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Leaching kinetics of scheelite in hydrochloric acid solution containing hydrogen peroxide as complexing agent

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ABSTRACT

The reaction kinetics for the leaching of scheelite with hydrogen peroxide and hydrochloric acid have been studied to determine the effect of process parameters, such as temperature, concentrations of hydrogen peroxide and hydrochloric acid and particle sizes. The Avrami–Erofeev equation and the Mampel equation were proposed based on the experimental data. Comparing the curve obtained from the kinetic model equation and experimental data, it was determined that both equations were well-fitted to the experimental data. Comparison of the results also demonstrated that Avrami–Erofeev equation was the best kinetic model equation. The Avrami–Erofeev equation was as follows:

$$[-\ln(1-x)] = \left(5.60 \times 10^2 \cdot C_{H_2O_2}^{0.29} \cdot e^{-\frac{38930}{RT}} \cdot t\right)^{1.01}.$$

1. Introduction

Scheelite is one of the main primary resources for tungsten extraction. Approximately two-thirds of the world tungsten reserves consist of scheelite deposits (Lassner and Schubert, 1999). Scheelite can be digested by HCl, NaOH and Na_2CO_3 (Forward and Vizsolyi, 1965; Li et al., 2001; Queneau et al., 1982). In the classical acid-leaching procedure, scheelite concentrates are decomposed to produce tungstic acid (H_2WO_4) by a hydrochloric acid solution (Eq. (1)).

$$CaWO_{4(S)} + 2HCl_{(aq)} = H_2WO_{4(S)} + CaCl_{2(aq)}. \tag{1}$$

According to Eq. (1), the dense solid layer of tungstic acid is formed and then covers the surface of the scheelite particles. Previous research has demonstrated that the scheelite leaching process is under the diffusion control because of the dense layer. To increase the leaching rate, some countermeasures, such as increasing the concentration of the reagents, elevating the reaction temperature and decreasing the initial particle size, are adopted. In addition, some strengthening methods, such as mechanical activation and ultrasonic technology, are also adopted to improve the leaching rate in some studies (Levenspiel, 1999; Narayana et al., 1997). However, as for the scheelite leaching with HCl solution, increasing the concentration of the reagents and elevating the reaction temperature are harmful to the environment due to the high volatility of HCl. Additionally, it demands expensive

acid-resistant equipment because of the strong corrosiveness of HCl. The decrease of initial particle size means higher grinding costs. The application of mechanical activation and ultrasonic technology can destroy the dense film and decrease the concentration and temperature. Nevertheless, the mechanical activation method requires a special thermal ball-milling reactor, and ultrasonic technology is now only suitable for experimental studies or small-scale production (Peng et al., 1989). Therefore, other effective methods should be utilised to eliminate the influence of the solid layer and increase the leaching rate.

Tungsten will form soluble complex compounds with the existence of oxalic, tartaric, citric, and phosphoric acid (Martins, 2003; Xuin et al., 1986). This means that tungstic acid will not be produced by adding one of these complexing agents during the process of scheelite acid-leaching. Recently, some studies have been performed to increase the decomposition rate through this method.

Some studies have been conducted on scheelite leaching with phosphoric and hydrochloric acid solution (Gurmen et al., 1999; Kahruman and Yusofoglu, 2006; Xuin et al., 1986). Instead of H_2WO_4, water-soluble compound hetero-poly-tungstic acid was formed during the leaching process and the decomposition rate was greatly enhanced. Gurmen et al. investigated the effect of important process parameters and obtained the optimum conditions for leaching low-grade scheelite concentrates: 353 K, 2 mol · L^{-1} HCl, 2 h leaching period, S/L ratio of 1/10, W/PO_4^{3-} weight ratio of 7/1, and stirring speed of 900 rpm. Xuin et al. and Kahruman et al. studied the leaching kinetics of synthetic $CaWO_4$ and scheelite concentrates and obtained the kinetic equation. They found that the reaction rate was controlled by the chemical reaction on the surface of solid particles. From above, it can be found that

adding the phosphate or phosphoric acid into hydrochloric acid can change the reaction control step, resulting in the decrease of reagent concentration and the reaction time.

