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Sustainable and efficient leaching of tungsten in ammoniacal ammonium carbonate solution from the sulfuric acid converted product of scheelite

Leiting Shen^{1,2}, Xiaobin Li^{1,*}, Qiusheng Zhou^{1,*}, Zhihong Peng¹, Guihua Liu¹, Tiangui Qi¹, Pekka

Taskinen²

¹ Central South University, School of Metallurgy and Environment, Changsha 410083, China

² Aalto University, School of Chemical Engineering, Metallurgical Thermodynamics and Modeling Research Group, Espoo 02150, Finland

*Corresponding authors, e-mail: x.b.li@csu.edu.cn; qszhou@csu.edu.cn

Abstract: To directly obtain solution of $(\text{NH}_4)_2\text{WO}_4$ instead of Na_2WO_4 is the key for developing a cleaner technology of ammonium paratungstate production. In this paper, ammoniacal ammonium carbonate solution was adopted for leaching tungsten from the converted product, a mixture of H_2WO_4 and CaSO_4 obtained by treating scheelite with sulfuric acid. The research indicates that tungsten can be efficiently extracted in form of ammonium tungstate solution with WO_3 leaching yield of $> 99.5\%$ under moderate leaching conditions. The WO_3 leaching yield is influenced by the transformation of calcium sulfate to calcium carbonate due to forming CaWO_4 through the secondary reaction between CaSO_4 and $(\text{NH}_4)_2\text{WO}_4$, whereas an excess $(\text{NH}_4)_2\text{CO}_3$ (≥ 0.64 mol/L) can suppress the secondary reaction by facilitating the transformation. Additionally, the consumed ammonium carbonate can be recovered by treating the leaching residue with ammonium sulfate solution at above 70°C . This work presents a cleaner and sustainable technique for producing ammonium paratungstate, with circulating the leaching reagents and bypassing the conversion of Na_2WO_4 to $(\text{NH}_4)_2\text{WO}_4$.

Keywords: Tungstic acid; Calcium sulfate; Leaching mechanism; Calcium carbonate; Ammonium paratungstate

1. Introduction

As a strategical rare metal, tungsten has wide industrial applications because of its remarkable physical and chemical properties (Lassner et al., 2012; Lassner and Schubert, 1999). Owing to lack of viable substitutes, tungsten was included in the list of critical metals by European Union (European Commission, 2014), and even ranked second among 41 critical elements by British Geological Survey (BGS, 2012). China has more than 60% of tungsten reserves, and accounts for about 80% of tungsten productions in the world (Gunn, 2014). The main natural tungsten minerals are scheelite and

wolframite, which respectively account for 70% and 30% of the resources (Gunn, 2014; BGS, 2012). With the progressive exhaustion of wolframite ore, scheelite has been the chief raw material to extract tungsten (Lassner et al., 2012; Lassner and Schubert, 1999). In the commercial production of ammonium paratungstate (APT), the main industrial intermediate product, caustic/soda or hydrochloric acid is usually used to decompose scheelite concentrate (Gaur, 2006).

Practically, soda or/and caustic soda are employed to decompose scheelite in digestion process producing soluble Na_2WO_4 and insoluble $\text{CaCO}_3/\text{Ca}(\text{OH})_2$, in which both excess reagents (≥ 2.5 stoichiometric ratio of Na_2O to WO_3) and elevated temperature ($> 150^\circ\text{C}$) are required to achieve high WO_3 recovery (Martins, 2014). The obtained sodium tungstate solution is then converted to ammonium tungstate in the purification operation by solvent extraction or ion exchange, simultaneously generating sodium chloride or sodium sulfate solution and thus consuming massive soda or caustic soda (Lassner, 1995). Additionally, vast volume of water is required in solvent extraction or ion exchange process (Yih and Wang, 1979), resulting in discharge of ~20 or 100 tons (Wan et al., 2012) of high-salinity wastewater for per ton APT production, where the later value was even reported as ~126 tons for ion exchange process (Wan et al., 2015a; Wan et al., 2015b). Furthermore, Leal-Ayala et al. (2015) pointed out that 4% of tungsten would be loss in APT production by these processes. Obviously, the caustic soda or soda process raises production cost, and especially poses serious environmental pollution, suggesting the difficulty in economic and cleaner production of tungsten (Liu and Xue, 2010; Li et al., 2017a).

