Kinetics of scheelite concentrate digestion with sulfuric acid in the presence of phosphoric acid

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Jiangtao Li [a], Zhongwei Zhao [a,b,*]

[a] School of Metallurgy and Environment, Central South University, Changsha 410083, Hunan, China
[b] Key Laboratory of Hunan Province for Metallurgy and Material Processing of Rare Metals, Changsha, 410083, Hunan, China

ABSTRACT

Considering the strict environmental requirements and cost of energy consumption, a cheap and non-volatile agent (H_2SO_4) was used to digest scheelite concentrate in the presence of phosphoric acid. In the digestion process, tungsten was completely leached in the form of a highly soluble 12-tungstophosphoric heteropoly acid ($H_3PW_{12}O_{40}$), and calcium remained in the residue as $CaSO_4 \cdot nH_2O$, which can be later used as cement raw materials. The effects of the leaching parameters, the concentrations of H_2SO_4 and H_3PO_4, the temperature and the particle size, were analysed to model the kinetics of scheelite decomposition. The kinetics data were consistent with the shrinking-core model, and the apparent activation energy of 63.8 kJ/mol shows that the system was under chemical reaction control.

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1. Introduction

Tungsten (W) is the most important member of the refractory metals and has been extensively used in various industrial fields such as cemented carbide, mechanical manufacturing industry, electronics, space navigation and chemical industry (Lassner and Schubert, 1999; Zhao, 2013; Li, 1999). The chief economic minerals of tungsten are wolframite and scheelite. Approximately two-thirds of the world tungsten reserves consist of scheelite deposits (Lassner and Schubert, 1999).

The main method to treat scheelite concentrates is to convert $CaWO_4$ in a soluble sodium tungstate into the leaching solution and to obtain insoluble calcium salts remained in the residue, such as soda autoclaving process and caustic soda autoclaving process. The soda autoclaving process is mostly applied in western countries, and the caustic soda autoclaving process is widely used in China (Queneau et al., 1982; Lassner, 1995; Li, 1996; Shamsuddin and Sohn, 1981; Fang, 2001). To obtain a satisfactory yield, these two methods usually require a high temperature and relatively large amounts of reagents, which necessitate the use of high-pressure and high-quality equipment. In addition, these methods inevitably cause soluble sodium salt discharge and leach residue treatment problems. The excess Na_2CO_3 is neutralized in the subsequent ion extraction process, and the surplus NaOH solution is discharged after the subsequent ion-exchange

procedure (Zhao et al., 2010). The $Ca(OH)_2$ residue from the caustic soda autoclaving process and the $CaCO_3$ residue from the soda autoclaving method must be buried underground.
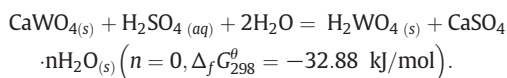
Hydrochloric acid digesting scheelite process was developed without the production of tungstic acid (Martins et al., 2003), which means no problems with diffusion. In this case, the temperature and amount of acid to achieve the complete conversion are much lower than those of common acid leaching (pH = 1.5–2.2; T = 70–80 °C; t = 45–210 min). In addition to the traditional method, Li (1998) shows that an amount of hydrochloric acid of approximately 1.5 times the equivalent to stoichiometric ratio can be used. The insoluble H_2WO_4 from these processes is used to prepare ammonium paratungstate (APT), whereas the leaching solution with $CaCl_2$ must be treated before discharge. To obtain a satisfactory yield of H_2WO_4, the contents of phosphorus, arsenic and other impurities in the scheelite concentrate should be strictly limited because they can cause loss of a large amount of H_2WO_4 into the leach solution in the form of a soluble heteropoly acid (for example, $[PW_{12}O_{40}]^{3-}$) (Xuin et al., 1986; Gürmen et al., 1999). In addition, the HCl agent is notably strongly corrosive and highly volatile, which causes difficulties in the operation. Thus, the conventional route for scheelitic ores is rarely adopted by tungsten metallurgical companies today. It should be noted that the process developed by Martins et al. (2003) was for synthetic scheelite.

To solve the corrosion and volatilization problems of HCl, sulfuric acid is considered an appropriate reagent to digest scheelite concentrates. In addition, sulfuric acid is notably cheap and easily obtained. The reaction trend between sulfuric acid and scheelite is also

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* Corresponding author at: School of Metallurgy and Environment, Central South University, Changsha, 410083, Hunan, China.
E-mail address: zhongweizhao@hotmail.com (Z. Zhao).

remarkable as follows (for example, $\Delta_f G_{298}^\theta$ is -32.88 kJ/mol when $CaSO_4$ is formed) (Martins, 2014).

$$CaWO_{4(s)} + H_2SO_{4\ (aq)} + 2H_2O = H_2WO_{4\ (s)} + CaSO_4$$
$$\cdot nH_2O_{(s)}\left(n = 0, \Delta_f G_{298}^\theta = -32.88\ \text{kJ/mol}\right).$$

Unfortunately, in the scheelite-digestion process using sulfuric acid, tungsten acid solid and calcium sulfate solid are formed and seriously hinder the reactant acid from penetrating into the core of the ores, which leads to a notably low leaching yield. Furthermore, the two solid products cannot be separated. In fact, tungsten acid is easily converted into a highly soluble 12-tungstophosphoric heteropoly acid in the presence of phosphoric acid; thus, apatite should be strictly controlled in scheelite concentrates for the HCl digestion process. However, this phenomenon implies that by intentionally introducing even a small amount of phosphoric acid into the leaching process, tungstic acid will transform into a highly soluble phosphotungstic heteropoly acid, whereas the calcium sulfate solid remains in the residue in the form of calcium sulfate. In addition, tungsten can also form soluble complex compounds with the existence of oxalic, tartaric, and citric (Martins, 2003; Kalpakli et al., 2012; Xuin et al., 1986; Gürmen et al., 1999). Thus, tungstic acid will not be produced by adding one of these complexing agents during the scheelite acid-leaching process.

