Scheelite conversion in sulfuric acid together with tungsten extraction by ammonium carbonate solution

Xiaobin Li, Leiting Shen, Qiusheng Zhou*, Zhihong Peng, Guihua Liu, Tiangui Qi

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

A B S T R A C T

Aiming to treat scheelite concentrate for producing ammonium paratungstate efficiently and cleanly, the conversion of scheelite to H_2WO_4 and $CaSO_4 \cdot nH_2O$ in H_2SO_4 solution was firstly studied in this work. The results show that H_2SO_4 concentration, temperature, time, stirring speed, and particle size affect the conversion efficiency. Moreover, this work reveals that solid H_2WO_4 layer on the surface of $CaWO_4$ particles forms and develops from thickness and looseness to thinness and denseness with increasing H_2SO_4 concentration, and thus hinders the conversion of $CaWO_4$ to H_2WO_4, whereas $CaSO_4 \cdot nH_2O$ almost does not deposit in the layer. Meanwhile, H_2WO_4 layer on $CaWO_4$ surface is resulted by isopolytungstate ions diffusion-tungstic acid deposition in diffusion layer. Additionally, the performance of separating H_2WO_4 from $CaSO_4 \cdot nH_2O$ by leaching the converted product with aqueous ammonium carbonate solution was examined, showing that the converted product has an excellent leachability of tungsten in aqueous ammonium carbonate solution at ambient temperature with WO_3 leaching efficiency of about 99%. This work has the potential to develop a novel technique for tungsten extraction from scheelite concentrate under atmospheric pressure, bypassing the conversion of Na_2WO_4 to $(NH_4)_2WO_4$.

1. Introduction

Tungsten, for its low vapor pressure and thermal expansion, high density and melting point, good thermal and electrical conductivity, high modulus of elasticity, has been increasingly used in many fields, such as hard materials, high temperature technology, lighting, X-ray technology, machine and engine construction, chemical industry, laser technology, armaments and aero-space industry (Lassner et al., 2012; Lassner and Schubert, 1999; Yang et al., 2016). While the main ore resources used for production of tungsten include wolframite and scheelite, and scheelite ($CaWO_4$) becomes a predominant raw material due to progressive exhaustion of wolframite (Lassner and Schubert, 1999). For extraction of tungsten from scheelite, there are mainly two approaches for decomposing ore, *i.e.*, dissolving tungsten in solutions and converting tungsten to tungstic acid.

Nowadays, the principal method for decomposing scheelite is dissolving tungsten in solutions. In present commercial applications, scheelite is mainly digested by either caustic soda or soda solutions in form of Na_2WO_4 (Queneau et al., 1982), in which a large amount of reagents and a high temperature are required. Typical digestion conditions are of 463–498 K temperature, 1.2–2.6 MPa pressure, and 2.5–4.5 stoichiometric ratio of Na_2O to WO_3 (Yih and Wang, 1979;
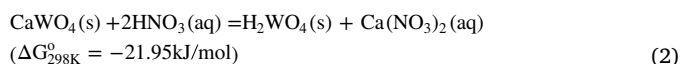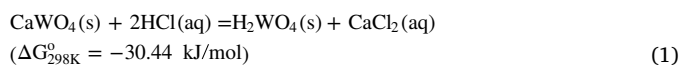
Lassner, 1995), and the ratio increases even to 5 if scheelite concentration is low (Burwell, 1966). Because caustic soda or soda is hard to be recycled (Lassner and Schubert, 1999), these processes have to discharge a large amount of high salinity wastewater, causing high production cost and environmental stress (Liu and Xue, 2010). Therefore, some researches proposed alternative methods to extract tungsten from scheelite to acid solution in the form of soluble tungstates. In the presence of phosphorus, the leaching processes of scheelite were investigated with hydrochloric acid or sulfuric acid (Xuin et al., 1986; Gurmen et al., 1999; Liu and Xue, 2010; Li and Zhao, 2016), in which the tungsten forms water-soluble phosphotungstic acid chelate compound (12-tungstophosphoric heteropoly acid, $H_3PW_{12}O_{40}$). Potashnikov et al. (1970) proposed a method to treat $CaWO_4$ with $H_2C_2O_4$ solution. Kalpakli et al. (2012) further studied the dissolution mechanism of synthetic $CaWO_4$ in $H_2C_2O_4$ solutions regarded it as forming water soluble hydrogen aqua oxalate tungstate ($H_2[WO_3(C_2O_4) H_2O]$). Moreover, Martins et al. treated synthetic scheelite forming soluble metatungstates by hydrochloric acid (Martins et al., 2003) or nitric acid (Martins, 2003) at a certain temperature and pH. Although these methods could effectively extract tungsten from scheelite to solution, there exist inherent disadvantages, *e.g.*, the expensiveness for phosphorus, nitric acid and oxalic acid, the strong corrosiveness and