Treating scheelite tungsten concentrate with an appropriate acid may avoid discharging high salinity wastewater. Hydrochloric acid or nitric acid can decompose scheelite tungsten by producing insoluble tungstic acid, which is subsequently leached in aqueous ammonia to obtain ammonium tungstate solution. Martins leached synthetic scheelite in hydrochloric acid (Martins et al., 2003) or nitric acid (Martins, 2003) with pH of 1.5–3.0 at a temperature range of 300–373 K to obtain soluble metatungstates. In the presence of phosphate or phosphoric acid as chelating agent, hydrochloric acid (Xuin et al., 1986; Gurmen et al., 1999; Kahruman and Yusufoglu, 2006; Liu and Xue, 2010) and nitric acid (Zhang et al., 2015) was used to decompose scheelite forming soluble phosphotungstic acid chelate compound ($\text{H}_3\text{PW}_{12}\text{O}_{40}$). The chelating agent can also be hydrogen peroxide with formation of soluble peroxotungstic acid ($[\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})_2]$) (He et al., 2014). However, the discharge of high-salinity wastewater of CaCl_2 or $\text{Ca}(\text{NO}_3)_2$ could not be eliminated in these methods. Potashnikov et al.

(1970) and Kalpakli et al. (2012) used oxalic acid to attack scheelite forming soluble hydrogen aqua oxalate tungstate ($\text{H}_2[\text{WO}_3(\text{C}_2\text{O}_4)\text{H}_2\text{O}]$) and solid CaC_2O_4 , in which no high-salinity wastewater is generated but oxalic acid is relatively expensive. An alternative approach is to use mixture sulfuric acid and phosphoric acid (Li and Zhao, 2016) to treat scheelite concentrate, generating soluble $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and insoluble CaSO_4 . Although this approach may effectively reduce high-salinity wastewater discharge, a certain amount of phosphorus is consumed.

Considering discharge of high-salinity wastewater, volatility, and cost, sulfuric acid is an appropriate candidate to decompose scheelite concentrate (Forward and Vizsolyi, 1965), forming solid H_2WO_4 and CaSO_4 . In our previous work, the conversion of tungsten concentrate in H_2SO_4 solutions was systematically studied, including the mechanism of H_2WO_4 layer formation on unreacted tungsten minerals (Li et al., 2017b; Shen et al., 2018a) and the kinetics of scheelite conversion in sulfuric acid (Shen et al., 2018b). It has been approved that tungsten concentrates can be completely converted in H_2SO_4 solution under appropriate conditions. Therefore, for developing a more sustainable cleaner production of APT in the sulfuric acid route, this work focused on sustainable and efficient leaching of tungsten from the sulfuric acid converted product of scheelite with a suitable leaching agent.

Due to the mature industrial recovery technique of ammonia and ammonium carbonate (Krop, 1999), they are widely used in vanadium (Li et al., 2017c), zinc (Lopez et al., 2017), tungsten (Li et al., 2015), copper (Bingöl et al., 2005), and nickel (Alguacil and Cobo, 1998) extraction processes. When ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solutions are employed to extract tungsten from the converted product of calcium-containing tungsten concentrate, H_2WO_4 reacts with NH_4OH to produce $(\text{NH}_4)_2\text{WO}_4$ according to Eq. (1), and CaSO_4 reacts with $(\text{NH}_4)_2\text{CO}_3$ to form more stable solid CaCO_3 and soluble $(\text{NH}_4)_2\text{SO}_4$ based on Eq. (2) (Murray et al., 2016; Mohammed et al., 2018). This is preliminarily evidenced by previous trial work with the converted products of synthetic scheelite, scheelite and mixed wolframite-scheelite concentrates (Li et al., 2017b; Shen et al., 2018a). Obviously, the secondary reaction (Eq. (3)) between CaSO_4 and $(\text{NH}_4)_2\text{WO}_4$ may take place in the leaching process and decrease the recovery of tungsten. Besides, ammonia and ammonium carbonate have considerably low decomposition temperatures, so that their aqueous solutions can be readily recycled. If $(\text{NH}_4)_2\text{SO}_4$ solution can react with the generated calcium carbonate at high temperature according to Eq. (4), the consumed ammonium carbonate can also be regenerated by absorbing NH_3 and CO_2 gases. In this case, it can not only gain $(\text{NH}_4)_2\text{WO}_4$ solution directly, but also realize the circulation of leaching reagents.

