sodium-salt roasting followed by water leaching and impurities removal. Then vanadium pentoxide product is obtained through a series of processes, including precipitation and calcination. As an indispensable part of the whole craft, vanadium precipitation is usually implemented using ammonium salt in acidic media. Due to the advantages of rapid precipitation, high purity of ammonium polyvanadate (APV) and high vanadium precipitation yield [8-10], acid ammonium salt precipitation technology has been generally prevalent in vanadium recovery plants worldwide. Nevertheless, the above-mentioned precipitation method produces large amounts of acidic wastewater with high salinity and ammonia nitrogen [11-13]. In modern factories, a treatment process of reduction neutralization and evaporation is usually utilized [14-16], creating significant additional costs. For example, if a qualified solution of 30 g/L is taken as raw liquid, nearly 25 m³ of

wastewater is to be generated during the manufacturing process of each ton of V_2O_5.

Industrial production statistics show that each increasing vanadium content of 1 g/L cuts down the wastewater yield by 0.8 m³/t V_2O_5, generating prominently economic and environmental perspectives. Beyond that, the utilization of high concentration of vanadium liquid can increase the capacity of single pot intermittent precipitation. At the same time, new water for leaching and steam, electric power, sulfuric acid for precipitation course will be greatly reduced. The cost-cutting of wastewater treatment is also achieved.

However, increased vanadium content also has some adverse effects on the precipitation process. The higher the vanadium content, the more prone for the hydrolysate to appear, contributing to an unqualified APV [17]. Owing to a larger solubility than APV, more vanadium remains in the solution as sodium polyvanadate, resulting in a low vanadium precipitation rate [1,18]. Consequently, the vanadium concentration of alkaline solution for acidic ammonium vanadium precipitation is not usually higher than 30 g/L in real application.

Considering hydrolysis of vanadium in a sodium-salt roasting leachate system, the hydrolysate was identified as a mixture of polyvanadic acid and sodium polyvanadate [18]. The formation course of sodium polyvanadate, e.g., $Na_2V_{12}O_{31}$ and $Na_2V_{12}O_{30}$ was also early expounded in 2006 [19]. Besides, the effect of Na on the precipitation of APV was studied at a low vanadium concentration of 10.97 g/L [20]. And the conclusions revealed that Na did not incorporate into the precipitate at a range of 0-8.33 g/L, and the crystal-

linity of the precipitate deteriorated with the increase of introduced Na. Whereas, there are few studies on the influence regularity of hydrolysis on precipitation from highly concentrated vanadium solution by acidic ammonium salt technology, which is of great significance to improve the quality and yield of precipitate.

In our study, the existence of forms of vanadium under different pH values was analyzed, and the effect of temperature and concentration on hydrolysis side reaction was, respectively, elucidated. Based on thermodynamic results, critical parameters such as pH value, temperature, and vanadium concentration, were investigated in detail using ICP-OES, SEM-EDS and XRD techniques. Combined with theoretical analysis, process test and morphology characterization, the influence mechanism of hydrolysis on vanadium precipitation by acid ammonium salt was elaborated in this research. The results suggest that hydrolysis of vanadium occurs simultaneously with ammonium precipitation, as a key factor controlling the quality of APV. For the popularity of high concentration vanadium precipitation technology, the reduction of negative hydrolysis reaction should be proposed as a technical difficulty in the future research.

EXPERIMENTAL

1. Materials and Analysis

The purified vanadium solution was provided by Pangang Group Vanadium & Titanium Co., Ltd., Panzhihua, China, with an initial pH value of 9.0. Its main chemical composition is exhibited in Table 1. The other chemical reagents utilized in this study were all analytical grade, including H_2SO_4 (95.0%-98.0%vol) and $(NH_4)_2SO_4$ (>99.0%wt). Deionized water was utilized in every experiment for sediment washing.

The content of V, Cr in qualified solution were determined by the method of ammonium persulfate oxidation and ammonium ferric sulfate titration. Inductively coupled plasma-optical emission spectroscopy (ICP-OES-OES, iCAP6300, Thermo Fisher Scientific, USA) was employed to analyze the other ions in qualified liquid, the residual V in the supernatant, as well as Na_2O and K_2O in APV. The pH value of vanadium liquid was examined by a digital pH meter (pHSJ-3F, INESA, China) with an accuracy degree of 0.01. The phase analysis of dried APV product was executed by X-ray diffractometer (Empyrean, PANalytical, Holland) using Co-Ka radiation (λ=0.154056 nm). The operating voltage was 35 kV and the current was 50 mA. The θ-2θ step-scan mode was used for scanning ranging from 10° to 80° with a scanning speed of 2°/min. Micro morphology and element distribution of APV samples were done with a scanning electron microscope (SEM, Sigma 500, ZEISS, Germany) equipped with an energy dispersive spectrometer (EDS, Oxford, UK).

