



Leaching kinetics of scheelite with nitric acid and phosphoric acid



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ABSTRACT

The extraction of tungsten from scheelite concentrate using phosphoric acid as chelating agent in nitric acid solutions was investigated. The effects of the leaching parameters, such as stirring speed, temperature, concentrations of HNO₃ and H₃PO₄ as well as particle size were examined in order to model the kinetics of scheelite dissolution. It was determined that the leaching rate was practically independent of stirring speed and H₃PO₄ concentration at an investigated range, while increased with increasing temperature and HNO₃ concentration. The leaching data agreed quite well with the shrinking core model, with surface chemical reaction as the rate-controlling step. The apparent activation energy was calculated as 52.91 kJ/mol, and the reaction order with respect to HNO₃ concentrations was determined to be 0.23. The leaching process using the shrinking sphere model was established as:

$$1 - (1 - x)^{1/3} = 3.2 \times 10^2 C_{\text{HNO}_3}^{0.23} r_0^{-1} \exp\left(\frac{-52910}{RT}\right).$$

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1. Introduction

Tungsten is usually found in nature in a hexavalent form and primarily exists in the form of wolframite and scheelite in nature. With progressive exhaustion of wolframite, scheelite has become the chief raw material for the production of tungsten [1].

Currently, the main process for scheelite treatment is to decompose the scheelite with sodium hydroxide or sodium carbonate through an autoclaving process [2–6]. Both methods, being widely applied on commercial scale, possessed a strong adaptability to raw materials and could effectively decompose scheelite concentrates and low grade ores, even the scheelite–wolframite blend concentrates. However, these two leaching processes usually require high temperature and relatively large amounts of reagents to obtain high yields, thus necessitating the use of high pressure and high-quality equipment [7,8]. In autoclave-soda process, the exorbitant initial concentration of sodium carbonate could cause a decrease of leaching rate [9,10]. The digestion had to be performed at high liquid/solid ratio, with a corresponding increase in heat consumption and decrease in the equipment capacity.

In the classical process, scheelite is treated with hydrochloric acid to produce tungstic acid [11]. Unfortunately, this process has a fatal shortcoming in that a solid-colloidal layer of H₂WO₄ will be formed and will cover the surface of the unreacted particle. With an extension of the reaction time, the thickness of the product layer increases and, thus,

hinders the reaction [12]. An alternative method that has been proposed to avoid the formation of insoluble H₂WO₄ takes advantage of the complex effect between W and chelating agents, such as oxalic, tartaric, citric, or phosphoric acid [13–15]. However, the process suffers from severe corrosion and volatilization of hydrochloric acid and in consequence it is environmentally harmful. Additionally, few effective ways have been found to deal with large quantity of residual hydrochloric acid, so that there is an increasing need to develop proper leaching system.

Compared with hydrochloric acid, nitric acid has advantages that it is less corrosive to equipment and the aqueous effluents could be treated for production of nitrogen fertilizer. Moreover, the use of nitric acid is constructive to the removal of flotation reagent on mineral surfaces due to its strong oxidation characteristics. Consequently, nitric acid utilized as leachant media could be appropriate for treating scheelite concentrate.

Davey [16] presented a method of extracting tungsten from scheelite and wolframite ores using two-step leaching. In first step, impurities are selectively dissolved and removed to form a mixture of a tungsten containing ore in mineral acids (H₂SO₄, HCl, HNO₃). The resulting tungsten mixture is dissolved as water-soluble compound by addition of organic acids (oxalic, tartaric and acetic acid etc.) in the second step. In his work, further, tungsten was recovered by heating the solution to precipitate H₂WO₄.

Lundquist [17] patented a process to recovery tungsten from tungsten bearing ores. According to this process, the tungsten ore is dissolved in a strong mineral acid solution (H₂SO₄, HCl, HNO₃) in the

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presence of phosphorus as complexing agent provided by adding phosphoric acid, calcium phosphate or phosphate rock. Leach solution was then treated by ammonium salt compound addition to precipitate the tungsten. However, the details of test parameters have not been disclosed.

In this paper, the dissolution of scheelite was carried out with phosphoric acid in nitric acid solution. The purpose was to investigate the kinetics of scheelite dissolution and the effects of stirring speed, temperature, nitric acid concentration, phosphoric acid concentration and particle size on the reaction rate. Furthermore, the controlling kinetic model of the reaction process was established.

2. Materials and methods

2.1. Materials

The scheelite concentrates used in experiment was taken from Jiangxi province of China. The mineral was ground and sieved to different size fractions ($-100/+74\ \mu\text{m}$, $-74/+61\ \mu\text{m}$, $-61/+50\ \mu\text{m}$, $-50/+38.5\ \mu\text{m}$). The composition and XRD pattern of the scheelite are presented in Table 1 and Fig. 1, respectively.

