



Dissolving behavior of ammonium paratungstate in (NH₄)₂CO₃–NH₃·H₂O–H₂O system

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Abstract: The effects of temperature, ammonia concentration and ammonium carbonate concentration on the dissolving behavior of ammonium paratungstate were studied in (NH₄)₂CO₃–NH₃·H₂O–H₂O system. The results show that rising temperature, prolonging duration, increasing ammonia concentration and decreasing ammonium carbonate concentration favor dissolving of ammonium paratungstate at temperature below 90 °C, while the WO₃ concentration decreases after a certain time at temperature above 100 °C. Furthermore, the undissolved tungsten exists in the form of either APT·4H₂O below 90 °C or pyrochlore-type tungsten trioxide above 100 °C. In dissolving process, the ammonium paratungstate dissolves into paratungstate ions followed by partially converting to tungstate ion, resulting in the coexistence of the both ions. This study may provide a new idea to exploit a novel technique for manufacturing ammonium paratungstate and pyrochlore-type tungsten trioxide.

Key words: ammonium paratungstate; dissolving behavior; ammonium carbonate; ammonia; pyrochlore-type tungsten trioxide

1 Introduction

Ammonium paratungstate (APT·4H₂O) is an important intermediate in the process of tungsten metallurgy. The main methods for most of the commercial production of APT·4H₂O are caustic soda leaching [1] and soda ash leaching [2], although the synergistic decomposition of scheelite by sulfuric–phosphorous mixed acid has been successfully applied in Xiamen Tungsten Co. Ltd., recently [3,4]. The impure sodium tungstate solution was obtained by decomposing tungsten concentrates, and then the ammonium tungstate solution was prepared by purification and conversion, finally the APT·4H₂O product was manufactured by evaporative crystallization [5]. But these methods consume a large amount of auxiliary materials and generate a lot of wastewater, leading to a serious environmental pollution [6]. The main reason is that, a mass of high salinity wastewater generated in the conversion process of sodium tungstate solution, and ammonia nitrogen wastewater created in the evaporative crystallization, are difficult to handle and unable to recycle economically [7]. So, these methods are difficult to meet the requirements of modern tungsten industry,

due to the increasingly strict environmental protection provisions.

In order to achieve solution circulation and reduce material consumption and effluent discharge, we proposed a novel extractive technology for tungsten metallurgy [8,9], in which ammonium tungstate solution was directly prepared by roasting tungsten concentrates followed by leaching the roasted product with aqueous ammonium carbonate solution. In this technology, tungsten-bearing minerals in tungsten concentrate were converted into Ca₃WO₆ and/or Ca₂FeWO₆ by roasting [10,11], and then the roasting product was leached by excess ammonium carbonate solution to obtain ammonium tungstate–ammonium carbonate–ammonia solution. And the leaching residue obtained can be reused as a raw material in the roasting process, and the carbon dioxide and ammonia generated in the evaporative crystallization can be absorbed to synthesize the leaching reagent, achieving a “closed-circulation” of main auxiliary materials used for producing APT·4H₂O.

The evaporative crystallization of APT·4H₂O and other tungsten compounds from ammonium tungstate solution is an important operation in tungsten metallurgy. Therefore, better understanding the dissolution/precipitation behavior of APT and other tungsten

compounds in ammonium tungstate systems, is vitally important for efficient operation and product quality control in evaporative crystallization. van PUT [12] studied the dissolution process of APT in aqueous ammonia. His results showed that, there mainly exist three kinds of tungstate species, i.e., paratungstate A ion ($[\text{HW}_6\text{O}_{20}(\text{OH})_2]^{5-}$), paratungstate B ion ($[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$) and tungstate ion, and they can transform mutually. The existence form of tungstate species is mainly influenced by pH value of the solution, and tungstate ion can be successively transformed into paratungstate A ion and paratungstate B ion with the decrease of pH. Duration has an important influence on the transformation of different tungstate species, and tungstate ion can convert to paratungstate A ion in some minutes, and to paratungstate B ion in some days. HARTL et al [13] believed that paratungstate A is $[\text{W}_7\text{O}_{24}]^{6-}$. Because the solubility of APT is the vital parameter affecting crystallization efficiency, van PUT et al [14] investigated APT dissolving in $\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$, and pointed out that WO_3 concentration in the solution still increased even after dissolving for 167 h, implying that it is difficult to obtain the accurate solubility data. LUTZ [15] studied the dissolving behavior of $5(\text{NH}_4)_2\text{O}\cdot 12\text{WO}_3\cdot 7\text{H}_2\text{O}$ in $\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$ system and reported that the dissolution quantity and rate of WO_3 decreased with the increase of initial ammonia concentration. WAN et al [16] tried to determine the solubility of $\text{APT}\cdot 4\text{H}_2\text{O}$ in $\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$ system and $\text{NH}_4\text{Cl}-\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$ system [17]. Their results showed that the dissolution quantity and rate of WO_3 increased with increasing temperature and duration, but the influence of initial ammonia concentration was contrary to that obtained by LUTZ [15]. It should be noted that, $\text{APT}\cdot 4\text{H}_2\text{O}$ was used and dissolved for only 22 h [17], meaning that they did not obtain the real solubility according to the research by van PUT [14]. These studies above contribute to comprehending the precipitation process of APT in $\text{NH}_3\cdot\text{H}_2\text{O}-(\text{NH}_4\text{Cl})-\text{H}_2\text{O}$ system, but the investigation report of APT dissolving in $(\text{NH}_4)_2\text{CO}_3-\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$ system is unavailable till now.