Therefore, we systemically studied the factors influencing the WO_3 leaching yield, such as stirring speed, solution compositions, temperature, and duration when using ammoniacal ammonium carbonate solution to extract tungsten from the sulfuric acid converted product of synthetic scheelite. An attempt was further made to reveal the leaching mechanism and avoid the occurrence of secondary reaction. Moreover, the regeneration of consumed ammonium carbonate was examined by reacting leaching residue with ammonium sulfate solution. This work is conducive to develop a cleaner and sustainable technology of manufacturing ammonium paratungstate, featuring sulfuric acid conversion and ammoniacal ammonium carbonate leaching.

2. Materials and methods

2.1 Materials

All the reagents used in this work were of analytically pure grades, including H_2SO_4 , $\text{NH}_3 \cdot \text{H}_2\text{O}$, Na_2WO_4 , CaCl_2 , and $\text{Ca}(\text{OH})_2$ purchased from Sinopharm Chemical Reagent Co., Ltd, and $(\text{NH}_4)_2\text{CO}_3$ from Aladdin Industrial Corporation.

Synthetic scheelite was prepared by the reaction between sodium tungstate solution and calcium chloride solution. The obtained precipitate (CaWO_4) was washed, dried, and calcined at 1000°C for 2h (Li et al., 2016). XRD pattern of synthetic scheelite is shown in Fig. 1 (a). Synthetic scheelite with fine particle size was decomposed in H_2SO_4 solution with free H_2SO_4 concentration of 1.0 mol/L at 90°C for 2 h. Subsequently, the slurry was filtered to obtain the solid converted product and filtrate. The converted product was washed and dried in an oven at 90°C for 12 h, then used for leaching experiments and XRD analysis. Fig. 1 (b) indicates that synthetic scheelite was completely converted and the converted product was a mixture of H_2WO_4 and CaSO_4 .

Synthetic calcium sulfate (CaSO_4) and synthetic calcium carbonate (CaCO_3) used in the secondary reaction experiments were obtained by adding $\text{Ca}(\text{OH})_2$ powder into H_2SO_4 and $(\text{NH}_4)_2\text{CO}_3$ solutions, respectively. The products were filtered, and the residues washed followed by drying in an oven at 90°C for 12 h. XRD patterns of synthetic calcium sulfate and synthetic calcium carbonate are present in

Fig. 2.

Fig.1. XRD patterns of (a) synthetic scheelite and (b) converted product of synthetic scheelite by sulfuric acid.

Fig. 2. XRD patterns of (a) synthetic calcium sulfate and (b) synthetic calcium carbonate.

2.2 Experimental procedures

2.2.1 Leaching

The leaching experiments were performed in a 100 mL three neck round-bottom flask, which was immersed in a thermostatic water bath with an electronic temperature-controller, in order to guarantee a tiny temperature fluctuation (± 0.5 °C). In each run, 60 mL ammoniacal ammonium carbonate solution was put into the flask and then heated to a preset temperature, followed by addition of 20 g converted product. The initial ratio of liquid (mL) to solid (g) is designated as L/S. The slurry was agitated by a single polytetrafluoroethylene (PTFE) coated impeller (diameter 35 mm, width 8 mm). After a certain duration, the resultant slurry was filtered to obtain a cake and a filtrate. The leaching residue was obtained by washing the cake using deionized water, and dried in an oven at 90 °C for 12 h.