2. Method

Vanadium precipitation tests in this research were carried out by a process of adding acid twice and ammonium salt once. First, each 200 mL of qualified solution was measured and poured into a beaker, heating it to 60 °C in water bath and regulating the pH value to 5.0-6.0 with H_2SO_4. Then, a certain amount of ammonium salt was added into the beaker. After stirring and dissolving, the pH value was further adjusted to 2.0. As far as the pH adjustment is concerned, a deviation of 0.05 is usually allowed. Continuing to heat to 95 °C, the precipitation reaction was kept under the conditions of stirring and boiling temperature for some time. Finally, solid-liquid separation and sediment washing were conducted. The upper liquid volume after precipitation was measured and the vanadium content was analyzed in order to calculate the vanadium precipitation rate. The main impurities content of obtained APV, such as K_2O and Na_2O, was detected after drying. The calculation formulas of ammonium salt addition coefficient K and vanadium precipitation rate φ were shown in Eq. (1) and (2), respectively.

$$K = \frac{m(NH_4)_2SO_4}{m(TV)} \tag{1}$$

$$\varphi = \frac{C_0 \times V_0 - C_1 \times V_1}{C_0 \times V_0} \times 100\% \tag{2}$$

Herein, $m((NH_4)_2SO_4)$ is the dosage of ammonium sulfate, g; $m(TV)$ is the total vanadium content in the solution, g; C_0 is the vanadium concentration of qualified solution, $g \cdot L^{-1}$; C_1 is the vanadium concentration in the upper liquid, $g \cdot L^{-1}$; V_0 is the volume of qualified liquid, mL; V_1 is the volume of upper liquid, mL.

Note that K and Na are the main impurities in APV crystallized from a sodium-salt roasting leachate with acidic ammonium salt precipitation. Metallurgical industry standard in China (YB/T 5304-2017) requires the total content of K_2O and Na_2O (a calculation form) in V_2O_5 (98.0-P) not to exceed 1.00%. After calcination and deamination of every 1,000 kg APV, the theoretical weight of V_2O_5 is 910 kg. Therefore, the total content of K_2O and Na_2O in APV has a standard critical value of 0.91% in theory. The K content in alkaline vanadium solution is usually very low, and the content of K_2O in APV is generally not more than 0.10%. Consequently, a single 0.81% of Na_2O content can be identical to the upper limit of APV quality criterion, which equals 0.60% in terms of Na.

RESULTS AND DISCUSSION

1. Thermodynamic Analysis

The occurrence form of vanadium in solution is closely related to pH value, temperature, and concentration [21,22]. In this part, the stable existing zone of different ionic forms of vanadium in solution was investigated. The transformation process of vanadium was studied in the process of vanadium precipitation by acidic ammonium salt, as well as the reaction conditions of hydrolysates and the quality of precipitation product.

1-1. V-pH Diagram

At room temperature, the existence form of vanadium in solution changing with pH value and concentration is demonstrated in Fig.

Table 1. Composition of test solution /g·L⁻¹

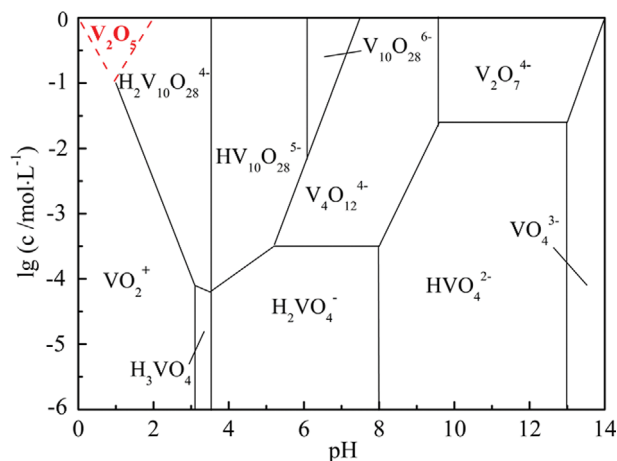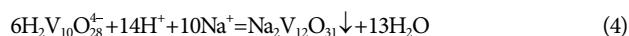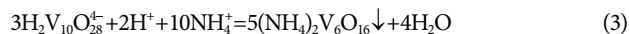| Elements	V	Cr	K	Na	Si	P
Qualified vanadium solution	46.25	2.38	0.224	43.6	1.31	0.012

Fig. 1. Existing form of vanadium at different pH values and concentrations (25 °C).