---

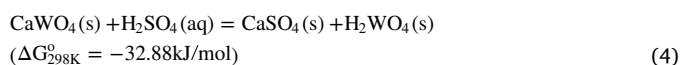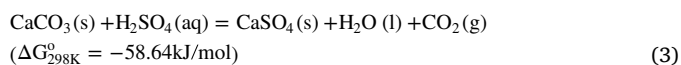volatilization for hydrochloric acid and nitric acid.

The other approach for decomposing scheelite is converting tungsten to insoluble tungstic acid. Using hydrochloric acid (Martins et al., 2003) or nitric acid (Martins, 2003) for decomposing scheelite according to reactions (1) and (2) (Martins, 2014), as a classical method, is a conventional industrial process, in which tungsten is converted to solid H_2WO_4 and most impurities are dissolved in solutions. Subsequently, the separated H_2WO_4 is leached in aqueous ammonia to obtain ammonium tungstate solution. Although this approach is cost-effective and simple compared with the dissolving tungsten method as mentioned previously, it is restricted by the high volatilization and notable corrosiveness of hydrochloric acid or nitric acid.

$$CaWO_4(s) + 2HCl(aq) = H_2WO_4(s) + CaCl_2(aq)$$
$$(\Delta G^o_{298K} = -30.44 \text{ kJ/mol}) \quad (1)$$

$$CaWO_4(s) + 2HNO_3(aq) = H_2WO_4(s) + Ca(NO_3)_2(aq)$$
$$(\Delta G^o_{298K} = -21.95 kJ/mol) \quad (2)$$

Considering the fact that sulfuric acid is low volatile and cheap, it is a preferred option to treat scheelite concentrate with H_2SO_4 as per reactions (3) and (4) (Martins, 2014). Being different from the conversion of scheelite by hydrochloric acid, it was thought that the formed insoluble H_2WO_4 and $CaSO_4 \cdot nH_2O$ in conversion by sulfuric acid were difficult to separate (Li and Zhao, 2016). The dihydric or polyhydric aliphatic alcohol leaching reagent was employed to separate H_2WO_4 from $CaSO_4 \cdot nH_2O$ based on a certain solubility of tungstic acid in such solutions (Forward and Vizsolyi, 1965), which is not suitable for commercial application due to poor solubility even at 170 °C($<$ 64 g/L, WO_3) and difficulty in separation of water and alcohol.

$$CaCO_3(s) + H_2SO_4(aq) = CaSO_4(s) + H_2O(l) + CO_2(g)$$
$$(\Delta G^o_{298K} = -58.64 kJ/mol) \quad (3)$$

$$CaWO_4(s) + H_2SO_4(aq) = CaSO_4(s) + H_2WO_4(s)$$
$$(\Delta G^o_{298K} = -32.88 kJ/mol) \quad (4)$$

Meanwhile, it was believed that decomposing scheelite by mineral acid resulted in a notably low conversion ratio. Li and Zhao (2016) considered that in the scheelite-treating process by sulfuric acid, the formed tungsten acid and calcium sulfate covered the ore and hindered seriously the reactant acid from penetrating into the core of the ore. It was noted that the similar trend was reported in the conversion of scheelite by hydrochloric acid (Martins et al., 2003). The tungsten conversion ratio in hydrochloric acid is often not high enough although the equilibrium constants of the reaction (1) (Martins, 2014) for 293 K and 373 K are respectively up to 1.0×10^4 and 1.5×10^4 (Meerson and Khavskii, 1961), which was also explained as that solid tungstic acid formed covered the surface of scheelite particles and blocked the further reaction of HCl with $CaWO_4$ particles (Martins et al., 2003). To increase the reaction rate and consequently the corresponding yield, some strategies are usually adopted, such as reducing the particle size (Fieberg and Coetzee, 1986), using a large excess of concentrated HCl (Vezina et al., 1970), utilizing heated ball mill reactors (Meerson and Khavskii, 1961). Unfortunately, the product layer wrapping the ore was never observed directly for scheelite conversion by either hydrochloric acid or sulfuric acid.