Aiming to understand the crystallization and dissolving behavior of APT in $(\text{NH}_4)_2\text{CO}_3-\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$ solution, we used dissolving balance method [18] to study the influences of temperature, ammonia concentration and ammonium carbonate concentration on the dissolving behavior of $\text{APT}\cdot 4\text{H}_2\text{O}$ in $(\text{NH}_4)_2\text{CO}_3-\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$ system. In addition, to provide a theoretical guidance for the preparation of tungsten compound in $(\text{NH}_4)_2\text{CO}_3-\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$ system containing tungsten, researches of tungstate species in solution and phase components of undissolved tungsten were conducted.

2 Experimental

2.1 Materials

Double-distilled water, analytically pure ammonium carbonate and ammonia were used in the experiments. The ammonium paratungstate provided by Jiangxi Rare Metals Tungsten Holdings Group Co., Ltd., China was zero grade $(\text{NH}_4)_{10}\text{H}_2\text{W}_{12}\text{O}_{42}\cdot 4\text{H}_2\text{O}$ and its X-ray diffraction (XRD) pattern is shown in Fig. 1.

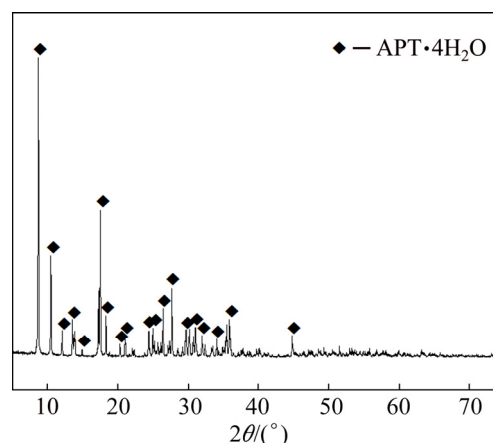


Fig. 1 XRD pattern of $\text{APT}\cdot 4\text{H}_2\text{O}$

2.2 Methods

$\text{APT}\cdot 4\text{H}_2\text{O}$ (30 g), ammonium carbonate/ammonia solution (100 mL), three big steel balls ($d=18$ mm) and three small steel balls ($d=8$ mm) were put into a steel bomb (150 mL) with teflon inner. The bomb was sealed, placed in glycerol at a preset temperature and then rotated for a certain time at 150 r/min to enhance agitation. The obtained slurry was filtrated, and the filtrate was analyzed by thiocyanate spectrometry with spectrophotometer of SP-752 (China) to determine WO_3 concentration, and by KBr tableting method with infrared spectrometer of Nicolet6700 (America) to survey tungstate species in the solution. The filter cake was washed with alcohol, dried at 70°C for 8 h and then analyzed to observe its phase and morphology by X-ray diffraction analyzer ($\text{Cu K}\alpha$, $8^\circ/\text{min}$) of Bruker D8-Advance (Germany) and scanning electron microscopy of JSM-6360LV (Japan), respectively.

3 Results and discussion

3.1 Influence of temperature

As temperature affects the dissolution of substance, the influence of temperature on the dissolving behavior of $\text{APT}\cdot 4\text{H}_2\text{O}$ in $(\text{NH}_4)_2\text{CO}_3-\text{NH}_3\cdot\text{H}_2\text{O}-\text{H}_2\text{O}$ system was first examined. The relationship between WO_3 concentration in the solution and the dissolving time of $\text{APT}\cdot 4\text{H}_2\text{O}$ at $60-120^\circ\text{C}$ is shown in Fig. 2.

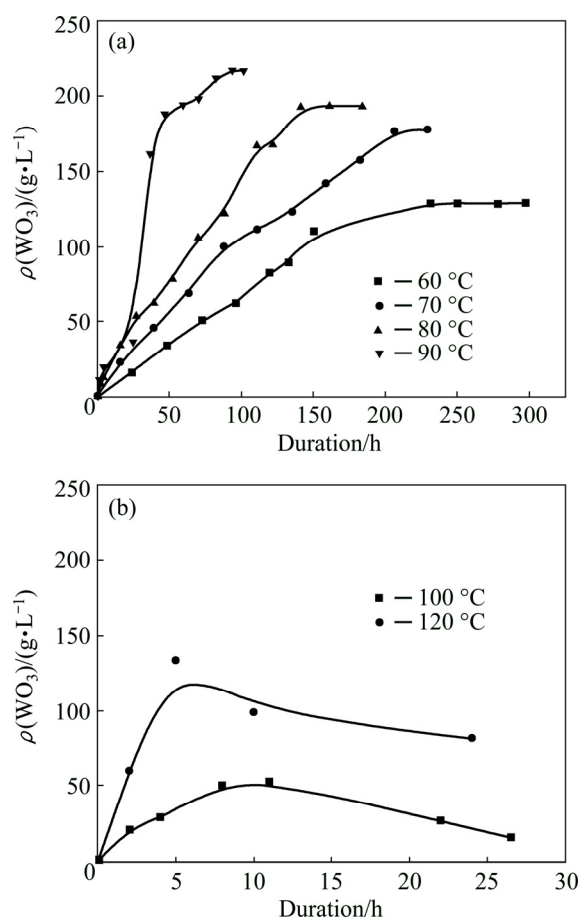


Fig. 2 Effect of temperature on concentration of tungsten in solution (470 g/L $(\text{NH}_4)_2\text{CO}_3$, 90 g/L NH_3)