Subsequently, the residue was weighed using an analytical balance, and its WO₃ content was measured using the thiocyanate method (Crouthamel and Johnson, 1954; Srivastava et al., 1996). The leaching yield of WO₃ in ammoniacal (NH₄)₂CO₃ solution was calculated by Equation (5). The standard deviation of the thiocyanate method is less than 2.5 % (Fogg et al., 1970), and thus the error of calculated WO₃ leaching yield is less than 1 %, which was confirmed by standard WO₃ sample in this work.

$$\eta(\text{WO}_3) (\%) = \left(1 - \frac{m_1 w_1}{m_0 w_0}\right) \times 100 \quad (5)$$

where, $\eta(\text{WO}_3)$ is the WO₃ leaching yield (%), m_0 is the initial weight of the converted product ($m_0 = 20$ g), m_1 is the weight of leaching residue (g), w_0 is the WO₃ content in the converted product (wt%), w_1 is the WO₃ content in the leaching residue (wt%).

2.2.2 Secondary reaction verification

The verification experiments were also carried out in a 100 mL three neck round-bottom flask. 2 g synthetic calcium sulfate or synthetic calcium carbonate was added into 50 mL prepared ammonium tungstate solution (0.6 mol/L WO_3 , 3 mol/L free $\text{NH}_3 \cdot \text{H}_2\text{O}$) containing $(\text{NH}_4)_2\text{CO}_3$ with different concentrations, and stirred for 1 h at 30 °C with 350 rpm. The obtained slurry was filtered, washed, and dried to get a sample used for determining WO_3 content.

Phase identification of the sample was performed on Bruker X-ray diffractometer (D8-Advance, Bruker Corporation) with Cu-K α monochromatic X-rays. The diffraction data for 2θ were recorded from 5° to 75° with 0.0085° step size at a scan rate of 2° min⁻¹, while the current and voltage of the X-ray generator were set to 30 mA and 40 kV.

3. Results and discussion

3.1. Leaching experiments

According to Eqs. (1) and (2), H_2WO_4 and CaSO_4 in the converted product have different reaction behaviors in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution. Hence, studies on the effects of stirring speed, $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration, $(\text{NH}_4)_2\text{CO}_3$ concentration, temperature, and duration on the WO_3 leaching yield and transformation of calcium sulfate were carried out.

3.1.1 WO_3 leaching yield

Fig. 3. Influence of stirring speed on WO_3 leaching yield of the converted product in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution (2 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, 2 mol/L $(\text{NH}_4)_2\text{CO}_3$, 30 °C, L/S 3).

First, the effect of stirring speed on the WO_3 leaching yield from the converted product was examined at the range of 250–450 rpm, as demonstrated in Fig. 3. The results indicate that stirring speed has a slight effect on the leaching yield at stirring speeds of 250–350 rpm, but has a negative influence at 450 rpm. The decrease of leaching yield at 450 rpm may be caused by some converted

product adhering to the flask walls or circulating along with stirrer at higher agitation speed. Therefore, stirring speed of 350 rpm was adopted for the subsequent experiments.

According to Eq (1), the concentration of $\text{NH}_3 \cdot \text{H}_2\text{O}$ obviously influences the WO_3 leaching yield from the converted product, as presented in Fig. 4. The WO_3 leaching yield rises remarkably with increasing $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration, and reaches the maximum of 99.9 % with $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration in excess of 2 mol/L. This is in agreement with the reported tendency of WO_3 or APT dissolving in ammonia (Van Put and De Koning, 1992; Van Put and Van Den Berg, 1988/1989).

The concentration of $(\text{NH}_4)_2\text{CO}_3$ may also affect the WO_3 leaching efficiency. As shown in Fig. 5, the WO_3 leaching yield also increases with increasing $(\text{NH}_4)_2\text{CO}_3$ concentration at the initial stage. These can be attributed to the fact that higher CO_3^{2-} concentration in the solution promotes the transformation of CaSO_4 to CaCO_3 according to Eq (2), either by increasing $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration to restrain the hydrolysis of CO_3^{2-} ($\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$) or by raising $(\text{NH}_4)_2\text{CO}_3$ concentration.

