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Leaching of WO_3 from sulfuric acid converted product of scheelite in $NH_3·H_2O$−NH_4HCO_3 solution

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Abstract: The leaching of sulfuric acid converted product of scheelite in $NH_3·H_2O$−NH_4HCO_3 solution was systemically studied to improve sulfuric acid conversion−ammonium salts leaching technology route for ammonium paratungstate production. The results showed that the WO_3 leaching efficiency was about 99% under optimal conditions of 350 r/min, liquid-to-solid ratio of 3 mL/g, 1 mol/L NH_4HCO_3, 4 mol/L $NH_3·H_2O$, 25 °C, and 15 min. During the leaching, $CaSO_4$ almost had no change and was still in a banding or rod-like shape in short leaching time, while conglobate $CaCO_3$ was gradually formed on the $CaSO_4$ surface. A secondary reaction might occur between $CaSO_4$ and WO_4^{2-}, which could be restrained by a certain amount of CO_3^{2-} in the solution. There was no $CaCO_3$ phase determined by XRD in leaching residue of converted product for scheelite concentrate under optimal conditions, which was different from that for synthetic scheelite. The leaching process could be explained by neutralization reaction of H_2WO_4 and solid transformation of $CaSO_4$ in $NH_3·H_2O$−NH_4HCO_3 solution.

Key words: tungstic acid; calcium sulfate; leaching mechanism; calcium carbonate; ammonium tungstate

1 Introduction

As a strategically rare metal, tungsten is widely applied in iron and steel, cemented carbide, aerospace, national defense industries because of its remarkable physical and chemical properties [1]. Due to the importance and lacking viable substitutes of tungsten, European Union, United States Geological Survey and British Geological Survey all consider tungsten as a critical metal [2]. Tungsten occurs as scheelite and wolframite minerals in nature [3], and scheelite has been the chief raw material for tungsten extraction due to the progressive exhaustion of wolframite [4]. Ammonium paratungstate (APT) is the main intermediate product in tungsten industrial practice produced by treating tungsten minerals [5].

In current industrial production technologies, soda or/and caustic soda are usually employed to discompose scheelite at high temperature and pressure in an autoclave to produce soluble Na_2WO_4 and insoluble $CaCO_3$/$Ca(OH)_2$. More than 2.5 times of stoichiometric Na_2O reagents are required in order to obtain a high WO_3 recovery, which is hard to economically recycle the excess caustic soda or soda [6,7]. Subsequently, sodium tungstate solution should be converted to ammonium tungstate solution by solvent extraction or ion exchange step [1,8]. The purified $(NH_4)_2WO_4$ solution was to produce ammonium paratungstate (APT) crystal via evaporative crystallization step. In order to reduce the soda and caustic soda consumption and increase tungsten leaching yield, the addition of sodium phosphate and calcium fluoride in the leaching [9,10] and pre-roasting of

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scheelite with $MgCl_2$ [11] was studied. However, there is about 4% tungsten loss in the present industrial practice [12]. 80−125 t of high-salinity wastewater by using ion exchange or about 25 t by using solvent extraction is discharged for per ton of APT production [13]. Therefore, the current caustic soda or soda process obviously has the disadvantages of excess raw material consumption, huge high-salinity wastewater discharge and low tungsten recovery, resulting in a high environmental and economic stress.

Acid method treating tungsten concentrate can avoid the conversion of Na_2WO_4 solution to $(NH_4)_2WO_4$ solution. Hydrochloric acid or nitric acid is traditionally employed to decompose scheelite with obtaining insoluble tungstic acid. The coarse H_2WO_4 is further purified by leaching in aqueous ammonia with generating ammonium tungstate solution, which subsequently is used to produce APT in evaporative crystallization step [14,15]. This process is subject to acid volatility, high requirement on tungsten concentrate grade, and tungstic acid layer formed in acid decomposition [2]. In order to improve the acid process, oxalic acid [16,17], $H_2C_2O_4$−H_2SO_4 mixed solution [18], HCl−H_3PO_4 mixed solution [19−21], HNO_3−H_3PO_4 mixed solution [22], HNO_3−H_3PO_4 mixed solution [23], H_2O_2−H_2SO_4 mixed solution [24−27] were used to decompose scheelite with forming soluble tungstate solution.

Tungsten concentrates can be directly and completely converted in low-volatile and inexpensive H_2SO_4 solution by controlling sulfuric acid concentration and adding an oxidizing agent, with producing a solid mixture of H_2WO_4 and $CaSO_4$ [28−30]. The subsequent step is finding a suitable method to extract tungsten from the sulfuric acid converted product. Because regenerative ammonium carbonate solution could leach $Ca_{3-x}(Fe,Mn)_xWO_6$ ($0\leq x\leq 1$) with directly obtaining $(NH_4)_2WO_4$ solution [31−33], ammoniacal ammonium carbonate solution was employed to leach the sulfuric acid converted product, with a tungsten leaching efficiency of about 99% [34,35]. The flowsheet of sulfuric acid conversion−ammonium salts leaching for ammonium paratungstate production is described in Fig. 1.

By considering the fact that NH_4HCO_3 is much cheaper and has similar property to $(NH_4)_2CO_3$, NH_4HCO_3 can be economically used in the leaching. Therefore, in this work the leaching of sulfuric acid converted product of scheelite in ammoniacal ammonium bicarbonate solution was systemically studied. The sulfuric acid converted product of scheelite was first characterized to understand its morphology and phase distribution. Then, the effect of leaching conditions on tungsten leaching efficiency from sulfuric acid converted product was investigated in detail. Finally, the leaching mechanism was revealed by combining the phase and morphology change. This work is beneficial to improving the sulfuric acid conversion-ammonium salts leaching route, resulting in a cleaner, sustainable and economical technology of ammonium paratungstate production by avoiding the conversion of sodium tungstate to ammonium tungstate solution.

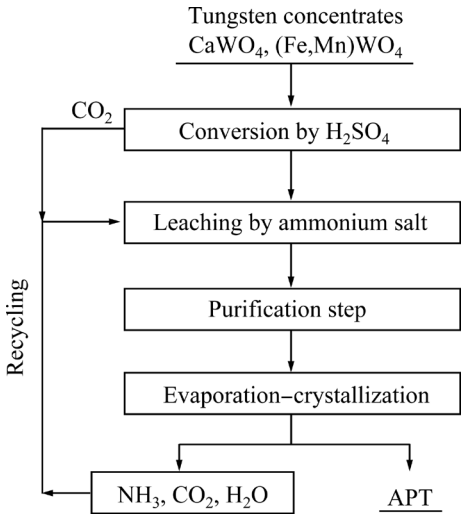

Fig. 1 Flowsheet of producing ammonium paratungstate by sulfuric acid conversion−ammonium salts leaching technology

2 Experimental

2.1 Materials

The reagents used in this work are of analytically pure grades. H_2SO_4 (98 wt.%), $NH_3\cdot H_2O$ (25 wt.% of NH_3), Na_2WO_4, and $CaCl_2$ were supplied by Sinopharm Chemical Reagent Co., Ltd., while NH_4HCO_3 was from Aladdin Industrial Corporation. The deionized water was used throughout the experiment.

Scheelite concentrate was provided by a tungsten company in Jiangxi, China. The chemical compositions of scheelite concentrate are given in Table 1. Synthetic scheelite was prepared by the

precipitation reaction between sodium tungstate solution and calcium chloride solution, which was washed by water and dried at 100 °C in an oven over night, and ground with particle size <45 μm.