1 [1].

Vanadium mainly exists in the form of pentavalent in alkaline vanadium solution with a high concentration usually ranging from 30 to 50 g/L and a pH value around 13.0. As can be seen from Fig. 1, a gradual transition from $V_2O_7^{4-}$ to $V_4O_{12}^{4-}$, $V_{10}O_{28}^{6-}$, $HV_{10}O_{28}^{5-}$, $H_2V_{10}O_{28}^{4-}$ and V_2O_5 occurs in the transformation process from basic to acidic solution. The definite pH range of vanadium precipitation with acidic ammonium salt is usually between 2.0 and 2.5.

Presumably, there simultaneously exists the following chemical precipitation reactions at 25 °C [19]:

$$3H_2V_{10}O_{28}^{4-}+2H^++10NH_4^+=5(NH_4)_2V_6O_{16}\downarrow+4H_2O \qquad (3)$$

$$6H_2V_{10}O_{28}^{4-}+14H^++10Na^+=Na_2V_{12}O_{31}\downarrow+13H_2O \qquad (4)$$

In the light of formula (4), $Na_2V_{12}O_{31}$ can be rewritten as $Na_2O\cdot 6V_2O_5$. In some relevant works, the hydrolysate of vanadium in alkaline solution is also written as $xNa_2O\cdot yV_2O_5\cdot zH_2O$ [1,9]. It can be observed that the occurrence of vanadate hydrolysis reaction leads to a certain amount of sodium polyvanadate in APV.

1-2. E-pH Diagrams

On account of the analysis in Section 3.1.1, the key factor affecting the content of Na in APV is the parallel hydrolysis reaction of $H_2V_{10}O_{28}^{4-}$. To further analyze the thermodynamic influence of higher temperature on hydrolysis process, the E-pH diagrams of V-H$_2$O system with a vanadium concentration of 0.8 mol/L (about 40 g/L) were drawn using FactSage 6.4 and shown in Fig. 2.

As seen in Fig. 2, the regions of VO_4^{3-}, $V_2O_7^{4-}$, $HV_2O_7^{3-}$ and $H_2V_{10}O_{28}^{4-}$ at 60 °C and 95 °C all fade away compared with those at 25 °C, indicating temperature has a great influence on the existing form of vanadium in solution. The vanadate is directly converted from HVO_4^{2-} to $HV_{10}O_{28}^{5-}$ in the process of pH adjustment before vanadium precipitation. Furthermore, the area of V_2O_5(s) region gradually shrinks with the increase of temperature, indicating that higher reaction temperature is beneficial to alleviate the hydrolysis
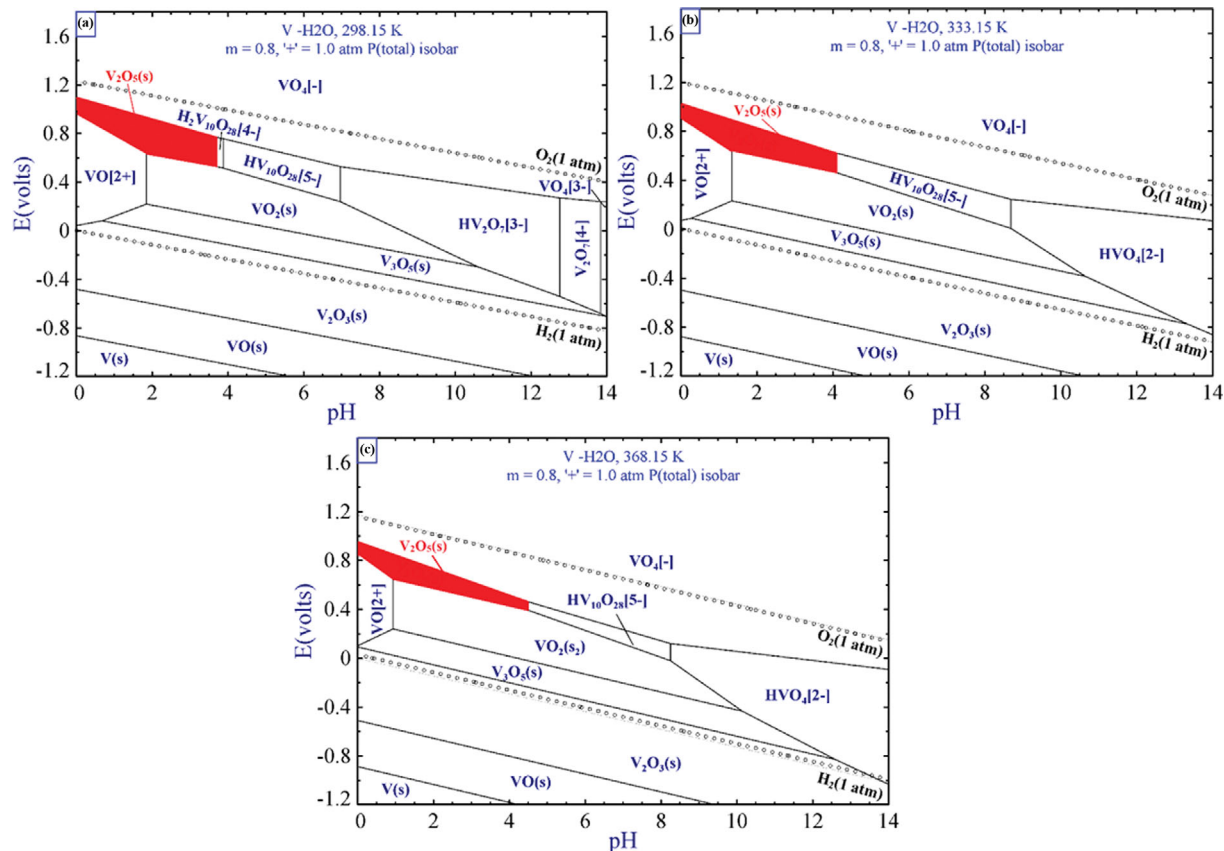