Fig. 4. The variation tendency of WO_3 leaching yield with $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution (350 rpm, 2 mol/L $(\text{NH}_4)_2\text{CO}_3$, 30 °C, 90 min, L/S 3).

Fig. 5. The relationship between WO_3 leaching yield and $(\text{NH}_4)_2\text{CO}_3$ concentration in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution (350 rpm, 30 °C, 90 min, L/S 3).

Conventionally, temperature plays an important role in the leaching process. As illustrated in Fig. 6, temperature has little influence on WO_3 leaching yield at $< 30^\circ\text{C}$, whereas increasing temperature reduces the yield at $> 30^\circ\text{C}$ especially with 2 mol/L $\text{NH}_3\cdot\text{H}_2\text{O}$. Van Put et al. (1991) stated that the amount of dissolved tungsten in aqua ammonia decreases at higher temperatures because of the low boiling point ($\sim 36^\circ\text{C}$) of $\text{NH}_3\cdot\text{H}_2\text{O}$, which supports the above result.

Fig. 6. Effect of temperature on WO_3 leaching yield from the converted product in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution (350 rpm, 2 mol/L $(\text{NH}_4)_2\text{CO}_3$, 90 min, L/S 3).

The effect of reaction time on the WO_3 leaching yield from the converted product is illustrated in Fig. 7. The results show that the dissolution reaction of H_2WO_4 in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solutions occurs almost instantaneously, with the WO_3 leaching yield of about 99% within only 15min. The obtained leaching yield varies little with time in the solution bearing 3 mol/L $\text{NH}_3\cdot\text{H}_2\text{O}$, while it slightly decreases with 2 mol/L $\text{NH}_3\cdot\text{H}_2\text{O}$. This implies occurrence of secondary reactions causing tungsten precipitating from the solution.

Fig. 7. Dependence of the WO_3 leaching yield on reaction time in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution (350 rpm, 2 mol/L $(\text{NH}_4)_2\text{CO}_3$, 30°C , L/S 3).

3.1.2 Phase transformation of residue

Conceivably, the behavior of calcium sulfate may affect the leaching process of converted product in ammoniacal ammonium carbonate solution. Hence, the transformation of calcium sulfate should be studied to better understand the leaching process, where the separation of tungstic and calcium is realized in the converted product. The phases in leaching residues obtained under different experimental conditions were investigated by XRD analyses.

Fig. 8 shows the phases of leaching residues obtained at 250 rpm and 450 rpm stirring speeds for different leaching time, indicating that calcium sulfate phase can transform fully to calcium carbonate for 90 min. Moreover, compared with low stirring speed (250 rpm), high stirring speed (450 rpm) seems to favor the formation of suspected hydrated hydroxyl calcium carbonate $[\text{Ca}_6(\text{CO}_{2.65})_2(\text{OH}_{0.657})_7(\text{H}_2\text{O})_2]$. There also exists scheelite in some samples especially at 450 rpm. These may be another reason for the observed decrease of WO_3 leaching yield at 450 rpm.

Fig. 8. Transformation of CaSO_4 in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution with different stirring speed (2 mol/L $\text{NH}_3\cdot\text{H}_2\text{O}$, 2 mol/L $(\text{NH}_4)_2\text{CO}_3$, 30 °C, L/S 3). A-calcium sulfate; B-hydrated hydroxyl calcium carbonate; C-vaterite; E-scheelite.

Fig. 9. Transformation of the leaching residue obtained with different $\text{NH}_3\cdot\text{H}_2\text{O}$ concentration (350 rpm, 2 mol/L $(\text{NH}_4)_2\text{CO}_3$, 30 °C, 90 min, L/S 3). B-hydrated hydroxyl calcium carbonate; C-vaterite; D-calcite; E-scheelite.