Table 1 Main chemical compositions of scheelite concentrate (wt.%)

WO_3	$CaCO_3$	H_2O	Fe	Mn	Mo	S	SiO_2
69.74	3.77	9.14	0.19	0.027	0.045	0.14	4.86

2.2 Experimental procedures

Synthetic scheelite and scheelite concentrate with fine particle size (<45 μm) were decomposed in H_2SO_4 solution with free H_2SO_4 concentration of 1.0 mol/L at 90 °C for 2 h [28]. Subsequently, the slurry was filtered to obtain the solid converted product and the filtrate. The converted product was washed and dried in an oven at 90 °C for 12 h, and then used in leaching experiments and analyses.

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

2.3 Analyses

Leaching residues and converted products were weighed using an analytical balance (accuracy of ±0.0001 g). The solid sample was fused with analytically pure Na_2O_2, and the WO_3 content was measured using the thiocyanate method [34]. The analysis error was less than 2.5%, which was further confirmed by standard WO_3 sample. Thus, the leaching efficiency of WO_3 in ammoniacal NH_4HCO_3 solution was obtained by Eq. (1):

$$\eta(\mathrm{WO_3}) = (1-\frac{m_1 w_1}{m_0 w_0})\times 100\% \quad (1)$$

where $\eta(WO_3)$ is the leaching efficiency of WO_3 (%), m_0 is the initial mass of the converted product (m_0=20 g), m_1 is the mass of leaching residue (g), w_0 is the WO_3 content in the converted product (wt.%), and w_1 is the WO_3 content in the leaching residue (wt.%).

Phase identification of the solid was performed with Cu K_α monochromatic X-ray using a X-ray diffractometer (Empyrean 2, PANalytical B.V.). The diffraction data for 2θ were recorded in 10°−70° with a step size 0.0085° at a scan rate of 10 (°)/min. SEM and EDS analyses were carried out by scanning electron microscope (JSM-7900F) and energy dispersive spectrometer (Symmetry S2, Oxford Instruments), respectively.

3 Results and discussion

3.1 Characteristic of sulfuric acid converted product of synthetic scheelite

In the technological route of extracting tungsten from scheelite by sulfuric acid, a sulfuric acid converted product is first obtained, which is used as raw material in subsequent leaching process. Therefore, the characterization of sulfuric acid converted product of synthetic scheelite was firstly carried out to understand the phase distribution of converted product. Figure 2(a) indicated that synthetic scheelite was completely converted with the product of a mixture of H_2WO_4 and $CaSO_4$. From Figs. 2(b−d), it could be seen that $CaSO_4$ was in a regular banding or rodlike shape, while H_2WO_4 existed in a fine sheet or grain-like shape. Fine H_2WO_4 mainly covered on the surface of $CaSO_4$, together with some in free distribution. H_2WO_4 and $CaSO_4$ particles were not intertwined in sulfuric acid converted product of synthetic scheelite.

3.2 Leaching WO_3 from sulfuric acid converted product of synthetic scheelite

By considering sulfuric acid converted product of synthetic scheelite consisting of H_2WO_4 and $CaSO_4$, the purpose of leaching step is separating H_2WO_4 and $CaSO_4$ by extracting WO_3 into the solution. Therefore, the effect of the leaching conditions such as stirring speed, liquid-to-solid ratio, $NH_3\cdot H_2O$ concentration, NH_4HCO_3 concentration, temperature, and reaction time on the WO_3 leaching efficiency and phase conversion of solid residue was systematically studied.

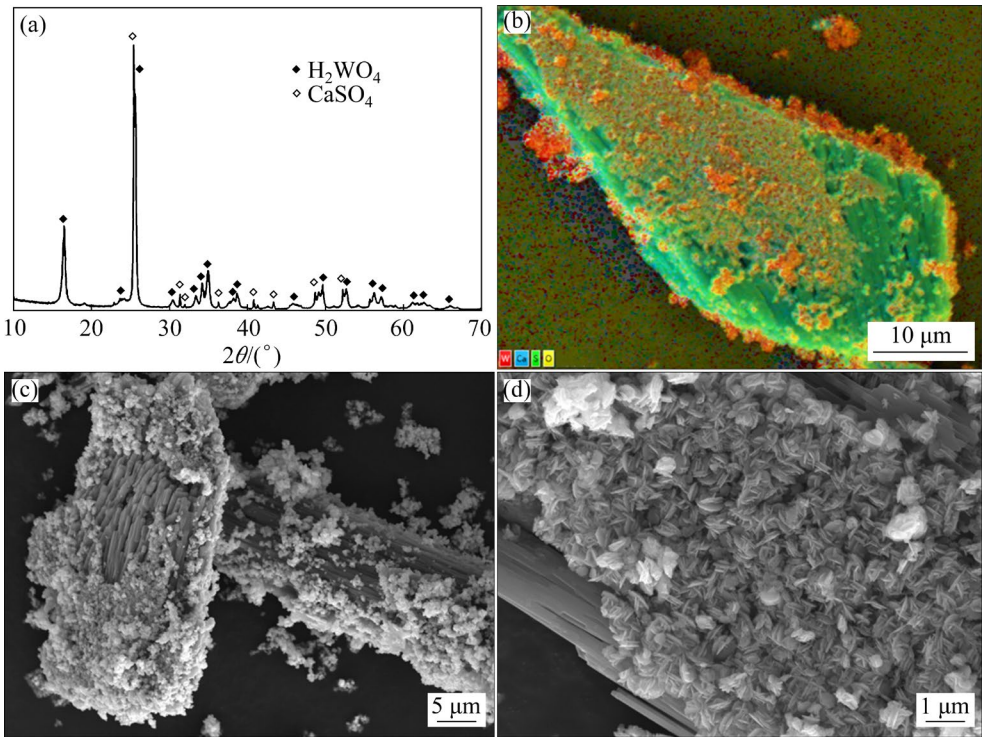

Fig. 2 XRD pattern (a), EDS map (b), and SEM images (c, d) of sulfuric acid converted product of synthetic scheelite

3.2.1 Leaching efficiency of WO_3

The influences of stirring speed, liquid-to-solid ratio, $NH_3·H_2O$ concentration, NH_4HCO_3 concentration, temperature, and reaction time on the WO_3 leaching efficiency from converted product were successively shown in Fig. 3.

From Fig. 3(a), the stirring speed had no obvious influence on WO_3 leaching efficiency, with leaching efficiency about 98% in a stirring speed range of 200−400 r/min. There existed the splashing of slurry with increasing stirring speed to 400 r/min. The suitable stirring speed was selected to be 350 r/min in the following experiments. As shown in Fig. 3(b), leaching efficiency of WO_3 increased from 91.56% to 99.35% with enhancing liquid-to-solid ratio from 2 to 4 mL/g, while the leaching efficiency changed slightly with liquid-to-solid ratios of 3 and 4 mL/g. The liquid-to-solid ratio of 3 mL/g was chosen to guarantee a high WO_3 concentration in leaching solution.