Because tungsten can easily form a soluble complex compound with the existence of phosphoric acid, we have improved a technology to treat scheelite concentrates using sulfuric acid and phosphoric acid (Zhao and Li, 2014). The use of cheap and non-volatile H_2SO_4 has significantly decreased the agent cost and improved the operating environment. Furthermore, phosphorus in the scheelite concentrates is no longer strictly controlled, which releases the pressure of the scheelite concentrate flotation process. We also choose phosphoric acid as the complexing agent because the phosphoric acid solution with a relatively high concentration can increase the solubility of calcium sulfate (Wu, 1987), which will effectively decrease the degree of supersaturation of calcium sulfate when the tungsten ore decomposes. Thus, large crystals easily form, a compact calcium sulfate is prevented, and the scheelite is leached effectively. In addition, the phosphotungstic heteropoly acid can be easily extracted using the cold crystallization process instead of the traditional ion exchange and solvent extraction, and the calcium sulfate residue can be used as cement raw materials. To investigate the leaching behaviors of scheelite concentrates, the effects of the H_2SO_4 and H_3PO_4 concentrations, temperature and particle size on the scheelite concentrate digestion were studied, and the kinetic model equation was established to determine the reaction control steps.

2. Experimental

2.1. Material

The scheelite concentrate samples were dried and sieved to different size fractions to examine the possible effect of the mineral particle size: $-180/+100$ μm, $-100/+74$ μm, $-74/+58$ μm and $-58/+45$ μm. The WO_3 contents in different size fractions are shown in Table 1. The XRD pattern of the scheelite concentrate is shown in Fig. 1.

The reagents (H_2SO_4 and H_3PO_4) in this work were chemically pure.

Table 1
Chemical analysis of the scheelite concentrate (wt.%).

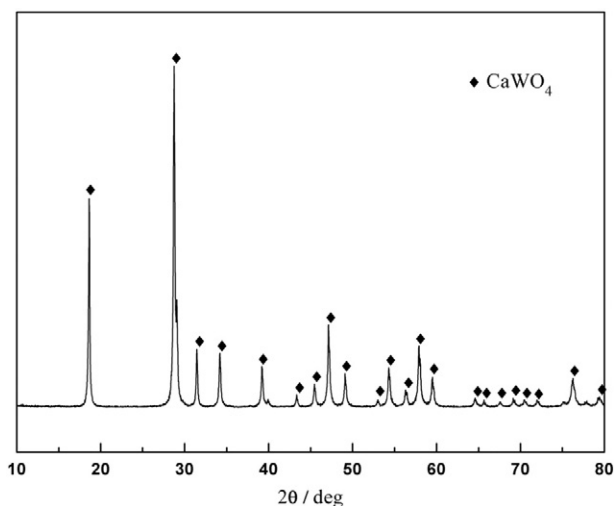| Mesh	μm	Mass fraction of WO_3(%)
$-80/+150$	$-180/+100$	71.94
$-150/+200$	$-100/+74$	72.06
$-200/+250$	$-74/+58$	70.81
$-250/+325$	$-58/+45$	71.97

Fig. 1. X-ray pattern of scheelite concentrates.

2.2. Leaching experiment

The scheelite concentrates were decomposed using sulfuric and phosphoric acids in a 1000-mL Pyrex reaction flask. The flask, which was equipped with an agitator, a thermometer and a reflux condenser, was heated using a thermostatically controlled water bath.

In each run, the flask with 500 mL of sulfuric–phosphoric mixture acid solution was heated to the required temperature (± 0.2 °C) before 5 g of sample was added. The contents were simultaneously well agitated. Then, 1 mL of the solution was sampled to measure the WO_3 content using ICP-AES (Intrepid IIXSP).

3. Results and discussion

3.1. Effect of H_3PO_4 and H_2SO_4 concentrations

The effect on tungsten extraction was studied by varying the H_2SO_4 concentrations from 50 g/L to 400 g/L and the H_3PO_4 concentrations from 50 g/L to 350 g/L at a reaction temperature of 80 °C and a particle size of $-74/+58$-μm. In the studied experiments, the range of H_3PO_4 concentration was 50–350 g/L, which corresponded to the W/P molar ratio range of 1:17 to 1:119. The H_3PO_4 dosage was sufficient for the scheelite concentrate to prevent the tungstic acid precipitation and to form the soluble phosphotungstic heteropoly acid ($H_3PW_{12}O_{40}$). Therefore, the H_3PO_4 concentration hardly affects the extraction rate of WO_3 in the investigated range as shown in Fig. 2.

The effect of the H_2SO_4 concentration on the scheelite concentrate decomposition is shown in Fig. 3. Increasing the H_2SO_4 concentration to an appropriate range positively affected the scheelite concentrate decomposition. However, the degree of supersaturation of calcium sulfate gradually decreased with the increase in H_2SO_4 concentration, and the supersaturated gypsum quickly nucleated and formed a large amount of fine crystals to wrap the unreacted minerals. Thus, the decomposition of scheelite concentrate slightly decreased when the H_2SO_4 concentration reached 400 g/L.

3.2. Effect of temperature

The effect of temperature on the leaching rate was examined at 50–90 °C for the $-74/+58$-μm particle size with 250 g/L H_2SO_4 and 350 g/L H_3PO_4 in the mixture solution. The results in Fig. 4 indicate that the temperature had a positive effect on the leaching rate of WO_3. For example, approximately 99% of the scheelite concentrate was digested at 90 °C after 40 min in comparison with 24% completion at 50 °C.