As seen in Fig. 2(a), the concentration of WO_3 in solution increases with the temperature rising, which indicates that the increase of temperature can promote the $\text{APT}\cdot 4\text{H}_2\text{O}$ dissolving. In addition, WO_3 concentration reaches a relatively stable value after a specific dissolving time at 60–90 °C, and the value increases with temperature increasing. When the temperatures were 60, 70, 80 and 90 °C, the relatively stable WO_3 concentrations were correspondingly 129, 178, 193 and 218 g/L, respectively. Furthermore, the increase of temperature can shorten the duration acquired for reaching the relatively stable WO_3 concentration in $\text{APT}\cdot 4\text{H}_2\text{O}$ dissolving. That is to say, in the range of 60–90 °C, the increase of temperature is conducive to the dissolution of APT in $(\text{NH}_4)_2\text{CO}_3\text{--NH}_3\cdot\text{H}_2\text{O--H}_2\text{O}$ system, which can be attributed to the endothermic reaction of this process.

The changes in WO_3 concentration with the dissolution time of $\text{APT}\cdot 4\text{H}_2\text{O}$ at 100 and 120 °C are shown in Fig. 2(b). The WO_3 concentration increases in the early stage and then decreases, which is obviously different from that at below 90 °C. For example, when the durations are 168 and 312 h, the corresponding concentrations of WO_3 are 74.5 and 47.9 g/L, being in

agreement with the dependence of the relatively stable WO_3 concentration on temperature in aqueous ammonia system reported by van PUT et al [19].

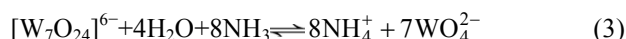
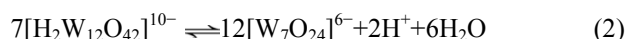
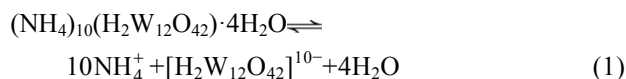
Theoretically, higher temperature should be favorable for the dissolution of $\text{APT}\cdot 4\text{H}_2\text{O}$, but at 100 and 120 °C the experimental phenomena, such as the dependence of WO_3 concentration on duration, the color of filter cake, are different from those at below 90 °C, suggesting that elevated dissolving temperature may cause solid phase transformation.

3.2 Effects of ammonia concentration

In the evaporative crystallization process of $\text{APT}\cdot 4\text{H}_2\text{O}$, the decrease of ammonia concentration in the solution leads to the drop of pH, causing that tungstate ion convert to paratungstate ions and $\text{APT}\cdot 4\text{H}_2\text{O}$ precipitates ultimately from the solution. Obviously, as the inverse process of crystallization, the dissolution of $\text{APT}\cdot 4\text{H}_2\text{O}$ is inevitably affected by the concentration of ammonia. Therefore, it is necessary to study the effect of ammonia concentration on the dissolving process of $\text{APT}\cdot 4\text{H}_2\text{O}$ and the experimental results are shown in Fig. 3.

Figure 3 shows that, at the same temperature, the dissolution rate of $\text{APT}\cdot 4\text{H}_2\text{O}$ and the relatively stable WO_3 concentration in the system increase with the increase of ammonia concentration. The dissolution rate of $\text{APT}\cdot 4\text{H}_2\text{O}$ is extremely small at 90 °C without ammonia, while the relatively stable WO_3 concentrations at 90 °C for 94 h with ammonia concentrations of 30, 60 and 90 g/L are 86, 158 and 217 g/L, respectively. With the increase of temperature, the time required to reach the relatively stable WO_3 concentration shortens, which has little to do with ammonia concentration. The increase of ammonia concentration enhances the dissolution of $\text{APT}\cdot 4\text{H}_2\text{O}$, which can be explained as follows.

According to the relationship between tungstate species and solution pH reported by van PUT [12], the dissolving process of $\text{APT}\cdot 4\text{H}_2\text{O}$ can be described as the following three steps in turn:



Due to the solubility and dissolution rate of $\text{APT}\cdot 4\text{H}_2\text{O}$ in water, Reaction (1) is not the rate-determining step of dissolving process. $[\text{W}_{12}\text{O}_{42}\text{H}_2]^{10-}$ is produced by the dissolving of $\text{APT}\cdot 4\text{H}_2\text{O}$, then converts to $[\text{W}_7\text{O}_{24}]^{6-}$ and H^+ by Reaction (2), and $[\text{W}_7\text{O}_{24}]^{6-}$ further transforms to WO_4^{2-} with the action of ammonia by Reaction (3). Obviously, the increase of ammonia concentration is beneficial to Reaction (3)