As shown in Fig. 3(c), $NH_3·H_2O$ concentration obviously influenced the leaching efficiency of WO_3 from sulfuric acid converted product. The leaching efficiency of WO_3 reached 98.67% at ≥4 mol/L $NH_3·H_2O$ from 80.87% at 2 mol/L. Another leaching reagent, $(NH_4)_2CO_3$, had no obvious effect on the WO_3 leaching efficiency with ≥0.864 mol/L NH_4HCO_3, where 0.864 mol/L NH_4HCO_3 was the stoichiometry from literature [34]. From Fig. 3(d), the optimized leaching efficiency of WO_3 was 98.67%, while the leaching efficiency slightly decreased with increasing $(NH_4)_2CO_3$ concentration with ≥1 mol/L NH_4HCO_3. In order to understand the influence of $NH_3·H_2O$ and $(NH_4)_2CO_3$ on the leaching efficiency of WO_3, ion concentration and pH changes of NH_3−NH_4HCO_3 solution were calculated by using ion concentration in solution instead of activity in the thermodynamic calculation based on the equilibrium principles and the matter conservation. The thermodynamic constants of corresponding equilibrium reactions at 25 °C were from the literature [35], with the calculated results drawn in Fig. 4. By combining the leaching results in Figs. 3(c, d) and 4, it could be concluded that increased pH and high NH_3 concentration facilitated the WO_3 leaching while the increased HCO_3^- concentration had a negative effect.

Figure 3(e) indicated that temperature played an important role in leaching efficiency of WO_3. Increasing temperature did not promote the WO_3 leaching from converted product. The WO_3 leaching efficiency was about 98% at 25 °C and 30 °C while it decreased to <90% at temperature

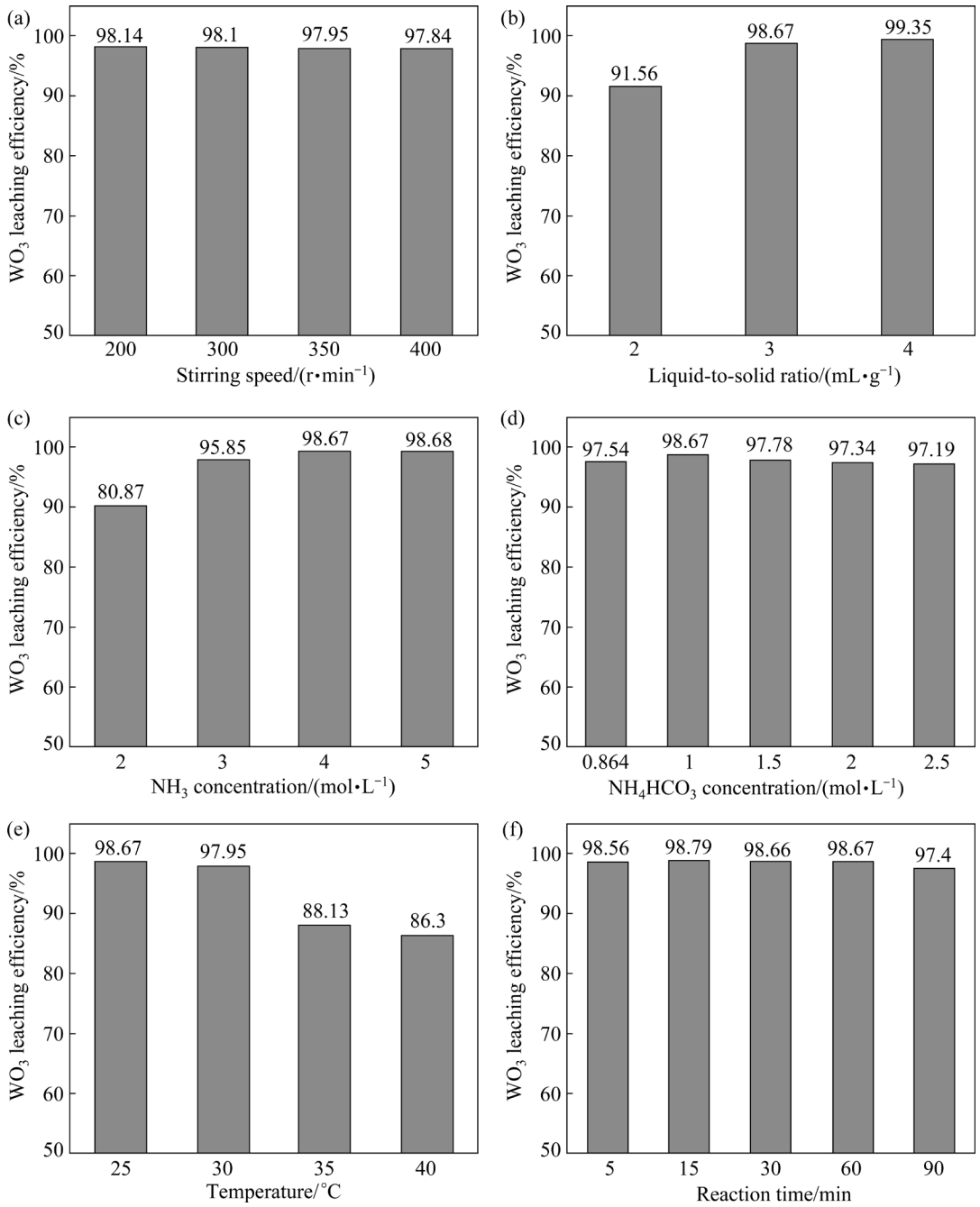

Fig. 3 Effect of reaction conditions on WO_3 leaching efficiency from sulfuric acid converted product of synthetic scheelite: (a) Stirring speed (30 °C); (b) Liquid-to-solid ratio; (c) NH_3 concentration, (d) NH_4HCO_3 concentration; (e) Temperature; (f) Reaction time (Other conditions: 1 mol/L NH_4HCO_3, 4 mol/L $NH_3·H_2O$, 60 min, 25 °C, 350 r/min, and liquid-to-solid of 3 mL/g)

≥30 °C. This could be attributed to the low decomposition temperatures and easy volatilization of $NH_3·H_2O$ and NH_4HCO_3 solutions. From Fig. 3(f), the leaching of H_2WO_4 in ammoniacal ammonium bicarbonate solution occurred very quickly, and the WO_3 leaching efficiency reached 98.56% within only 5 min. Extending reaction time had no obvious effect on WO_3 leaching efficiency, showing only a slight decrease in 90 min.

3.2.2 Phase conversion of leaching residue

Reaction of calcium sulfate conversion to other solid phase was investigated to obtain a better understanding on the leaching process. The XRD patterns of leaching residues under different leaching conditions are shown in Fig. 5.

XRD patterns of leaching residues obtained at stirring speed of 200−450 r/min are shown in Fig. 5(a), with the main phases of $CaSO_4$, $CaCO_3$

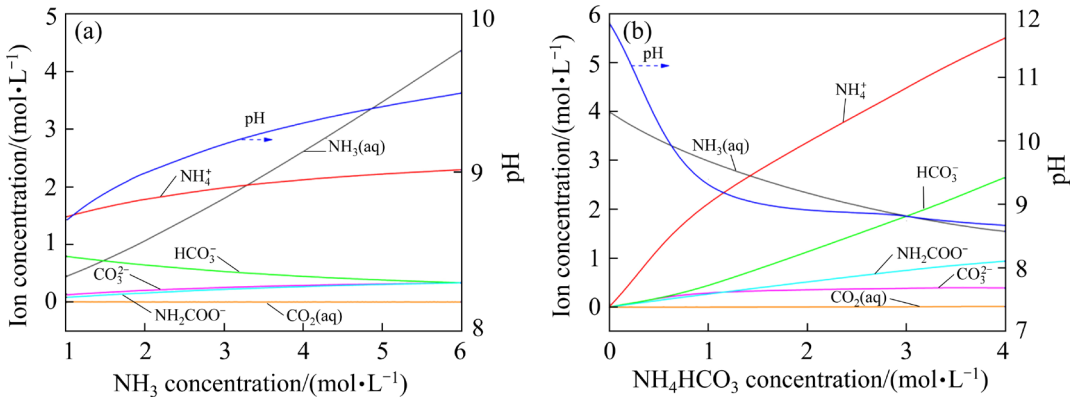

Fig. 4 Ion concentration and pH changes of NH_3–NH_4HCO_3 solution with different NH_3 and NH_4HCO_3 concentrations: (a) NH_3 concentration (1 mol/L NH_4HCO_3); (b) NH_4HCO_3 concentration (4 mol/L NH_3)