Therefore, aiming to intensify the conversion of scheelite concentrate by sulfuric acid, this work attempted to investigate the formation of product layer and determine appropriate conversion conditions including H_2SO_4 concentration, temperature, time, stirring speed, and particle size. In addition, considering the extremely small solubility of $CaCO_3$ and the possibility of regenerating $(NH_4)_2CO_3$ from $(NH_4)_2SO_4$, separating H_2WO_4 from $CaSO_4 \cdot nH_2O$ was preliminarily examined by using aqueous ammonium carbonate solutions as leaching agent at ambient temperature. It should be noted that this work only focused on the behaviors of W and Ca in the conversion and leaching process, and those of impurities in scheelite concentrate would be studied in later.

This work may favor to exploit a simple and cleaner process for manufacturing ammonium paratungstate.

2. Materials and methods

2.1. Materials

The reagents used in this work were analytically pure. H_2SO_4 solution was prepared by diluting H_2SO_4 (Sinopharm Chemical Reagent Co., Ltd) with deionized water, and its concentration was determined by volumetric analysis using 0.1 M standard NaOH solution and methyl orange indicator. While aqueous ammonium carbonate solution was obtained by dissolving $(NH_4)_2CO_3$ (Aladdin Industrial Corporation) in deionized water.

The original scheelite concentrate was provided by Jiangxi Rare Metals Tungsten Holdings Group Co., Ltd., China. Synthetic scheelite was prepared by the reaction of sodium tungstate solution and calcium chloride solution, then washed, dried and calcined at 1273 K for 2 h (Li et al., 2015). 100 g original scheelite concentrate was ground by vibrating mill (FM-1, Beijing Yongguangming Medical Instruments Co., Ltd., China) to obtain scheelite concentrate with particle size -150 μm. The chemical components of scheelite concentrate and synthetic scheelite determined by chemical analysis following the national standard of China (GB/T 14352.1-2010) were shown in Table 1, and their X-ray diffraction (XRD) patterns shown in Fig. 1 indicated that scheelite concentrate consisted of $CaWO_4$ and $CaCO_3$ while the synthetic scheelite comprised only $CaWO_4$.

2.2. Experimental procedure

The conversion experiments were performed in a 250 mL three neck round-bottom flask, which was immersed in a thermostatic glycerol bath pot with an electronic temperature-controller in order to guarantee tiny temperature fluctuation ($\pm$ 1 °C). The sulfuric acid solution (120 mL) was put into the flask and then heated to a preset temperature, followed by adding 30 g–40 g scheelite concentrate. The slurry was agitated by a single impeller (diameter 65 mm, width 12 mm) coated by polytetrafluoroethylene (PTFE) at 300 rpm stirring speed. After a certain duration, the resultant slurry was filtered to obtain a cake (converted product) and a filtrate. The converted product was washed using deionized water and dried in an oven at 90 °C for 12 h, then used for XRD and SEM analyses and testing its leachability in aqueous ammonium carbonate solution.

2.3. Analysis methods

Phase analysis was performed with Cu-Kα monochromatic X-ray using a Bruker X-ray diffractometer (D8-Advance, Bruker Corporation).The data were recorded for 2θ from 5° to 75° and 0.0085° step size was used at a scan rate of 1° min^{-1}, and the current and voltage of the generator were respectively set at 30 mA and 40 kV (Li et al., 2015).

For convenience, the mass fractions of H_2WO_4 and $CaWO_4$ in the converted product were calculated semi-quantitatively by Relative Intensity Ratio (RIR) method ($<$ 5% error) based on XRD analysis (Al-Jaroudi et al., 2007), according to the following equation:

Table 1
The main chemical components of tungsten-bearing materials (mass, %).

Tungsten-bearing materials	WO$_3$	Ca	Fe	Mn	Mo	S	Si
Synthetic scheelite	80.55	13.89					
Scheelite concentrate	51.88	24.05	0.27	0.16	0.33	0.31	0.27