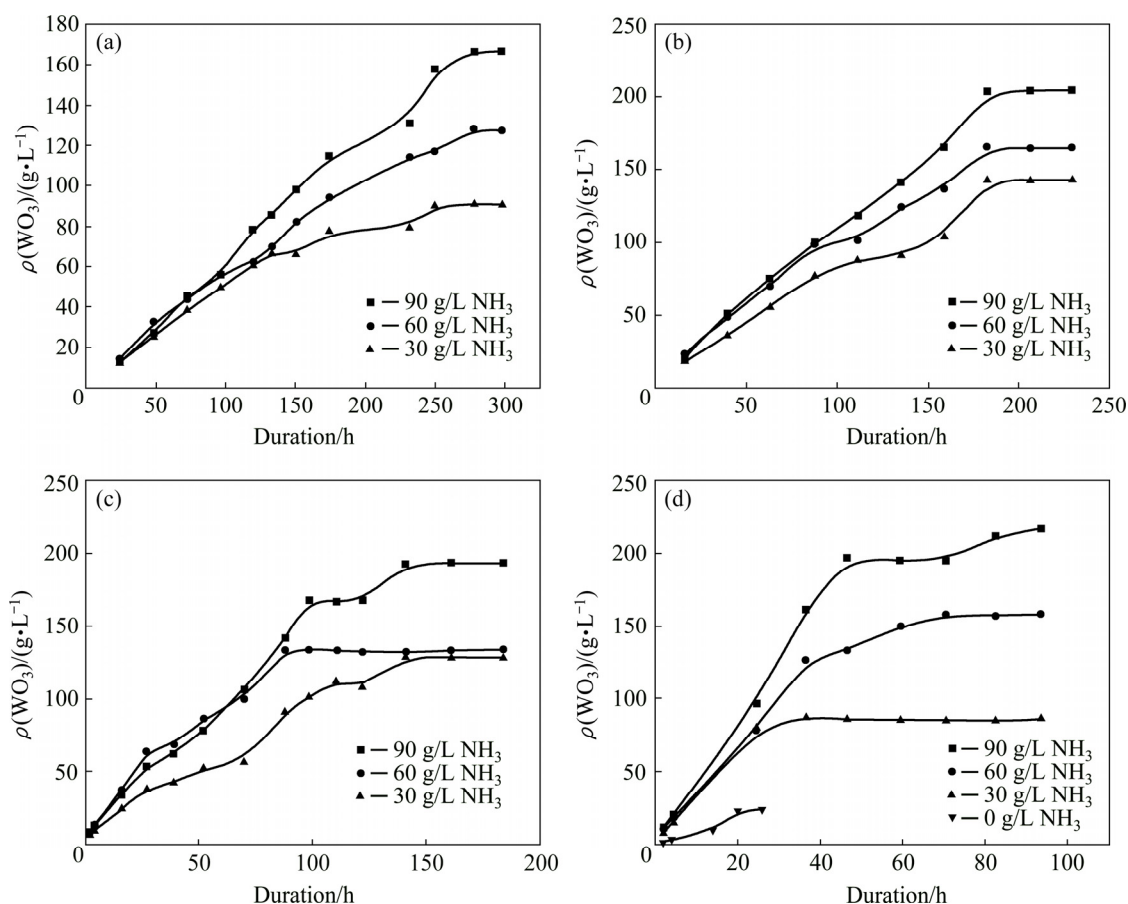


Fig. 3 Effect of NH_3 concentration on WO_3 concentration in solution with 470 g/L $(\text{NH}_4)_2\text{CO}_3$ at different temperatures: (a) 60 °C; (b) 70 °C; (c) 80 °C; (d) 90 °C

forwards. On the other hand, H^+ concentration reduces by the neutralization of OH^- and the combination of the lone pair electrons of NH_3 with H^+ , promoting Reaction (2) forwards. So, the increase of ammonia concentration contributes to the dissolution of $\text{APT} \cdot 4\text{H}_2\text{O}$.

3.3 Influence of ammonium carbonate concentration

According to Reactions (1) and (3), the concentration of NH_4^+ will also influence the dissolving process of $\text{APT} \cdot 4\text{H}_2\text{O}$, and it will change with the variation of $(\text{NH}_4)_2\text{CO}_3$ concentration in solution. So, experiments for the effect of ammonium carbonate concentration on the dissolving process of $\text{APT} \cdot 4\text{H}_2\text{O}$ were carried out and the results are depicted in Fig. 4.

As we can see in Fig. 4, when the $(\text{NH}_4)_2\text{CO}_3$ concentration ranges from 230 to 470 g/L, ammonium carbonate concentration has no obvious effect on the dissolving process of $\text{APT} \cdot 4\text{H}_2\text{O}$ at 60 and 70 °C, while the dissolution rate of $\text{APT} \cdot 4\text{H}_2\text{O}$ decreases with the increase of ammonium carbonate concentration at 80 and 90 °C. The relatively stable WO_3 concentration decreases with the increase of ammonium carbonate concentration in this system. In the dissolving process of $\text{APT} \cdot 4\text{H}_2\text{O}$, the time needed for reaching the relatively stable WO_3

concentration reduces with increasing temperature, and is little related to the concentration of ammonium carbonate.

The phenomenon that ammonium carbonate to some extent inhibits the dissolution of $\text{APT} \cdot 4\text{H}_2\text{O}$ can be interpreted as follows. On one hand, the increase of ammonium carbonate concentration raises the concentration of NH_4^+ in solution, which hinders the Reactions (1) and (3) progressing towards right. On the other hand, the hydrolysis ability of NH_4^+ ($\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 \cdot \text{H}_2\text{O} + \text{H}^+$) is stronger than that of CO_3^{2-} ($\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$), which leads to the generation of H^+ and thus inhibits Reaction (2) forwards.

3.4 pH variation in dissolving process of $\text{APT} \cdot 4\text{H}_2\text{O}$

According to Reactions (1)–(3), besides the tungstate species in the solution, the concentrations of NH_4^+ , H^+ and NH_3 will change and thus cause pH variation of the solution in dissolving process of $\text{APT} \cdot 4\text{H}_2\text{O}$. Therefore, it is necessary to examine the pH variation in the dissolving process of $\text{APT} \cdot 4\text{H}_2\text{O}$ in $(\text{NH}_4)_2\text{CO}_3$ – $\text{NH}_3 \cdot \text{H}_2\text{O}$ – H_2O system with different concentrations of ammonia and ammonium carbonate.