Fig. 2. E-pH diagrams of V-H₂O system at different temperatures ((a) 25 °C, (b) 60 °C, (c) 95 °C).
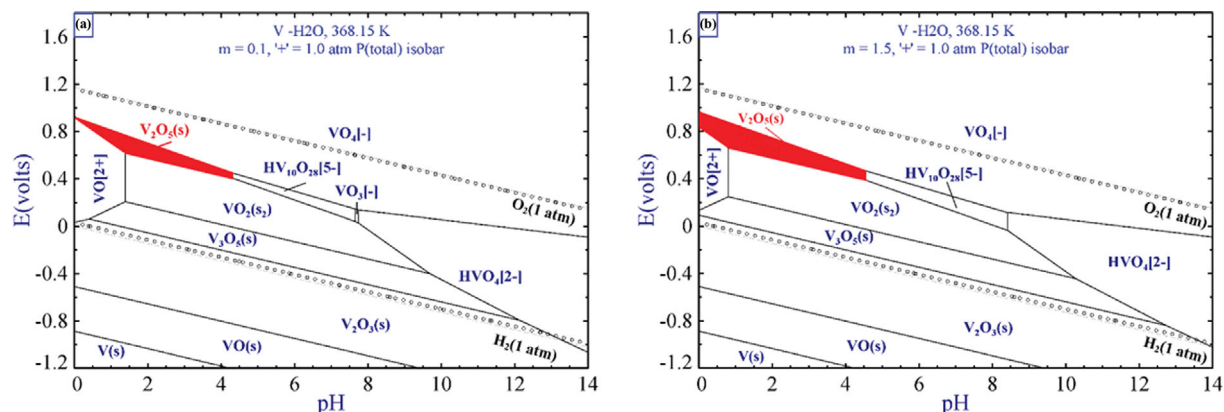
Fig. 3. E-pH diagrams of V-H$_2$O system at different concentrations ((a) 0.1 mol/L, (b) 1.5 mol/L).
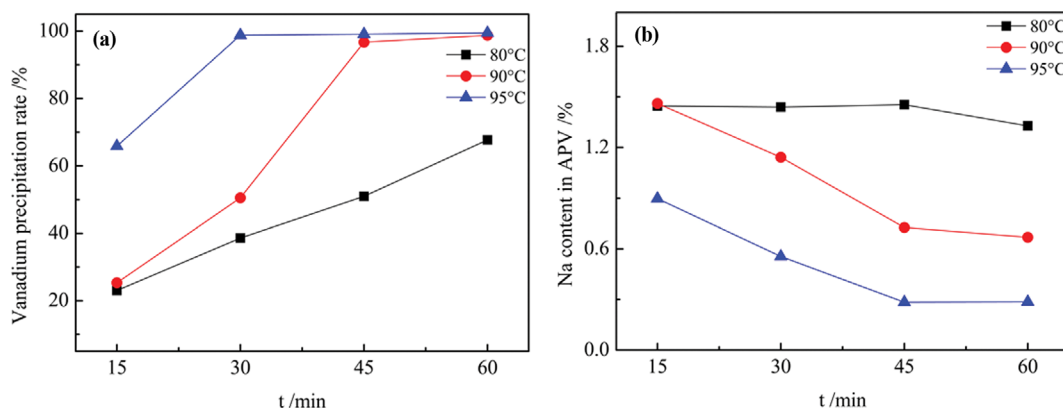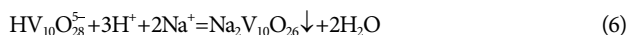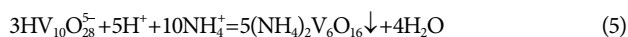

