



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

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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 $(\text{NH}_4)_2\text{WO}_4$.

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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, 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

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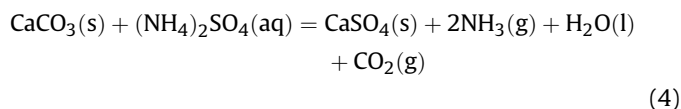
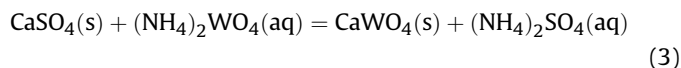
soda process raises production cost, and especially poses serious environmental pollution, suggesting the difficulty in economic and cleaner production of tungsten (Liu and Xue, 2015; Li et al., 2017a).

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 (Xu et al., 1986; Gurmen et al., 1999; Kahruman and Yusufoglu, 2006; Liu and Xue, 2015) 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 Vizolyi, 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 2 h (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.

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 ($\pm 0.5^\circ\text{C}$). 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)

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