As shown in Fig. 5(a), at different ammonia concentrations, solution pH declines slowly in the APT·4H₂O dissolving, which was caused by the continually generating H⁺ by Reaction (2). The higher the ammonia concentration, the higher the pH in dissolving process, promoting both Reactions (3) and (2) towards right, which can further explain the conclusion in section 3.2 that the increase of ammonia concentration favors the dissolution of APT·4H₂O. Figure 5(b) shows that solution pH decreases slightly with the increase of

ammonium carbonate concentration and dissolution time. These experimental results match with the conclusion that ammonium carbonate blocks the dissolution of APT·4H₂O in section 3.3.

3.5 Structural changes of tungstate species in dissolving process

To reveal the mechanism of APT·4H₂O dissolving process, the structural changes of tungstate species in dissolution were studied by FTIR.

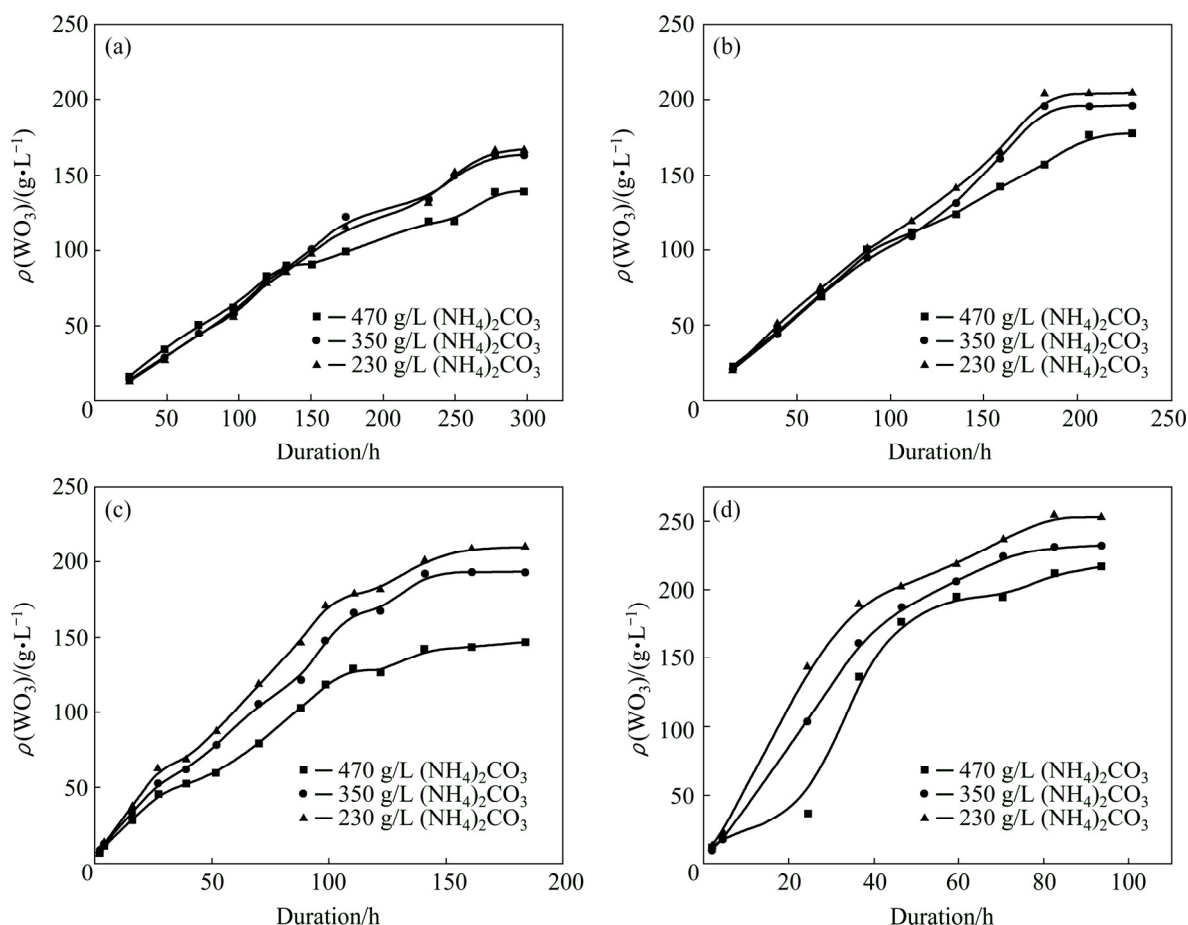


Fig. 4 Effect of $(\text{NH}_4)_2\text{CO}_3$ concentration on WO_3 concentration in solution with 90 g/L NH_3 at different temperatures: (a) 60 °C; (b) 70 °C; (c) 80 °C; (d) 90 °C