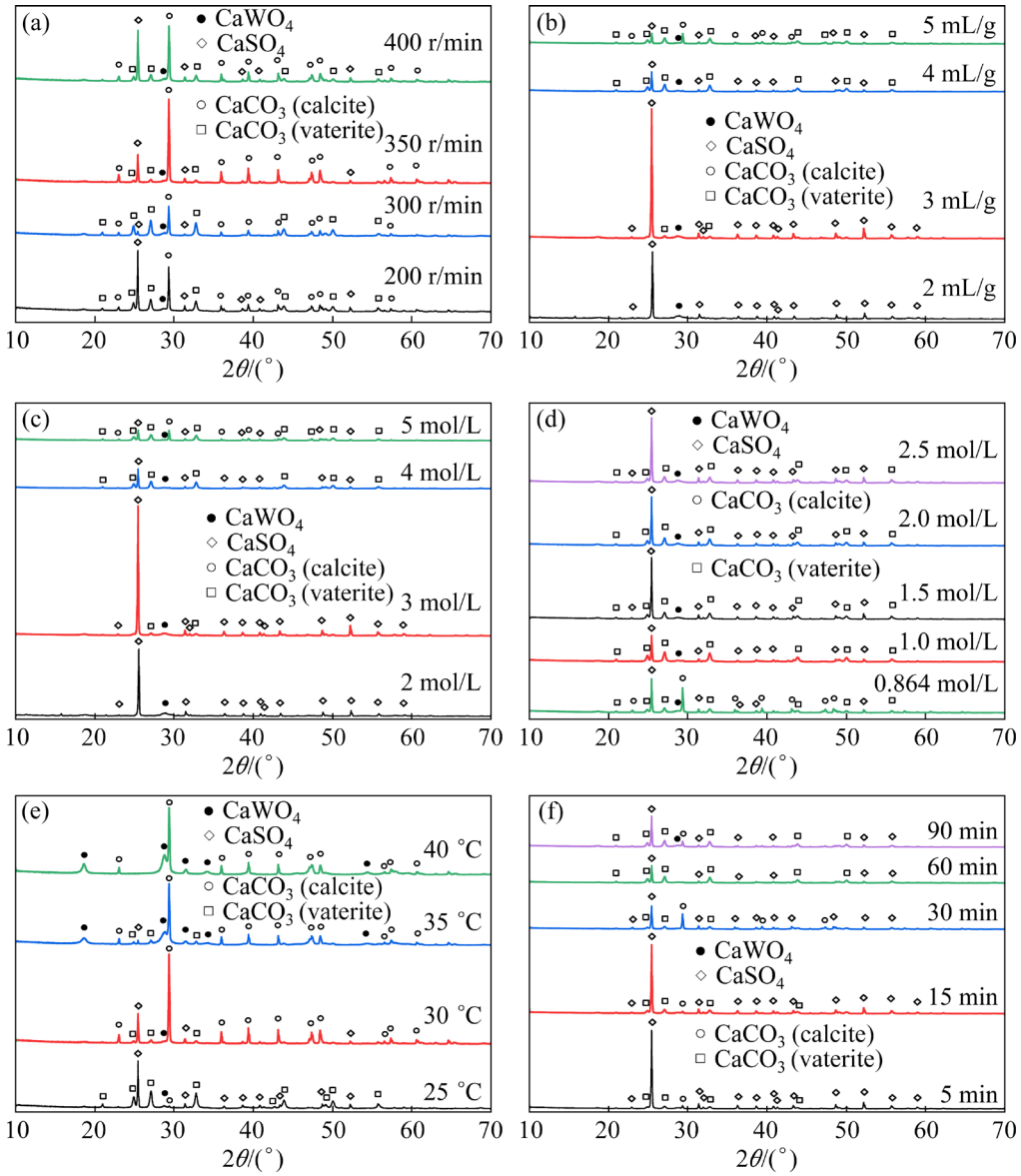

Fig. 5 XRD patterns of leaching residues under different reaction conditions: (a) Stirring speed (30 °C); (b) Liquid-to-solid ratio; (c) NH_3 concentration; (d) NH_4HCO_3 concentration; (e) Temperature; (f) Reaction time (Other conditions: 1 mol/L NH_4HCO_3, 4 mol/L $NH_3·H_2O$, 60 min, 25 °C, 350 r/min, and liquid-to-solid ratio of 3 mL/g)

(calcite and vaterite), and minor $CaWO_4$. Calcium sulfate phase would convert to calcite and vaterite in the leaching, and the diffraction peak of calcite intensified with increasing stirring speed. Phase conversion of $CaSO_4$ seemed to have no effect on WO_3 leaching efficiency under different stirring speeds, while the existence of minor $CaWO_4$ could explain the WO_3 leaching efficiency of about 98%. From Fig. 5(b), it could be seen that $CaSO_4$ did not change at liquid-to-solid ratio of 2 mL/g, while $CaSO_4$ converted to vaterite at liquid-to-solid ratio of 3 mL/g, and further converted to vaterite and calcite at liquid-to-solid ratio of 4 mL/g.

As shown in Fig. 5(c), when NH_4HCO_3 concentration was 1 mol/L, $CaSO_4$ kept stable with 2 mol/L $NH_3·H_2O$, and $CaSO_4$ started to convert to vaterite with increasing $NH_3·H_2O$ concentration, while calcite phase appeared in 5 mol/L $NH_3·H_2O$. The XRD patterns of leaching residues obtained with different NH_4HCO_3 concentrations are shown in Fig. 5(d). Calcite phase only appeared in 0.864 mol/L NH_4HCO_3, while $CaSO_4$ and vaterite $CaCO_3$ coexisted with increasing NH_4HCO_3 concentration.

Temperature seriously affected the phase conversion of leaching residue, as shown in Fig. 5(e). Increasing temperature intensified the phase conversion of $CaSO_4$, and $CaSO_4$ phase disappeared at 40 °C. $CaCO_3$ had phases of vaterite and calcite at low temperature, while only calcite phase existed at 40 °C. Additionally, the diffraction peak of $CaWO_4$ increased with increasing the temperature, meaning that secondary reaction occurred between tungstate ions and calcium compounds. As for the influence of reaction time shown in Fig. 5(f), the diffraction peak of $CaSO_4$ decreased with extending the reaction time, while there was no obvious distribution regularity for $CaCO_3$ phase.

3.2.3 Characteristic of leaching residue under optimized conditions

According to above experimental results of WO_3 leaching efficiency and phase conversion of leaching residue under different leaching conditions, the leaching of H_2WO_4 to $(NH_4)_2WO_4$ occurred very quickly with a leaching efficiency of 98.56% in only 5 min, while the conversion of $CaSO_4$ to $CaCO_3$ needed much more time. The optimal leaching conditions for extracting WO_3 from sulfuric acid converted product of synthetic scheelite were stirring speed of 350 r/min, liquid-to-solid ratio of 3 mL/g, 1 mol/L NH_4HCO_3, 4 mol/L $NH_3·H_2O$, 25 °C, and 15 min. Under these conditions, the WO_3 leaching efficiency was 98.79%.