Fig. 4. Vanadium precipitation result obtained at different temperatures.

reaction. Above 60 °C, the following chemical precipitation reactions can be deduced:

$$3HV_{10}O_{28}^{5-}+5H^++10NH_4^+=5(NH_4)_2V_6O_{16}\downarrow+4H_2O \qquad (5)$$

$$HV_{10}O_{28}^{5-}+3H^++2Na^+=Na_2V_{10}O_{26}\downarrow+2H_2O \qquad (6)$$

On the other hand, the E-pH diagrams of different vanadium concentrations at 95 °C are described in Fig. 3, including Fig. 2(c). Here, a phenomenon is not difficult to figure out that V$_2$O$_5$(s) region exists at every concentration and the vanadium hydrolysis reaction tends to appear when the pH is less than 4.5. The larger the vanadium concentration, the larger V$_2$O$_5$(s) interval area, representing the easier to form hydrolysate.

The above thermodynamic results indicate that an inevitable hydrolysis reaction coexists in the vanadium precipitation process by acid ammonium salt technology. In the hope of an excellent quality of APV, it is a priority to mitigate the degree of hydrolytic vanadium.

2. Process Research

In this part, the ammonium addition coefficient (K) of 1.6 was fixed. The effects of reaction temperature, time, pH value and vanadium concentration on vanadium precipitation result were principally investigated.

2-1. Reaction Temperature and Time

The reaction temperature of vanadium precipitation directly affects

the chemical reaction rate and determines the dissolution rate of hydrolysate. Higher temperature can accelerate the diffusion rate of APV crystal and the reaction process at the liquid-solid interface, which is conducive to crystal growth [23,24]. At a suitable temperature, sufficient reaction time is also a guarantee of good crystallization. The qualified solution exhibited in Table 1 was diluted to get a solution with vanadium content of 30 g/L. Vanadium precipitation experiments were executed at 80, 90, 95 °C for 15, 30, 45 and 60 min, respectively, and the result is presented in Fig. 4.

The data in Fig. 4 demonstrates that the vanadium precipitation rate is less than 70% even if kept for 60 min at 80 °C, and Na content in the deposit is 1.33%, which cannot meet the production standard. At the precipitation temperature of 90 °C and maintaining time of 45 min, vanadium precipitation rate increases to 99% above, while Na content in APV is 0.73%. Even though the precipitation time is increased to 60 min, vanadium precipitation rate and Na content have no significant changes. When the reaction temperature continues to rise to 95 °C, vanadium precipitation rate can reach more than 99% after only 30 min. In the meantime, Na content in APV is 0.55%, which satisfies the subsequent needs. Hence, vanadium precipitation by acidic ammonium salt should be done at a higher temperature, which is consistent with the results of thermodynamic analysis in Section 3.1.2. After the vanadium precipitation time increased to 45 min at 95 °C, Na content decreased to 0.28%. According to the results in reference [22], vanadium precipitation rate could
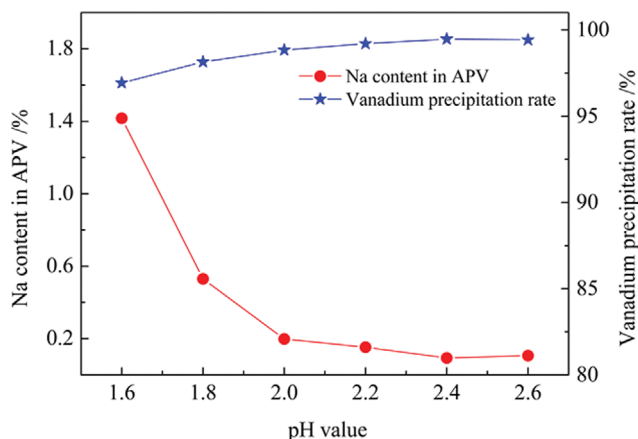
Fig. 5. Vanadium precipitation result obtained at different pH values.