The effect of $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration on the transformation of calcium compounds in the leaching is presented in Fig. 9. With increasing $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration, calcium compounds formed in the leaching residue change from hydrated hydroxyl calcium carbonate, vaterite ($K_{\text{sp}}, 10^{-7.91}$, metastable $\mu\text{-CaCO}_3$) (Plummer and Busenberg, 1982) to calcite ($K_{\text{sp}}, 10^{-8.47}$) (Speight, 2005). This phenomenon is very similar to the process of amorphous calcium carbonate crystallization to calcite, *via* vaterite, in which the transformation of vaterite to calcite is very slow (Rodriguez-Blanco et al., 2011). Moreover, Fig. 9 also shows that scheelite precipitates in $\leq 1 \text{ mol/L}$ $\text{NH}_3 \cdot \text{H}_2\text{O}$ solutions, resulting in a low WO_3 leaching yield.

Fig. 10. Effect of $(\text{NH}_4)_2\text{CO}_3$ concentration on phase transformation of leaching residue obtained in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution (350 rpm, 30 °C, 90 min, L/S 3): (a) 2 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, (b) 3 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$. A-calcium sulfate; B-hydrated hydroxyl calcium carbonate; C-vaterite; D-calcite; E-scheelite.

Fig. 10 shows the effect of $(\text{NH}_4)_2\text{CO}_3$ concentration on the transformation of CaSO_4 in the leaching process. With 2 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ in the solution, both hydrated hydroxyl calcium carbonate and calcium sulfate exist in the leaching residue with $\leq 1.5 \text{ mol/L}$ $(\text{NH}_4)_2\text{CO}_3$, and disappear with 3 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ solutions. Furthermore, scheelite generates in the solution with 2 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$

solution, while its diffraction peaks disappear with 3 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ solutions and ≥ 1.5 mol/L $(\text{NH}_4)_2\text{CO}_3$ (about 0.64 mol/L excess $(\text{NH}_4)_2\text{CO}_3$). It should be noted that the stoichiometric consumption of $(\text{NH}_4)_2\text{CO}_3$ is about 0.86 mol/L according to the reaction (2).

As shown in Fig. 11, increasing temperature accelerates the transformation of calcium sulfate to carbonate. Calcium sulfate does not completely convert to calcium carbonate in 90 min at ≤ 25 °C, which can also explain the high WO_3 leaching yield obtained at 30 °C in Fig. 6. In addition to that, most calcium sulfate has transformed to hydrated hydroxyl calcium carbonate, accompanying with scheelite co-precipitation above 40 °C (see Fig. 8, Fig. 9, Fig. 10 (a) and Fig. 11 (a)). This implies that hydrated hydroxyl calcium carbonate is a metastable phase and facilitates scheelite precipitation in the leaching process.

Fig.11. Effect of temperature on transformation of CaSO_4 in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solutions (350 rpm, 2 mol/L $(\text{NH}_4)_2\text{CO}_3$, 90 min, L/S 3): (a) 2 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, (b) 3 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$. A-calcium sulfate; B-hydrated hydroxyl calcium carbonate; C-vaterite; D-calcite; E-scheelite.

The calcium sulfate transformations in the leaching residue with different durations are illustrated in Fig. 12. The diffraction peaks of calcium sulfate decrease with prolonging the reaction time, and

disappear after 90 min. However, scheelite forms readily in 2 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (Fig. 12 (a)), which can be avoided in 3 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (Fig. 12 (b)) with complete transformation of calcium sulfate to calcium carbonate.

Fig.12. XRD patterns of leaching residues for different reaction time in ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solutions (350 rpm, 2 mol/L $(\text{NH}_4)_2\text{CO}_3$, 30 °C, L/S 3): (a) 2 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, (b) 3 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$. A-calcium sulfate; B-hydrated hydroxyl calcium carbonate; C-vaterite; D-calcite; E-scheelite.

From the discussion on the phase transformation of leaching residues, it can be deduced that high concentrations of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$ promote the transformation of calcium sulfate to vaterite and calcite, and that scheelite forms readily in solutions with low concentrations of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (<2 mol/L) and $(\text{NH}_4)_2\text{CO}_3$ (<2 mol/L).