In order to further clarify the leaching process, the phase, morphology and element distribution of leaching residue obtained under optimal conditions were analyzed, as shown in Fig. 6. The main phase of leaching residue was $CaSO_4$, together with small amount of vaterite and calcite. The existence of $CaWO_4$ indicated that secondary reaction occurred between tungstate ions and calcium-containing compound, leading to uncompleted leaching of WO_3. This was verified by the experiment that leaching 5 g sulfuric acid converted product of synthetic scheelite in 100 mL 2 mol/L Na_2CO_3− 1 mol/L NaOH solution at 25 °C for 60 min obtained a WO_3 leaching efficiency of >99.95%. From SEM and EDS analyses of leaching residue in Figs. 6(b, c), $CaSO_4$ phase was still in a banding or rodlike shape, meaning that $CaSO_4$ almost had no change in the leaching. The formed conglobate $CaCO_3$ and trace $CaWO_4$ adhered on the $CaSO_4$ surface.

3.3 Leaching of sulfuric acid converted product of scheelite concentrate

From the above experiment results, WO_3 could be efficiently leached in ammoniacal NH_4HCO_3 solution for sulfuric acid converted product of synthetic scheelite. To verify its efficiency of industrial application, the sulfuric acid converted product of scheelite concentrate was tested in the leaching process under optimal conditions. XRD patterns, SEM images, and EDS maps of converted product and leaching residue are presented in Figs. 7 and 8, respectively.

From the XRD analyses in Fig. 7(a), the existing phases were $CaSO_4$, H_2WO_4, and SiO_2 in the converted product. The leaching experiment of 5 g converted product in 100 mL 2 mol/L Na_2CO_3− 1 mol/L NaOH solution at 25 °C for 60 min was carried out to further verify the conversion of scheelite concentrate, obtaining a WO_3 leaching efficiency of 98.32%. This indicated almost complete conversion of scheelite concentrate. $CaWO_4$ in leaching residue could not be determined

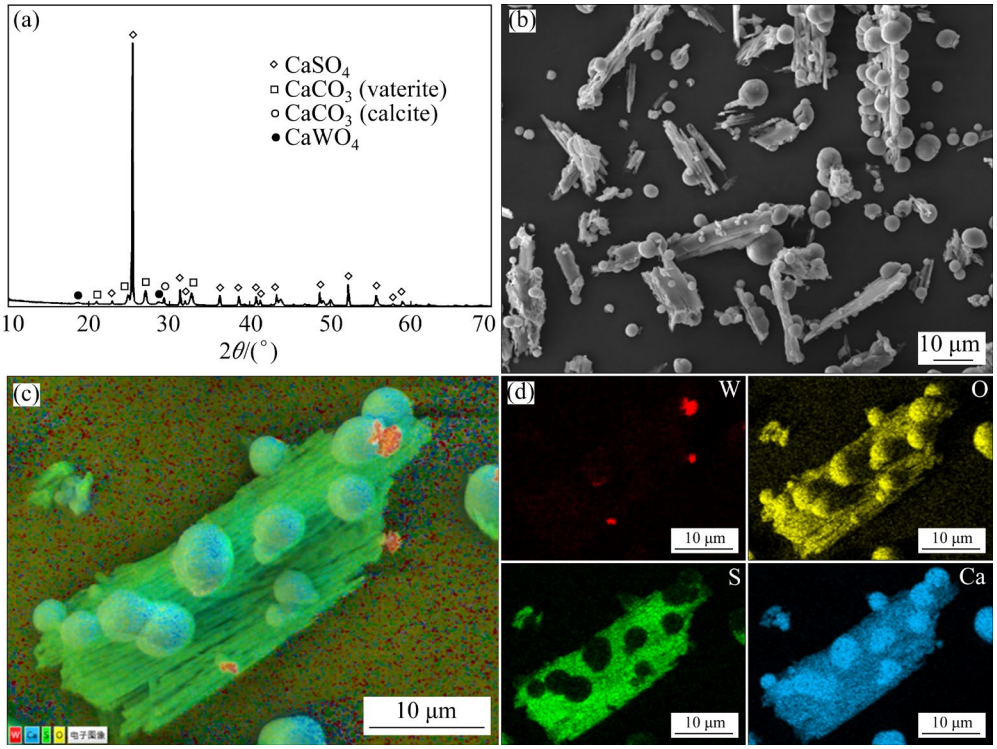

Fig. 6 XRD pattern (a), SEM image (b), and EDS mappings (c, d) of leaching residues for sulfuric acid converted product of synthetic scheelite

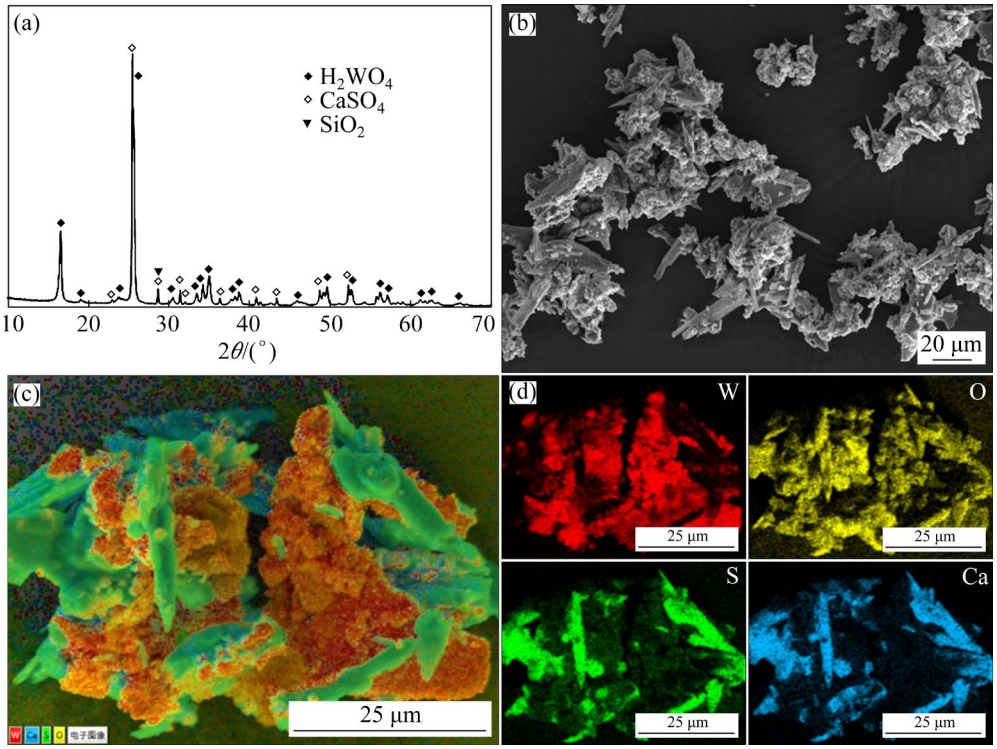

Fig. 7 XRD pattern (a), SEM image (b), and EDS mappings (c, d) of sulfuric acid converted product of scheelite concentrate

in XRD analyses. From SEM images and EDS mappings in Figs. 7(b−d), the distribution of H_2WO_4 and $CaSO_4$ in converted product of scheelite concentrate was more disordered than that of synthetic scheelite. $CaSO_4$ was in an unregular rod-like shape, while H_2WO_4 existed in a fine grain-like shape. Fine H_2WO_4 and rod-like $CaSO_4$ mutually adhered with each other.