Fig. 6. Effect of concentration on vanadium precipitation.

reach above 99.38% and Na content drop to 0.30% under the optimal conditions of pH 2.0-2.5 and reaction temperature over 95 °C for 120 min. Nevertheless, the effect of holding time was not described too much.

To ensure a higher vanadium precipitation rate and better product quality, reduce energy consumption and improve the production efficiency, an optimum precipitation operation should be kept at 95 °C for 45 min.

2-2. pH Value

In addition to temperature, pH value in the vanadium precipitation course also has a great influence on the composition and impurity of crystal product. A diluted vanadium solution with concentration of 30 g/L was adopted to test and precipitate for 45 min at 95 °C. The influence of precipitation pH value on vanadium precipitation result is displayed in Fig. 5.

It can be seen from Fig. 5, when the precipitation pH value is between 1.6 and 2.6, vanadium precipitation rate increases first and then tends to be basically stable after 2.0, with a value of above 99%. On the other hand, Na content in APV gradually decreases with the increase of pH value. When pH is 1.6, the content of Na in APV is 1.42%, the precipitates are reddish brown and a side reaction of hydrolysis is obvious. When pH value is not less than 1.8, Na content in APV drops significantly below 0.60%. Due to the decrease of hydrogen ion concentration in the solution, the hydrolysis reaction is gradually replaced by the substitution reaction of NH_4^+, and Na content decreases accordingly. Moreover, when the pH value is higher than 2.4, the loose density of APV decreases to less than 0.5 g/cm³, resulting from the change of APV aggregation state [17,25]. Therefore, the appropriate vanadium precipitation pH value should be 2.2 in the consideration of vanadium precipitation rate and product quality.

2-3. Vanadium Concentration

The qualified alkaline solution provided in Table 1 was considered as the feed solution. The experimental vanadium solution with different concentrations was prepared through dilution or evaporation to ensure a proper V/Na ratio. The influence of vanadium concentration on precipitation effect was investigated and the results are shown in Fig. 6.

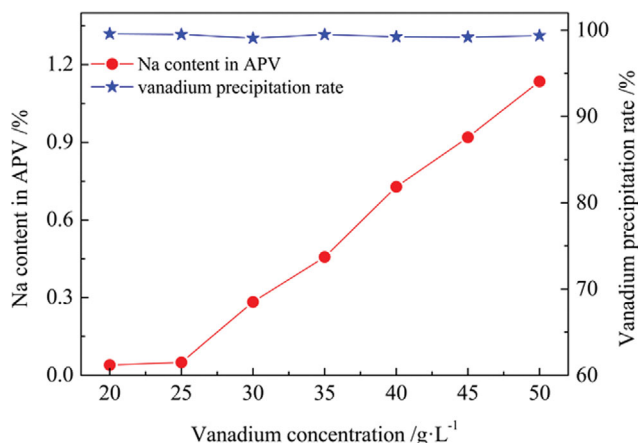As seen in Fig. 6, the vanadium precipitation rate has little change

with increasing concentration of vanadium in solution, which is all above 99%. The vanadium concentration in the upper liquid can be reduced below 0.15 g/L. The content of Na in APV increases with the improvement of vanadium concentration in the range of 20 to 50 g/L. When vanadium concentration exceeds 25 g/L, the Na content in APV rises greatly. At the vanadium content of 35 g/L, Na in APV has a content of 0.46%. With increasing the concentration of vanadium, the value of Na is about to excess 0.6%, which does not meet the criteria requirement.

In relevant published works, vanadium concentration is currently being studied using artificial prepared vanadium liquid [24], which cannot reflect the actual composition and proportion. Under another specific condition that vanadium liquid was added into the beaker drop by drop, the maximum allowable concentration of vanadium reached 70 g/L [17]. Admittedly, taking such an approach, local overconcentration in the solution was prevented from generating burst nucleation. But the dropwise addition operation is time consuming and impractical.