In total, based on the above discussion, the WO_3 leaching yield closely relates to phases of calcium compounds in the leaching residue. The established calcium compounds formed in the leaching process, vaterite and calcite, facilitate the achievement of a high WO_3 recovery, rather than the uncompleted conversion of calcium sulfate and formation of hydrated hydroxyl calcium carbonate. Therefore, the optimal leaching conditions for extracting WO_3 from the converted product are a

combination of stirring speed of 350 rpm in 2 mol/L $(\text{NH}_4)_2\text{CO}_3$ and 3 mol/L $\text{NH}_3\cdot\text{H}_2\text{O}$ solutions, at 30 °C for 90 min. Under these conditions, the WO_3 leaching yield reaches over 99.5%, and crystalline vaterite and calcite are obtained in the leaching residue.

3.2 Secondary reactions and leaching mechanism

Considering that WO_3 can be almost completely leached from the converted product in 15 min, while complete transformation of calcium sulfate needs more than 90 min, and scheelite would form in the leaching process, there may exist secondary reactions between tungstate ions and calcium compounds. Therefore, focused verification experiments were carried out at 30 °C by adding synthetic calcium sulfate and calcium carbonate crystals into ammonium tungstate solution with different $(\text{NH}_4)_2\text{CO}_3$ concentrations.

The results of verification experiments are presented in Table 1, with the obtained XRD patterns shown in Fig. 13 and Fig. 14. We can see that a secondary reaction between tungstate ions and calcium sulfate occurs strongly with formation of scheelite (Fig. 13). Increasing $(\text{NH}_4)_2\text{CO}_3$ concentration can lower the WO_3 content of solid residue, indicating that ammonium carbonate can suppress the secondary reaction between tungstate ions and calcium sulfate. It thus facilitates the conversion of calcium sulfate to carbonate. By the way, calcium sulfate still exists in the residue with 1 mol/L and 1.5 mol/L $(\text{NH}_4)_2\text{CO}_3$ in Fig. 13, which agrees with that 90 minutes is required for complete conversion of calcium sulfate to carbonate in Fig. 8 and Fig. 12. Furthermore, the secondary reaction between tungstate ions and calcium carbonate only takes place without ammonium carbonate in the solution (Fig. 14).

Table 1 The results of the verification experiments with different $(\text{NH}_4)_2\text{CO}_3$ concentrations.

Calcium-bearing compounds	$(\text{NH}_4)_2\text{CO}_3$ concentrate (mol/L)	WO_3 in the solid residue (%)
Synthetic $\text{CaSO}_4\cdot\text{nH}_2\text{O}$	0	77.85
	0.25	73.28
	0.5	58.28
	1.0	8.47
	1.5	2.79
Synthetic CaCO_3	0	15.62
	0.25	0
	0.5	0
	1.0	0

30 °C, 350 rpm, 60 min, L/S 25, 0.6 mol/L WO_3 , 3 mol/L free $\text{NH}_3\cdot\text{H}_2\text{O}$.

It can be therefore concluded that the secondary reaction in the leaching process mainly occurs

between tungstate ions and calcium sulfate. A certain concentration of $(\text{NH}_4)_2\text{CO}_3$ present in the leaching solution can prevent the secondary reactions. The reason can be attributed to solubility performances of CaSO_4 , CaCO_3 and CaWO_4 in ammoniacal ammonium carbonate solutions, with their solubility products K_{sp} of $10^{-4.38}$, $10^{-7.91\sim-8.47}$, and $10^{-8.06}$, respectively (Plummer and Busenberg, 1982; Speight, 2005).

Fig. 13. XRD patterns of the solid residues obtained by adding synthetic calcium sulfate into ammonium tungstate solution (30 °C, 350 rpm, 60 min, L/S 25, 0.6 mol/L WO_3 , 3 mol/L free $\text{NH}_3\cdot\text{H}_2\text{O}$). A-calcium sulfate; D-calcite; E-scheelite.

Fig. 14. XRD patterns of the solid residues obtained by adding synthetic calcium carbonate into ammonium tungstate solution (30 °C, 350 rpm, 60 min, L/S 25, 0.6 mol/L WO_3 , 3 mol/L free $\text{NH}_3\cdot\text{H}_2\text{O}$). C-vaterite; D-calcite; E-scheelite; F-Aragonite.