The leaching efficiency of WO_3 from sulfuric acid converted product of scheelite concentrate under optimal leaching conditions was 97.64%. Compared with the leaching efficiency of 98.32% for this converted product in Na_2CO_3−NaOH solution, the leaching efficiency was 99.3%, meaning that there was no obvious difference between converted product of synthetic scheelite and scheelite concentrate in leaching process. The importance of obtaining a high WO_3 extraction was to guarantee the complete conversion of tungsten-containing mineral in sulfuric acid converting.

The phase, morphology and element distribution of leaching residue obtained under optimal conditions are shown in Fig. 8. The main phases of leaching residue were $CaSO_4$, SiO_2 and some $CaWO_4$. There was no $CaCO_3$ phase determined in XRD patterns. The existence of $CaWO_4$ was attributed to the uncompleted scheelite in conversion and secondary reaction in the leaching. SEM and EDS results of leaching residue indicated that H_2WO_4 was leached while $CaSO_4$ was retained in the leaching process. The morphology of $CaSO_4$ almost kept unchanged while there were some ravines on its surface.

3.4 Leaching mechanism of sulfuric acid converted product

From the experimental results above-mentioned, the WO_3 in sulfuric acid converted product of scheelite concentrate and synthetic scheelite was efficiently leached in ammoniacal ammonium bicarbonate solution. The leaching process could be explained by the neutralization reaction of H_2WO_4 and solid transformation of $CaSO_4$ including following aspects. The leaching schematic is shown in Fig. 9.

(1) With adding the sulfuric acid converted product of scheelite into ammoniacal ammonium bicarbonate solution, acidic H_2WO_4 reacted with alkaline solution by producing tungstate ion. This neutralization reaction could be finished in a very short time after the homogenization of slurry:

$$H_2WO_4(s)+2OH^-(aq)=WO_4^{2-}(aq)+2H_2O(l) \quad (2)$$

(2) Solid $CaSO_4$ ($K_{sp}=10^{-4.31}$) was more stable than H_2WO_4 in ammoniacal ammonium bicarbonate solution. It could react with CO_3^{2-} ions with forming stabler $CaCO_3$ solid ($K_{sp}=10^{-7.91}$−$10^{-8.47}$) [36], accompanied with producing soluble SO_4^{2-}. But this reaction was very slow and needed much more time to completely transform at low temperature:

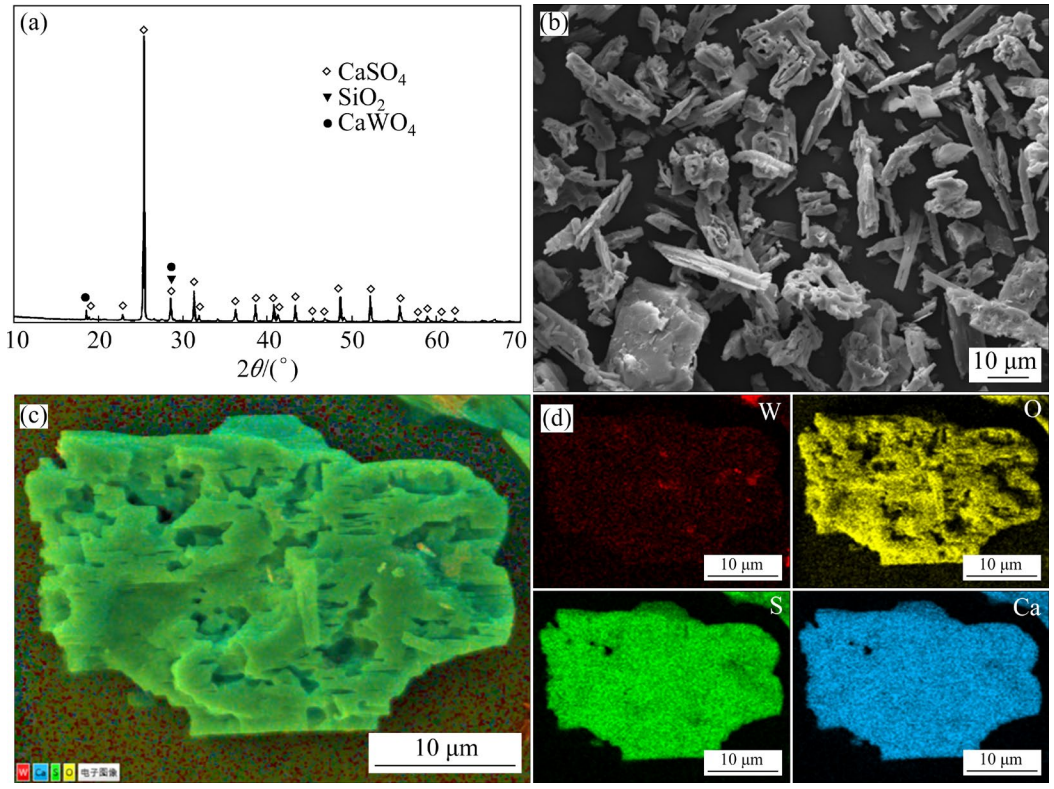

Fig. 8 XRD pattern (a), SEM image (b), and EDS mappings (c, d) of leaching residues for sulfuric acid converted product of scheelite concentrate

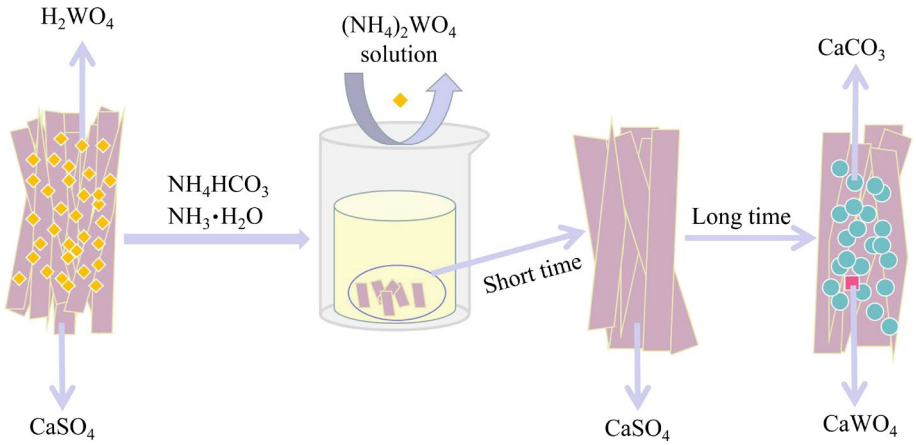

Fig. 9 Leaching schematic for sulfuric acid converted product of scheelite in ammoniacal ammonium bicarbonate solution

$$CaSO_4(s)+CO_3^{2-}(aq)=CaCO_3(s)+SO_4^{2-}(aq) \quad (3)$$

(3) With the increase of WO_4^{2-} in the solution, $CaSO_4$ ($K_{sp}=10^{-4.38}$) possibly reacted with WO_4^{2-}, resulting in the formation of solid $CaWO_4$ ($K_{sp}=10^{-8.06}$) [36], which would reduce the leaching efficiency of WO_3. The existence of CO_3^{2-} in the solution could prevent the secondary reaction due to the very close K_{sp} values of $CaCO_3$ and $CaWO_4$:

$$CaSO_4(s)+WO_4^{2-}(aq)=CaWO_4(s)+SO_4^{2-}(aq) \quad (4)$$

During the leaching of sulfuric acid converted product, the reaction of H_2WO_4 to $(NH_4)_2WO_4$ occurred very quickly with a leaching efficiency of 98.56% in only 5 min, while the conversion of $CaSO_4$ to $CaCO_3$ needed much more time. Increasing $NH_3·H_2O$ concentration or amount led to the increase of NH_4^+ concentration and pH of solution, resulting in a high WO_3 leaching efficiency. However, the increase of NH_4HCO_3 concentration would increase at an early stage but later reduce CO_3^{2-} concentration. Prolonging reaction time had no much influence on WO_3 leaching, but promoted the transformation of $CaSO_4$ to $CaCO_3$. Secondary reaction between $CaSO_4$ and WO_4^{2-} might occur, which could be restrained by a certain amount of CO_3^{2-} in the leaching solution.