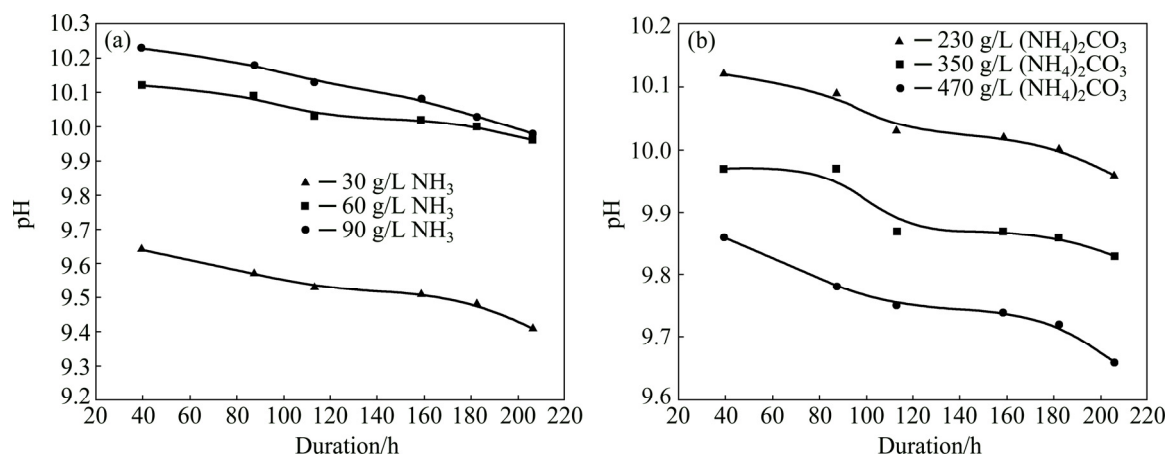


Fig. 5 Variation of solution pH with dissolution time of APT·4H₂O at 70 °C: (a) 470 g/L $(\text{NH}_4)_2\text{CO}_3$; (b) 90 g/L NH_3

The infrared spectra of solution were recorded after $\text{APT} \cdot 4\text{H}_2\text{O}$ dissolving at 70°C for different time in the solution with 90 g/L ammonia and 470 g/L ammonium carbonate, as shown in Fig. 6. It was reported that 834 cm^{-1} corresponds to vibration bands of WO_4 tetrahedron [20] and 931 cm^{-1} to vibration bands of WO_6 hexahedron [21], respectively representing tungstate ion and paratungstate ions. In the dissolving process, the intensities of characteristic peaks of 834 and 931 cm^{-1} increase gradually, but the increase of peak 834 cm^{-1} is stronger. This means that paratungstate ions form and then convert to tungstate ion in $\text{APT} \cdot 4\text{H}_2\text{O}$ dissolving, resulting in the coexistence of paratungstate and tungstate ions in the system. It should be noted that, the slight position deviation of the two peaks can be attributed to the variations of both system composition and solution pH in dissolving process.

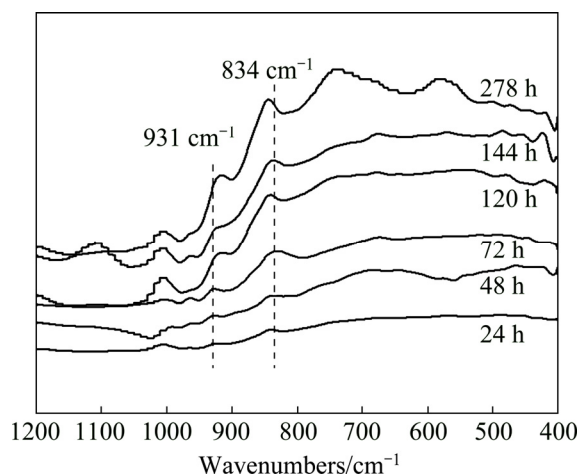


Fig. 6 FTIR spectra of solutions obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ for different time (470 g/L $(\text{NH}_4)_2\text{CO}_3$, 90 g/L NH_3 , 70°C)

Figure 7 represents the effect of ammonia concentration on the FTIR spectra of solutions obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ at 70°C for 175 h with 470 g/L ammonium carbonate. The characteristic peaks at 834 and 931 cm^{-1} become strong with ammonia concentration increasing from 30 to 90 g/L, while the change of characteristic peak centred at 834 cm^{-1} is more obvious. It can be deduced that, increasing ammonia concentration accelerates paratungstate ions converting to tungstate ion and thus benefits $\text{APT} \cdot 4\text{H}_2\text{O}$ dissolving. Additionally, 680 and 1003 cm^{-1} respectively correspond to bending vibration band of CO_3^{2-} and stretching vibration band of HCO_3^- [20].

Finally, the influence of ammonium carbonate concentration on the FTIR spectra of solutions prepared by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ at 70°C for 175 h with 90 g/L ammonia, is shown in Fig. 8. With the concentration of ammonium carbonate increasing from 230 to 470 g/L,

the characteristic peak intensity of tungstate ion (834 cm^{-1}) reduces slightly while that of paratungstate ions (931 cm^{-1}) increases, attributing to solution pH increase caused by increasing ammonium carbonate concentration.

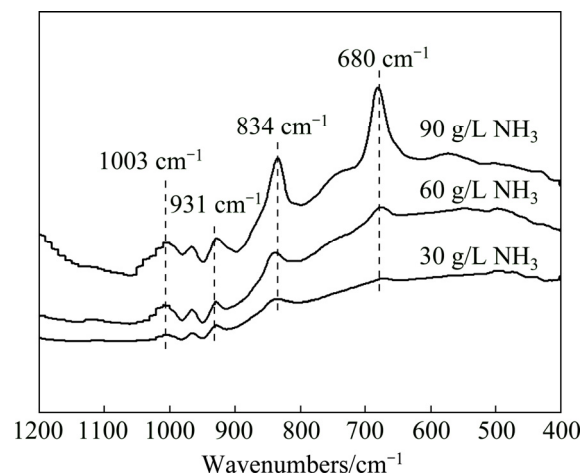


Fig. 7 FTIR spectra of solutions obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ with different NH_3 concentrations at 70°C (470 g/L $(\text{NH}_4)_2\text{CO}_3$, 175 h)