2-4. Phase and Morphology

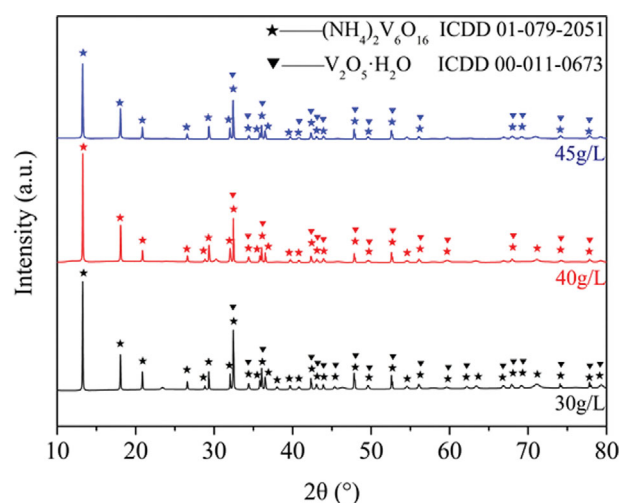In accordance with the optimization of process parameters, the

Fig. 7. XRD patterns of precipitated products at different vanadium concentrations.

following conditions were acquired: K=1.6, precipitation pH of 2.2, temperature of 95 °C and holding time of 45 min. The XRD patterns of the precipitated products at 30 g/L, 40 g/L and 45 g/L are exhibited in Fig. 7.

It can be seen that the precipitate is mainly composed of $(NH_4)_2V_6O_{16}$ and $V_2O_5 \cdot H_2O$. Additionally, $V_2O_5 \cdot H_2O$ appears in all these deposits, indicating the hydrolyzed reaction cannot be avoided in the process of vanadium precipitation by acidic ammonium salt, which is consistent with the thermodynamic result. Compared with the XRD spectrum of the precipitated product at 30 g/L, the diffraction peak intensity of $(NH_4)_2V_6O_{16}$ in the spectra at 40 g/L and 45 g/L is clearly weakened, illustrating that crystallinity decreases with the increase of vanadium concentration.

At a low vanadium concentration of 10.97 g/L, Na content with a range of 0-8.33 g/L had no effect on the precipitate composition, which always remained in the form of $(NH_4)_2V_6O_{16}$ [20]. Meanwhile, some previous findings showed that the precipitate mainly consists of $NH_4V_3O_8 \cdot 0.5H_2O$ with a concentration range of 30-50 g/L [17,22]. At a precipitation pH of 2.0, temperature of 90 °C and precipitation time of 60 min, the vanadium precipitate contains $NaV_3O_8 \cdot xH_2O$ and $Na_2V_6O_{16} \cdot 3H_2O$, except for the purpose component of $(NH_4)_2V_6O_{16}$ [9]. That temperature and pH value have a major effect on the precipitate composition is further illustrated.

The microscopic morphology of different sediments at a vanadium concentration of 30 g/L, 40 g/L and 45 g/L is demonstrated in Fig. 8.

It can be observed that the precipitated particles from alkaline

Table 2. EDS analysis result of different areas shown in Fig. 8 /wt%

Label	Blocky areas			Acicular areas		
	1	3	5	2	4	6
Na	0.01	0.92	0.06	2.25	2.54	2.02
V	62.62	61.25	64.53	65.90	66.76	65.98