4 Conclusions

(1) The optimal conditions for leaching WO_3 from sulfuric acid converted product of scheelite were stirring speed of 350 r/min, liquid-to-solid ratio of 3 mL/g, 1 mol/L NH_4HCO_3, 4 mol/L $NH_3·H_2O$, 25 °C, and 15 min. Under these conditions, the WO_3 leaching efficiency was 98.79%. During the leaching, $CaSO_4$ almost had no change and was still in a banding or rod-like shape in a short leaching time, while conglobate $CaCO_3$ was gradually formed on the $CaSO_4$ surface.

(2) Based on the leaching efficiency, there was no obvious difference on WO_3 leaching between converted product of synthetic scheelite and scheelite concentrate in leaching under optimal conditions. The difference was that there was no $CaCO_3$ phase determined by XRD in leaching residue for converted product of scheelite concentrate under optimal conditions. The complete conversion of tungsten-containing mineral in sulfuric acid solution was very important to obtain a high WO_3 extraction efficiency in subsequent leaching process.

(3) The leaching of WO_3 from sulfuric acid converted product of scheelite could be explained by neutralization reaction of H_2WO_4 and solid transformation of $CaSO_4$ in ammoniacal ammonium bicarbonate solution. During the leaching, a secondary reaction between $CaSO_4$ and WO_4^{2-} might occur, which could be restrained by a certain amount of CO_3^{2-} in solution.

CRediT authorship contribution statement

Lei-ting SHEN: Conceptualization, Methodology, Validation, Writing – Review & editing, Funding acquisition, Supervision; **Yu LIU:** Software, Investigation, Data curation, Writing – Original draft; **Juan-Lang GUO:** Experiment, Data curation, Writing – Original draft; **Qiu-sheng ZHOU:** Writing – Review &

editing; **Tian-gui QI**: Investigation, Writing – Review & editing; **Zhi-hong PENG:** Writing – Review & editing; **Gui-hua LIU:** Writing – Review & editing; **Xiao-bin LI:** Conceptualization, Methodology, Supervision, Writing – Review & editing.

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 paper.

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References

[1] TRASORRAS J R L, WOLFE T A, KNABL W, VENEZIA C, LEMUS R, LASSNER E, SCHUBERT W D, LUDERITA E, WOLF H. Tungsten, tungsten alloys, and tungsten compounds [M]//Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co, Weinheim: KGa A, 2016.

[2] SHEN Lei-ting, LI Xiao-bin, TASKINEN P, LINDBERG D. Tungsten extractive metallurgy: A review of processes and their challenges for sustainability [J]. Minerals Engineering, 2019, 142: 105934.

[3] GUNN G. Critical metals handbook, chapter 16, tungsten [M]. British Geological Survey/American Geophysical Union/John Wiley & Sons, Ltd, 2014: 385−413.

[4] WANG Xu, QIN Wen-qin, JIAO Fen, DONG Liu-yang, GUO Jian-gen, ZHANG Jian, YANG Cong-ren. Review of tungsten resource reserves, tungsten concentrate production and tungsten beneficiation technology in China [J]. Transactions of Nonferrous Metals Society of China, 2022, 32: 2318−2338.

[5] GAUR R P S. Modern hydrometallurgical production methods for tungsten [J]. JOM, 2006, 58: 45−49.

[6] MARTINS J I. Leaching systems of wolframite and scheelite: A thermodynamic approach [J]. Mineral Processing and Extractive Metallurgy Review, 2014, 35: 23−43.

[7] SHEN Lei-ting, LI Xiao-bin, TASKNIEN P. Thermodynamics of tungsten ores decomposition process options [C]//Extraction 2018, Part C-1. Ottawa, Canada, 2018: 26−29.

[8] XIA Xin-bin, ZHANG Gui-qing, GUAN Wen-juan, ZENG Li, WU Sheng-xi, Li Qing-gang, CAO Zuo-ying. Mathematical model and reaction mechanism of molybdenum and tungsten extraction with TRPO from peroxide solution [J]. Transactions of Nonferrous Metals Society of China, 2022, 32: 3123−3135.

[9] YANG Liang, ZHANG Xin-ying, CAO Cai-fang, XUE Xiang, WAN Lin-sheng. A new process for the efficient decomposition of low-grade scheelite based on the formation of insoluble calcium fluorophosphate [J]. Minerals Engineering, 2022, 177: 107372.

[10] GONG Dan-dan, ZHANG Yong, WAN Lin-sheng, QIU Ting-sheng, CHEN Yun-nen, REN Si-li. Efficient extraction of tungsten from scheelite with phosphate and fluoride [J]. Process Safety and Environmental Protection, 2022, 159: 708−715.

[11] GONG Dan-dan, ZHOU Kang-gen, PENG Chang-hong, LI Jun-jie, CHEN Wei. Sequential extraction of tungsten from scheelite through roasting and alkaline leaching [J]. Minerals Engineering, 2019, 132: 238−244.

[12] LEAL-AYALA D R, ALLWOOD J M, PETAVRIETZ E, BROWN T J, GUNN G. Mapping the global flow of tungsten to identify key material efficiency and supply security opportunities [J]. Resources Conservation and Recycling, 2015, 103: 19−28.

[13] WAN Lin-sheng, YANG Liang, CHEN Yong-ming, ZHAO Li-fu, LI Hong-chao. Synthesis of scheelite with wolframite and calcium carbonate by a direct solid-state synthesis route [J]. Int. Journal of Refractory Metals and Hard Materials, 2015, 48: 301−304.

[14] MARTINS J I, MOREIRA A, COSTA S C. Leaching of synthetic scheelite by hydrochloric acid without the formation of tungstic acid [J]. Hydrometallurgy, 2003, 70: 131−141.

[15] MARTINS J I. Leaching of synthetic scheelite by nitric acid without the formation of tungstic acid [J]. Industrial & Engineering Chemistry Research, 2003, 42: 5031−5036.

[16] POYASHNIKOA Y M, GAMOL'SKII A M, MOKHOSOEV M V, KOALOVA F M. Kinetics of the dissolution of calcium tungstate in oxalate acid solution [J]. Zh. Neorg. Khim, 1970, 15(2): 502−508.

[17] KALPAKLI A O, ILHAN S, KAHRUMAN C, YUSUFOGLU I. Dissolution behavior of calcium tungstate in oxalic acid solutions [J]. Hydrometallurgy, 2012, 121/121/123/124: 7−15.