Combining the analyses of leaching experiments with secondary reactions, the leaching mechanism of extracting tungsten from the converted product in ammoniacal ammonium carbonate solution can be summarized as the following steps.

1. Solid H_2WO_4 quickly reacts with $\text{NH}_3\cdot\text{H}_2\text{O}$, generating soluble $(\text{NH}_4)_2\text{WO}_4$;
2. More stable CaCO_3 is slowly formed by reactions of CaSO_4 with $(\text{NH}_4)_2\text{CO}_3$, accompanying with the production of soluble $(\text{NH}_4)_2\text{SO}_4$;

3. Secondary reactions may occur by CaSO_4 reacting with $(\text{NH}_4)_2\text{WO}_4$, resulting in the formation of solid CaWO_4 and lowering the leaching yield.

Due to the very close K_{sp} values of CaCO_3 and CaWO_4 , the concentrations of CO_3^{2-} and WO_4^{2-} in the solution have a crucial influence on the final leaching residue. With a certain concentration of free $(\text{NH}_4)_2\text{CO}_3$ in the leaching solution, CaCO_3 will be formed more easily than CaWO_4 , thus suppressing the secondary reaction from lowering the WO_3 leaching yield.

3.3 Recovery test of leaching reagents

In the sulfuric acid conversion – ammoniacal ammonium carbonate leaching route for ammonium paratungstate production, the purified tungsten-containing ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution will be evaporated at a elevated temperature. There $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$ volatilize or decompose forming gaseous NH_3 , CO_2 and H_2O , and ammonium paratungsten (APT) is crystallized out (Gaur, 2006). NH_3 and CO_2 gases can be absorbed in water at room temperature under atmospheric pressure, with high efficiency and loading capacity (Mani et al., 2006; Bai and Yeh, 1997; Kurz et al., 1995). After APT crystallization, the residual WO_3 in the spent liquid can be precipitated in form of H_2WO_4 by adding sulfuric acid, obtaining $(\text{NH}_4)_2\text{SO}_4$ in the solution. The H_2WO_4 may be recycled to the leaching process. To avoid the discharge of high salinity wastewater, recovering consumed ammonium carbonate based on Eq. (4) was preliminarily examined by adding leaching residue into $(\text{NH}_4)_2\text{SO}_4$ solution.

Fig. 15. XRD pattern of the solid residue obtained by $(\text{NH}_4)_2\text{SO}_4$ solution reacting with leaching residue.

50 g leaching residue was added in 250 mL 2 mol/L $(\text{NH}_4)_2\text{SO}_4$ solution with continuous stirring and heating on a hot plate, in which gas bubble was observed when temperature reached $\sim 70^\circ\text{C}$, and temperature did not rise until the termination of gas release. Subsequently, the solid residue was

washed, dried, and then examined with XRD analyses. The XRD pattern in Fig. 15 shows that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the main phase, together with small fraction CaWO_4 which originally existed in the leaching residue. The results indicate that consumed ammonium carbonate can be recovered by treating the leaching residue with an ammonium sulfate solution at temperatures above 70 °C.

4. Conclusions

(1) The optimal leaching conditions for extracting WO_3 from the converted product of scheelite by sulfuric acid are in 2 mol/L $(\text{NH}_4)_2\text{CO}_3$ and 3 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ solutions with a stirring speed of 350 rpm at 30 °C leaching temperature for 90 min. The WO_3 leaching yield reaches ~99.5 %, with CaCO_3 remaining in the leaching residue.

(2) Complete transformation of calcium sulfate to crystalline calcium carbonate requires longer time than WO_3 leaching from the converted product. Formations of vaterite and calcite in the leaching process facilitate the WO_3 leaching. The secondary reaction of CaSO_4 with $(\text{NH}_4)_2\text{WO}_4$ may occur forming a scheelite precipitate, which can be suppressed by adding excess $(\text{NH}_4)_2\text{CO}_3$ in the leaching solution.

(3) Consumed ammonium carbonate in the leaching can be recovered and recirculated feasibly by adding the leaching residue into ammonium sulfate solution, suggesting the feasibility of a closed internal chemicals circulation for APT manufacture.

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