2.2. Methods

Leaching experiments were carried out by placing 250 mL leaching solution into round-bottom flask and heating to desired temperature in a water bath with constant stirring. 1 g sample was added to the solution when the operating temperature had stabilized. 1 mL liquor sample was periodically withdrawn from the reactor for determination of leaching rate through analyzing the concentration of W by ICP-AES instrument. After each sampling, 1 mL of fresh lixiviant was added to the reactor to keep the volume of the solution constant during the experiments. When experiment completed, the mixture in the reactor was filtered to separate the solid and solution.

3. Result and discussion

3.1. Effect of stirring speed

The effect of stirring speed on the dissolution of scheelite was examined in the range from 200 rpm to 400 rpm. As presented in Fig. 2, the leaching rate was practically independent of stirring speed, which indicates that the mass transfer was not influenced by fluid film around the solid particles and scheelite dissolution was under chemical reaction control. Therefore, stirring speed of 300 rpm was used for all subsequent experiments.

3.2. Effect of temperature

The leaching results obtained at different temperatures (323 K–363 K) are shown in Fig. 3. It was observed that the extraction of tungsten was significantly sensitive to temperature and increased with an increase in temperature. For example at 363 K, the dissolution of scheelite was almost accomplished after 45 min, compared with 24.7% completion at 323 K.

Table 1

The chemical composition of scheelite concentrate (wt.%).

Element	WO ₃	H ₂ O	Mo	MnO	P	Sn	S	SiO ₂	Cu	As
Content (%)	67.47	0.23	0.04	0.50	0.029	0.080	0.240	1.800	0.100	0.040

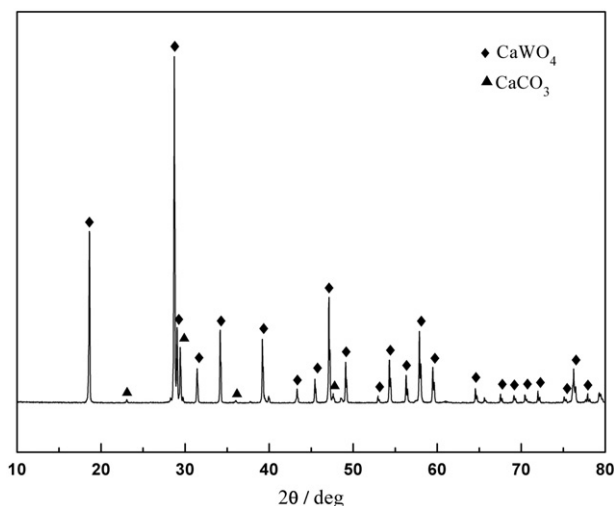


Fig. 1. XRD pattern of scheelite concentrate.

3.3. Effect of nitric acid

The effect on tungsten extraction was studied by varying the nitric acid concentration from 0.5 mol/L to 3.0 mol/L. The results obtained are shown in Fig. 4. The dissolution curves show an increase in tungsten recovery with increasing nitric acid concentration. After 2 h, the leaching rate reached 92.3% at a HNO₃ concentration of 3.0 mol·L⁻¹, whereas the leaching rate was 77.3% at a HNO₃ concentration of 0.5 mol·L⁻¹.

3.4. Effect of phosphoric acid

Leaching experiments for phosphoric acid concentration ranging from 0.1 mol/L to 0.75 mol/L were performed in order to investigate the influence of phosphoric acid concentration. Results in Fig. 5 show that the variations in H₃PO₄ concentration had no significant effect on tungsten extraction at an investigated range. According to the literature, polytungstate species in aqueous solutions varies during the dissolution of scheelite depending on the W/P ratio, and the stoichiometric W/P ratio is $\leq 12/1$ [18,19]. When the H₃PO₄ concentration was 0.1 mol/L, the W/P ratio is 1/8.5. The experiments suggest that 0.1 mol/L H₃PO₄

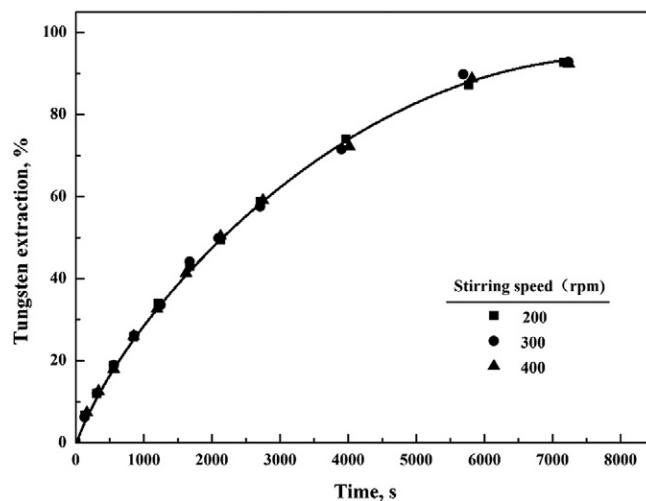


Fig. 2. Effect of stirring speed on tungsten extraction (Temperature: 343 K; HNO₃ concentration: 3.0 mol/L; H₃PO₄ concentration: 0.5 mol/L; particle size: $-50 + 38.5\ \mu\text{m}$).

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