Recently, Kalpakli et al. performed research on the dissolution of $CaWO_4$ in oxalic acid solution (Kalpakli et al., 2012). The results showed that the dissolution reaction was conducted in two steps: intermediate product $Ca[WO_3(C_2O_4)H_2O]$ was yielded initially and was transformed to $H_2[WO_3(C_2O_4)H_2O]$ as the final product. The solid product $CaC_2O_4H_2O$ formed a protective layer at high temperature (>343 K). Tungstic acid can be precipitated from the leaching solutions containing tungsten as $H_2[WO_3(C_2O_4)H_2O]$ by increasing the temperature of the solution to the boiling point. Therefore, the oxalic acid solution is a good complexing agent for scheelite leaching when the temperature is below 343 K.

Hydrogen peroxide is a low-cost and clean complexing agent; its addition does not introduce impurity ions that may be harmful to the subsequent process or the environment (Guan et al., 2012). In some research, H_2O_2 solution is used to dissolve the tungsten wire and powder to prepare the tungsten compounds or to analyse the tungsten samples (Murau, 1961). In the dissolving process, tungstate peroxide is formed. The properties of tungstate peroxide have been used to separate molybdenum and tungsten by solvent extraction from ammonium solution (Guan et al., 2012).

Meanwhile, the structure of peroxo tungsten compounds has been discussed (Lassner and Schubert, 1999; Pecquenard et al., 1998). Hydrogen peroxide may be regarded as a bidentate ligand that substitutes the oxygen ligands at the tungstate ion. The 3-membered ring configuration

$\begin{smallmatrix} O \\ | \\ O \end{smallmatrix}\!\!>\!\!w$ is thermodynamically more stable than the $W\!\overset{H_2O}{=}\!O$ or $w\!\!<\!\!\begin{smallmatrix} OH \\ OH \end{smallmatrix}$ bonding configurations when the hydrogen peroxide concentration is high enough (Lassner and Schubert, 1999). In addition, when tungsten powder is dissolved in hydrogen peroxide, or when WO_3 reacts with hydrogen peroxide, peroxotungstic acid with the $\begin{smallmatrix} O \\ | \\ O \end{smallmatrix}\!\!>\!\!w$ structure will be generated, And the peroxy compounds, in which the ratio of (O_2):W is 4:1, 3:1, 2:1 and 1:1, are formed depending on the pH value (Bailar et al., 1973; Dickman and Pope, 1994; Lassner and Schubert, 1999). Based on the conductometric and potentiometric titration of peroxotungstic acid, Richardson found that the H_2WO_4 solid disappeared as hydrogen peroxide was added; two peroxotungstic acids with (O_2):W ratios of 1:1 and 4:1 were formed during the whole pH range (Richardson, 1960). However, all peroxo tungsten compounds are unstable. The degree of instability increases with increasing W:(O_2) ratio. As the pH of peroxide-rich solutions of tungstate is lowered, the tetraperoxoanions are converted into dimers of diperoxo species (Lassner and Schubert, 1999). From this, it is concluded that when a solid particle of scheelite concentrate is in contact with the aqueous solution of hydrogen peroxide and hydrochloric acid in the leaching process, the soluble peroxotungstic acids $[WO(O_2)_2(H_2O)_2]$ will form in the solution (Eq. (2)) (Pecquenard et al., 1998). And the product of peroxotungstic acids may be decomposed to tungstic acid at high temperature, which will be a new method for producing tungstic acid.

$$CaWO_{4(S)} + 2HCl_{(aq)} + 2H_2O_{2(aq)} \rightarrow [WO(O_2)_2(H_2O)_2]_{(aq)} + CaCl_{2(aq)} + H_2O_{(l)}. \tag{2}$$
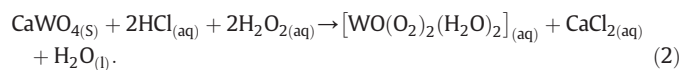
However, up to now, there has not been a detailed study on scheelite leaching with H_2O_2 in HCl solution. It is meaningful for tungsten

Table 1
Quantitative chemical analysis results of major elements of scheelite concentrate.