vanadium solution using acidic ammonium salt method are not of uniform size. Most crystal grains are present in blocky form and some in needle form. Both blocky crystals and acicular crystals are randomly distributed and disordered. In view of the EDS analysis results of different regions listed in Table 2, Na content in nubbly grains (points 1, 3 and 5) is significantly lower than that in flocculent grains (points 2, 4 and 6). Combined with XRD results, it can be inferred that the phase composition of blocky grain is $(NH_4)_2V_6O_{16}$ (APV), while the acicular grain mostly consists of $V_2O_5 \cdot H_2O$. No diffraction peak of sodium vanadate is found in Fig. 7, indicating Na possibly precipitates in $V_2O_5 \cdot H_2O$ in the form of amorphous body or chemical absorption. Obviously, the presence of Na has a certain effect on the crystal morphology of APV. In terms of the previous study [20], at a low vanadium concentration of 10.97 g/L, the crystallinity of APV increased first and then decreased with the increase of Na concentration from 0 to 8.33 g/L. The introduced Na did not incorporate into the precipitate. The morphology of the precipitate is free from the effect of Na and always remains flaky. As to high concentration of vanadium solution, the crystallinity of APV may be synergistically affected by the content of V and Na.
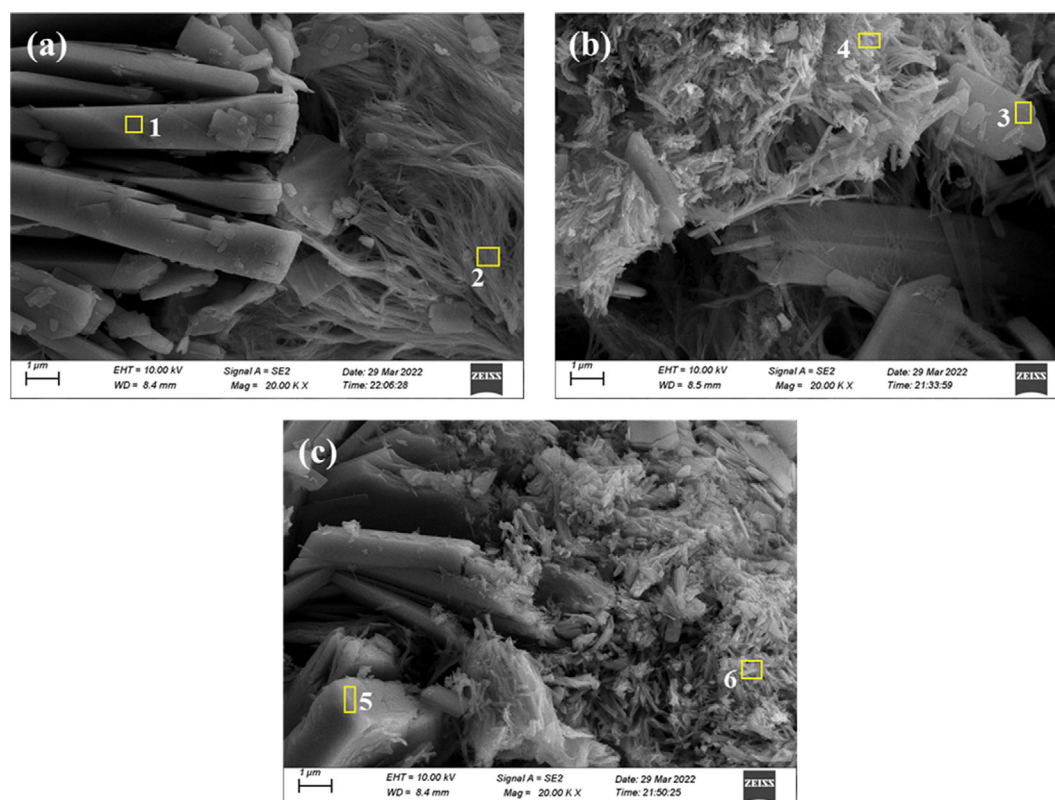

Fig. 8. SEM of precipitation products at different concentrations ((a) 30 g/L, (b) 40 g/L, (c) 45 g/L).

CONCLUSIONS AND RECOMMENDATION

This paper reports an experimental work on the effect of hydrolysis on acidic ammonium salt vanadium precipitation that has been applied to extract high-purity APV compounds from a sodium-salt roasting leachate. From the theoretical analysis and experimental results, the following conclusions are summarized.

(1) According to the thermodynamics analysis of V-H_2O system, it is first confirmed that negative hydrolysis reaction is unavoidable in the precipitation process with acid ammonium salt from high concentration of alkaline vanadium solution.

(2) An allowable maximum vanadium content is obtained in the optimal condition of ammonium salt dosage, pH, reaction temperature and time. In the hope of qualified APV product, the concentration of vanadium precipitation should not exceed 35 g/L.

(3) By combining the results of XRD and SEM-EDS, the acidic ammonium salt precipitate is mainly the mixture of APV and $V_2O_5 \cdot H_2O$, which is mingled with a certain amount of Na. For the application of vanadium precipitation with high concentrated solution, the first concern should be given to the mitigation of hydrolysis.

In summary, to reduce the adsorption of Na in hydrolysate and obtain a favorable quality of APV, it is essential to restrain the hydrolysis in the precipitation process of highly concentrated vanadium solution. The reasonable use of crystal seed and the exploitation of continuous vanadium precipitation technology are expected to be the focus of future research.

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DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this work.

Authorship Contribution Statement

Lin Jiang: Conceptualization, Investigation, Data arrangement, Manuscript writing. Guangchao Du: Review and Graphic processing. Hao Zheng: Editing and Characteristic analysis. Wenyi He: Methodology and Software. Yi Peng: Formal analysis and Supervision.

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