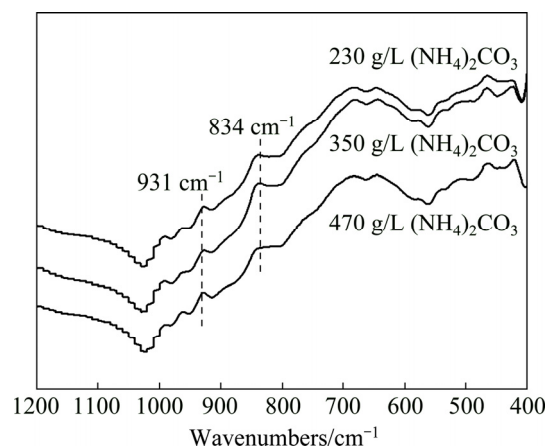


Fig. 8 FTIR spectra of solutions obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ with different $(\text{NH}_4)_2\text{CO}_3$ concentrations (70°C , 90 g/L NH_3 , 175 h)

3.6 Solid phase analysis and morphology evolution

It has been described in section 3.1 that, the phase of the residual solid after $\text{APT} \cdot 4\text{H}_2\text{O}$ dissolving at below 90°C may be different from that at above 100°C . The solid phases after reaction at 70 and 120°C were analyzed by XRD and scanning electron microscope (SEM).

The XRD patterns of residual solids are shown in Fig. 9, where the residual solids were obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ at 70°C for 167 h with different concentrations of ammonium carbonate and ammonia. Figure 9 shows that the residual solids are still $\text{APT} \cdot 4\text{H}_2\text{O}$ and no new solid phase appears.

As shown in Fig. 10, the XRD patterns of the obtained residual solids manifest that there exists $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ besides $\text{APT} \cdot 4\text{H}_2\text{O}$ after $\text{APT} \cdot 4\text{H}_2\text{O}$ dissolving at 100 and 120 °C for 12 h, which signifies that $\text{APT} \cdot 4\text{H}_2\text{O}$ dissolves into tungstate species and then forms $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ precipitates. This can explain that WO_3 concentration increased first and then decreased

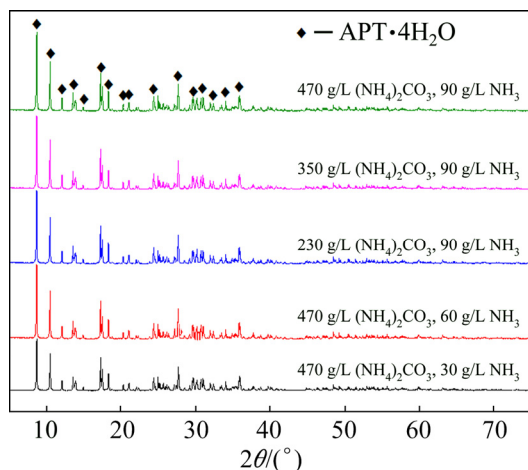


Fig. 9 XRD patterns of residual solids obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ at 70 °C for 167 h

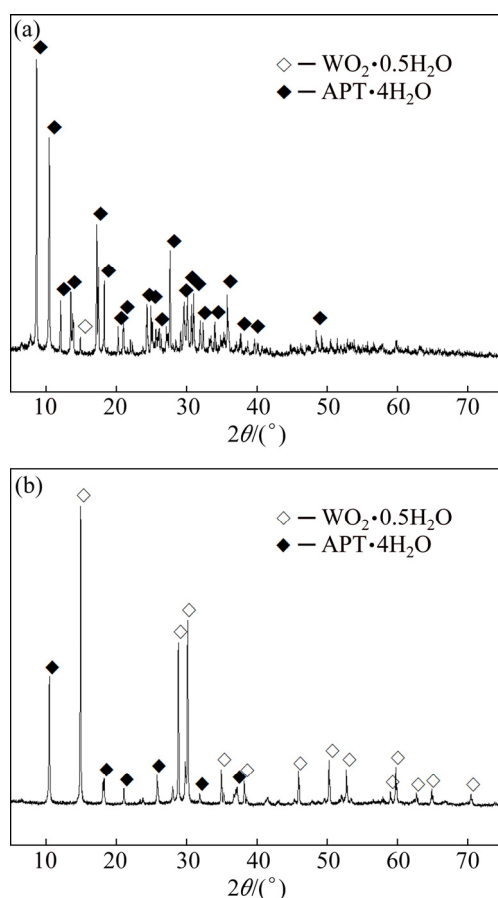


Fig. 10 XRD patterns of solid phase obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ at 100 (a) and 120 °C (b) (90 g/L NH_3 , 470 g/L $(\text{NH}_4)_2\text{CO}_3$, 12 h)

above 100 °C (Fig. 2). However, van PUT et al [19] ascribed the fact that relatively stable WO_3 concentration at 93 °C is lower than that at 65 °C in aqueous ammonia to the lower solubility of ammonia at higher temperatures. Furthermore, the finding means that $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ might be prepared in $(\text{NH}_4)_2\text{CO}_3$ – $\text{NH}_3 \cdot \text{H}_2\text{O}$ – H_2O system containing tungstate, which will be investigated in our future work.