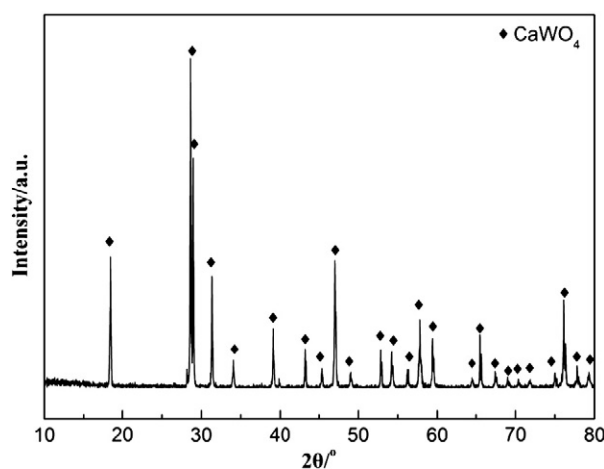| Size fractions (μm)	WO$_3$ (%)	Ca (%)	Sn (%)	Fe (%)	Si (%)	Al (%)	Mn (%)
−180 + 100	71.94	14.69	1.553	0.9014	0.4112	0.3794	0.3233
−100 + 74	72.06	14.58	1.747	0.9350	0.3546	0.3233	0.4054
−74 + 58	70.81	14.93	1.162	0.8492	0.4382	0.3997	0.3172
−58 + 45	71.97	14.61	1.686	0.9095	0.3783	0.3673	0.3318

Fig. 1. XRD patterns of scheelite concentrate.

extraction from scheelite concentrates with acid solution containing H_2O_2 as a complexing agent.

In this paper, the leaching of scheelite with H_2O_2 in HCl solution was studied to investigate the effect of temperature, H_2O_2 concentration, HCl concentration and particle sizes on the reaction rate. More importantly, the reaction mechanism for the extraction process will be discussed, corresponding to the final-deduced kinetic model equations being obtained.

2. Experiments

2.1. Materials and reagents

The samples of scheelite concentrates were from Chongyi Zhangyuan Tungsten Co. Ltd (Jiangxi province, China). Scheelite concentrates were dried and sieved to different size fractions. The WO_3 contents of scheelite concentrates are presented in Table 1. The XRD patterns of the scheelite concentrates are shown in Fig. 1. Hydrogen peroxide functioned as a complexing agent and hydrochloric acid as the leaching agent. All reagents used in the test were of analytical grade.

2.2. Apparatus and experimental procedure

A 500 mL Pyrex flask fitted with an agitator, a thermometer and a reflux condenser was used as the reactor. The flask was put into a thermostatically controlled water bath.
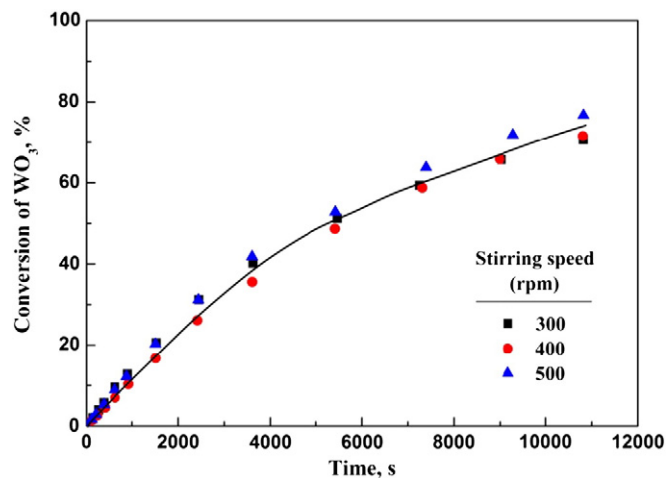

Fig. 2. Effect of stirring speed on the conversion of WO$_3$ (Temperature: 303 K; HCl concentration: 2.0 mol · L^{-1}; H$_2$O$_2$ concentration: 1.6 mol · L^{-1}; particle size: −100 + 74 μm).