[18] LIU Q S, TU T, GUO H, CHENG H, WANG X Z. Complexation extraction of scheelite and transformation behavior of tungsten-containing phase using H_2SO_4 solution with $H_2C_2O_4$ as complexing agent [J]. Transactions of Nonferrous Metals Society of China, 2021, 31: 3150−3161.

[19] XUIN G H, YU D Y, SU Y F. Leaching of scheelite by hydrochloric acid in the presence of phosphate [J]. Hydrometallurgy, 1986, 16: 27−40.

[20] GURMEN S, TIMUR S, ARSLAN C, DUMAN I. Acid leaching of scheelite concentrate and production of heteropoly−tungstate salt [J]. Hydrometallurgy, 1999, 51: 227−238.

[21] KAHRUMAN C, YUSUFOGLU I. Leaching kinetics of synthetic $CaWO_4$ in HCl solutions containing H_3PO_4 as chelating agent [J]. Hydrometallurgy, 2006, 81: 182−189.

[22] ZHANG Wen-juan, LI Jian-tao, ZHAO Zhong-wei. Leaching kinetics of scheelite with nitric acid and phosphoric acid [J]. Int. Journal of Refractory Metals and Hard Materials, 2015, 52: 78−84.

[23] LI Jiang-tao, ZHAO Zhong-wei. Kinetics of scheelite concentrate digestion with sulfuric acid in the presence of phosphoric acid [J]. Hydrometallurgy, 2016, 163: 55−60.

[24] HE Gui-xiang, ZHAO Zhong-wei, WANG Xiao-bo, LI Jiang-tao, CHEN Xing-yu, HE Li-hua, LIU Xu-heng. Leaching kinetics of scheelite in hydrochloric acid solution containing hydrogen peroxide as complexing agent [J]. Hydrometallurgy, 2014, 144/145: 140−147.
[25] YIN Chang-sheng, JI Lei, CHEN Xing-yu, LIU Xu-heng, ZHAO Zhong-wei. Efficient leaching of scheelite in sulfuric acid and hydrogen peroxide solution [J]. Hydrometallurgy, 2020, 192: 105292.
[26] ZHANG Wen-juan, CHEN Yong-qiang, CHE Jian-yong, WANG Cheng-yan, MA Bao-zhong. Green leaching of tungsten from synthetic scheelite with sulfuric acid-hydrogen peroxide solution to prepare tungstic acid [J]. Separation and Purification Technology, 2020, 241: 116752.
[27] ZHANG Wen-juan, WEN Pei-cheng, XIA Liu, CHEN Jun, CHE Jian-yong, WANG Cheng-yan, MA Bao-zhong. Understanding the role of hydrogen peroxide in sulfuric acid system for leaching low-grade scheelite from the perspective of phase transformation and kinetics [J]. Separation and Purification Technology, 2021, 241: 119407.
[28] LI Xiao-bin, SHEN Lei-ting, ZHOU Qiu-sheng, PENG Zhi-hong, LIU Gui-hua, QI Tian-gui. Scheelite conversion in sulfuric acid together with tungsten extraction by ammonium carbonate solution [J]. Hydrometallurgy, 2017, 171: 106−115.
[29] SHEN Lei-ting, LI Xiao-bin, ZHOU Qiu-sheng, PENG Zhi-hong, LIU Gui-hua, QI Tian-hua, TASKINEN P. Kinetics of scheelite conversion in sulfuric acid [J]. JOM, 2018, 70: 2499−2504.
[30] SHEN Lei-ting, LI Xiao-bin, ZHOU Qiu-sheng, PENG Zhi-hong, LIU Gui-hua, QI Tian-gui, TASKINEN P. Wolframite conversion in treating a mixed wolframite-scheelite concentrate by sulfuric acid [J]. JOM, 2018, 70: 161−167.
[31] LI Xiao-bin, XU Xiang-ming, XU Wang, ZHOU Qiu-sheng, QI Tian-gui, LIU Gui-hua, PENG Zhi-hong, CUI Yuan-fa, LI Jian-pu. $Ca_{3-x}(Fe,Mn)_xWO_6$ ($0<x\leq1$) prepared from tungsten-containing materials and its leachability in aqueous ammonium carbonate solution [J]. Int. Journal of Refractory Metals and Hard Materials, 2016, 57: 93−100.
[32] LI Xiao-bin, XU Xiang-ming, ZHOU Qiu-sheng, QI Tian-gui, LIU Gui-hua, PENG Zhi-hong, CUI Yuan-fa, LI Jian-pu. Ca_3WO_6 prepared by roasting tungsten-containing materials and its leaching performance [J]. Int. Journal of Refractory Metals and Hard Materials, 2015, 52: 151−158.
[33] XU Xiang-ming, ZHOU Ke-chao, LI Xiao-bin, ZHOU Qiu-sheng, QI Tian-gui, LIU Gui-hua, PENG Zhi-hong. Leaching of synthetic Ca_3WO_6 with ammoniacal ammonium carbonate solution under atmospheric pressure: A fundamental study [J]. Hydrometallurgy, 2019, 184: 55−66.
[34] SHEN Lei-ting, LI Xiao-bin, ZHOU Qiu-sheng, PENG Zhi-hong, LIU Gui-hua, QI Tian-gui, TASKINEN P. Sustainable and efficient leaching of tungsten in ammoniacal ammonium carbonate solution from the sulfuric acid converted product of scheelite [J]. Journal of Cleaner Production, 2018, 197: 690−698.
[35] LI Xiao-bin, SHEN Lei-ting, TONG Xiao-yi, QI Tian-gui, ZHOU Qiu-sheng, LIU Gui-hua, PENG Zhi-hong. Thermodynamic modeling on reaction behavior of silicates in $(NH_4)_2WO_4$−$(NH_4)_2CO_3$−NH_3−H_2O system [J]. Transactions of Nonferrous Metals Society of China, 2018, 28: 2324−2350.
[36] SPEIGHT J G. Lange's handbook of chemistry [M]. 16th edition. New York: McGraw-Hill, 2005.

$NH_3·H_2O$−NH_4HCO_3 溶液中白钨矿硫酸转化产物浸出 WO_3

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摘 要：为优化硫酸转型−铵盐浸出制备仲钨酸铵工艺路线，系统研究了白钨矿硫酸转化产物在 $NH_3·H_2O$−NH_4HCO_3 溶液中的浸出过程。结果表明：在 350 r/min、液固比 3 mL/g、1 mol/L NH_4HCO_3、4 mol/L $NH_3·H_2O$、温度 25 ℃、时间 15 min 的浸出条件下，WO_3 浸出率可达 99%左右。浸出过程中，短时间内 $CaSO_4$ 几乎没有变化，仍呈带状或棒状；随着浸出时间延长，球状 $CaCO_3$ 在 $CaSO_4$ 表面逐渐形成。$CaSO_4$ 与溶液中的 WO_4^{2-} 可能发生二次反应，溶液中一定量的 CO_3^{2-} 可抑制二次反应。与合成白钨矿不同，优化条件下白钨矿精矿转化产物浸出渣中 XRD 检测不到 $CaCO_3$ 生成。该浸出机理可解释为 $NH_3·H_2O$−NH_4HCO_3 溶液中 H_2WO_4 的酸碱中和反应和 $CaSO_4$ 的固相转化。

关键词：钨酸；硫酸钙；浸出机理；碳酸钙；钨酸铵

(Edited by Bing YANG)