Figure 11 shows the change in morphology of residual solids obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ at different temperatures in solutions with 90 g/L ammonia and 470 g/L ammonium carbonate. Obviously, there is a large difference in the morphology between the starting sample and the residual solids. Compared with the starting $\text{APT} \cdot 4\text{H}_2\text{O}$ particles as cubic, coarse and clear surface (Fig. 11(a)), the residual solid obtained at 70 °C

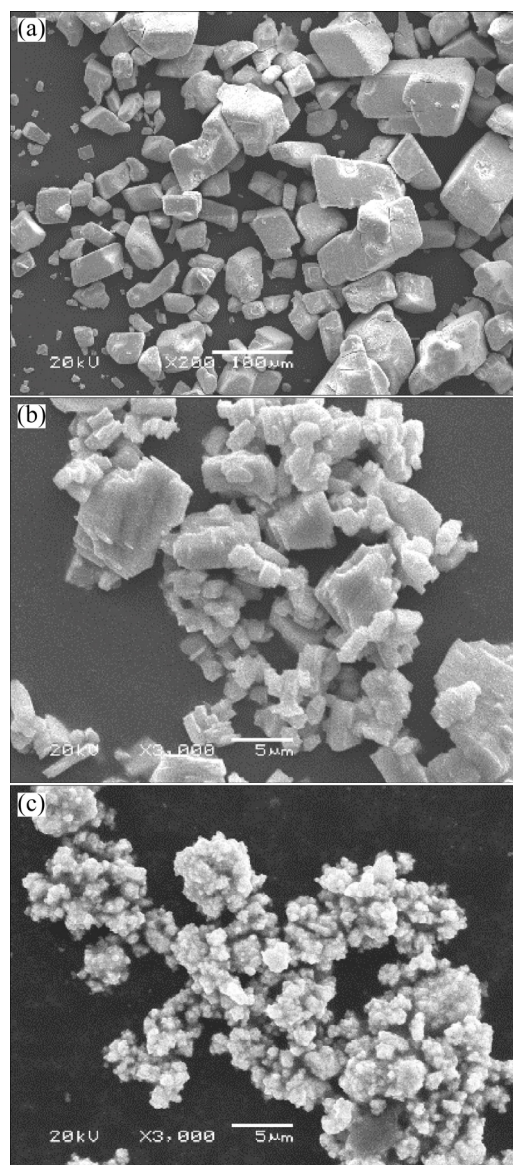


Fig. 11 SEM images of starting $\text{APT} \cdot 4\text{H}_2\text{O}$ (a) and residual solids obtained by dissolving $\text{APT} \cdot 4\text{H}_2\text{O}$ in solution with 90 g/L ammonia and 470 g/L ammonium carbonate at 70 °C after 229 h (b) and at 120 °C after 30 h (c)

after 229 h becomes smaller and more irregular (Fig. 11(b)), while that obtained at 100 and 120 °C after 30 h becomes aggregate with much finer grains (Fig. 11(c)). This suggests that $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ is generated through nucleation from the solution, and may provide a new idea for preparing pyrochlore-type tungsten trioxide, being quite different from those methods reported in Ref. [22].

4 Conclusions

1) In the dissolving process of $\text{APT} \cdot 4\text{H}_2\text{O}$ in $(\text{NH}_4)_2\text{CO}_3\text{--NH}_3 \cdot \text{H}_2\text{O--H}_2\text{O}$ system, WO_3 concentration in solution increases with increasing temperature, reaction time and ammonia concentration at below 90 °C, while it decreases with increasing ammonium carbonate concentration. Whereas, WO_3 concentration in solution increases and then decreases with the extension of reaction time at above 100 °C.

2) In the $\text{APT} \cdot 4\text{H}_2\text{O}$ dissolving process, paratungstate ions form and then convert to tungstate ions, resulting in coexistence of paratungstate and tungstate ions. Increasing reaction time and ammonia concentration can promote paratungstate ions transforming to tungstate ion, while increasing ammonium carbonate concentration impedes the transformation.

3) $\text{WO}_3 \cdot 0.5\text{H}_2\text{O}$ can precipitate from solution in the $\text{APT} \cdot 4\text{H}_2\text{O}$ dissolving process at above 100 °C, which leads to the relatively stable WO_3 concentration decreasing. By contrast, there is no new solid phase emerging at below 90 °C.

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仲钨酸铵在 $(\text{NH}_4)_2\text{CO}_3\text{--NH}_3\cdot\text{H}_2\text{O--H}_2\text{O}$ 体系中的溶解行为

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摘 要: 研究 $(\text{NH}_4)_2\text{CO}_3\text{--NH}_3\cdot\text{H}_2\text{O--H}_2\text{O}$ 体系中温度、氨水浓度和碳酸铵浓度对仲钨酸铵($\text{APT}\cdot 4\text{H}_2\text{O}$)溶解行为的影响。结果表明: 当温度低于 90 °C 时, 随着温度的升高、时间的延长、氨水浓度的增加和碳酸铵浓度的降低, $\text{APT}\cdot 4\text{H}_2\text{O}$ 溶解量增大; 而当温度高于 100 °C 时, 溶解过程中 $\text{APT}\cdot 4\text{H}_2\text{O}$ 溶解量先升高再下降; 当温度低于 90 °C 时, 未溶解物仍以 $\text{APT}\cdot 4\text{H}_2\text{O}$ 形态存在; 当温度高于 100 °C 时, 未溶解物则主要以焦绿石型三氧化钨($\text{WO}_3\cdot 5\text{H}_2\text{O}$)形态存在; 溶解过程中, $\text{APT}\cdot 4\text{H}_2\text{O}$ 先溶解为仲钨酸根离子继而部分转变为正钨酸根离子, 最终溶液中正钨酸根离子和仲钨酸根离子共存。该研究可为 $\text{APT}\cdot 4\text{H}_2\text{O}$ 生产新工艺的开发和 $\text{WO}_3\cdot 5\text{H}_2\text{O}$ 的制备提供新思路。

关键词: 仲钨酸铵; 溶解行为; 碳酸铵; 氨水; 焦绿石型三氧化钨

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