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# Comparative kinetic analysis of conventional and ultrasound-assisted leaching of scheelite by sodium carbonate

Jin-hong YANG, Li-hua HE, Xu-heng LIU, Wen-tao DING, Yun-feng SONG, Zhong-wei ZHAO

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

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**Abstract:** For further comprehending the mechanism of the intensification of ultrasound for extraction, the difference of leaching kinetics between the ultrasound-assisted and conventional sodium carbonate leaching of scheelite was studied, and the corresponding kinetic equations were established. The results indicate that the obtained apparent activation energy with or without ultrasound is same 72 kJ/mol, and both reactions are controlled by surface chemical reaction. By comparing the leaching kinetics of scheelite by $Na_2CO_3$, NaOH and $Na_3PO_4$ reactants with or without ultrasound, a general conclusion for scheelite hydrometallurgy is obtained. For the process with the formation of compact product layer, the intensification of the tungsten extraction with ultrasound mainly reflects in the stripping and elimination of product layer, corresponding to the transformation of kinetic controlling step from diffusion controlling step and reduction of apparent activation energy. For the one without compact product layer or with a loose and porous product layer, the intensification mainly embodies in the increase of frequency factor, and the controlling step and apparent activation energy of the reaction always remain constant.

**Key words:** scheelite; kinetics; ultrasound; ultrasonic chemistry; activation energy

## 1 Introduction

Tungsten is widely applied in machine equipment manufacturing, chemical industry, national defense industry, and so on. Unfortunately, scheelite ($CaWO_4$), as one of the most important commercial raw minerals for the extraction of tungsten metal (the tungsten reserves of China are the first in the world, and about 70% of the tungsten is hosted in scheelite deposits), is a typical refractory ore for metallurgy [1]. Up to now, the main technologies for scheelite extraction are caustic decomposition and sodium carbonate decomposition. However, both of them were operated at a high temperature and pressure situation in autoclave. For example, in the sodium carbonate decomposition process, the decomposition temperature was usually controlled to be 200−230 °C, and the dosage of $Na_2CO_3$ was 2.5−3.5 times of the theoretical amount [1−3]. Especially with the consumption of the high-quality tungsten resources, the treatment of low-grade tungsten ores causes more serious challenges for the tungsten metallurgy.

Therefore, how to intensify the tungsten extraction process attracts more and more attention now. And researches have been done to improve the leaching process and to obtain a high yield of tungsten by applying mechanical activation [4−6], microwave-assisted heating [7,8] and reactive extrusion [9]. In recent years, ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems [10,11]. And it has successfully increased the conversion, improved the yield, changed the reaction pathway, and initiated the reaction in biological, chemical, and electrochemical systems [12,13]. Additionally, ultrasound may have other mechanical effects on the reaction, such as increasing the surface area between the reactants, accelerating the dissolution, and renewing the surface of a solid reactant [12,14,15]. Those characters of the ultrasound are beneficial for the intensification of scheelite decomposition, because in the process of caustic decomposition and sodium carbonate decomposition, solid resultant ($Ca(OH)_2$ or $CaCO_3$) will be formed and coated on the surface of the scheelite ores, which is possible to restrict the leaching reactions.

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**Corresponding author:** Li-hua HE; Tel: +86-731-88830476; E-mail: helihua@csu.edu.cn

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Actually, the effects of ultrasound on the kinetics of scheelite leaching with sodium hydroxide [16] and sodium phosphate [17] were studied, and the results reveal that ultrasound can improve the tungsten extraction effectively. However, there were few reports on the leaching kinetic of scheelite by sodium carbonate with ultrasound. Therefore, the purpose of this work is to study the leaching kinetics of scheelite by sodium carbonate with or without ultrasound. Based on that, the apparent activation energy and frequency factor were calculated. Furthermore, the controlling steps of chemical reactions were determined, and the final-deduced kinetic equations were obtained.

## 2 Experimental

### 2.1 Experimental materials and devices

The samples of the scheelite concentrates are provided by Chongyi Zhangyuan Tungsten Co., Ltd., Jiangxi, China. Before the leaching experiments, the scheelite concentrate was dried and sieved to yield a particle size distribution between 38 and 80 μm. The $WO_3$ contents of scheelite concentrates in different size fractions are listed in Table 1, and the XRD pattern is shown in Fig. 1.

**Table 1** Chemical compositions of scheelite

| Sample No. | Particle size/μm | Mass fraction of $WO_3$/% |
|---|---|---|
| 1 | 58−80 | 62.25 |
| 2 | 45−58 | 64.72 |
| 3 | 38−45 | 65.22 |

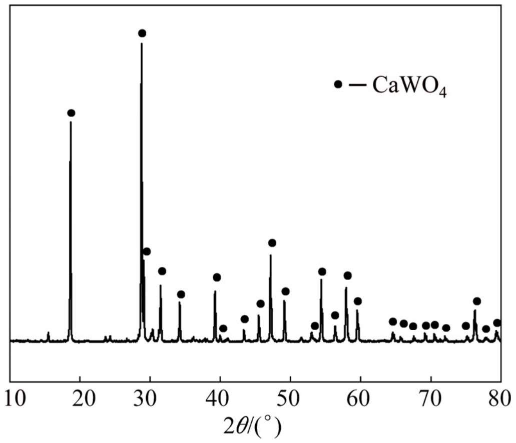

**Fig. 1** XRD pattern of scheelite concentration

The schematic illustration of the experimental setup is shown in Fig. 2. The ultrasonic instrument (GY-USM−1000, Beijing Iron and Steel Research Institute, China) has two transducers and can be operated at a frequency of (20±2) kHz and a rated power of 1 kW, companying with a water bath (*d*150 mm × 150 mm). The extraction experiment was carried out in a 500 mL three-necked flask equipped with an agitator, a thermometer and a reflux condenser, and the three-necked flask was heated using a thermostatical controller in water bath. For each experiment, 8 g scheelite concentrate was added at one time to the agitated $Na_2CO_3$ solution (300 mL) at a required temperature with or without ultrasound. $WO_3$ content was measured by ICP−AES (IRIS intrepid XSP, Thermo Electron Corporation), and X-ray diffraction (XRD) profiles of the sample were measured with TTR-III (Cu $K_\alpha$ radiation, Rigaku Corporation) at a speed of 4 (°)/min.

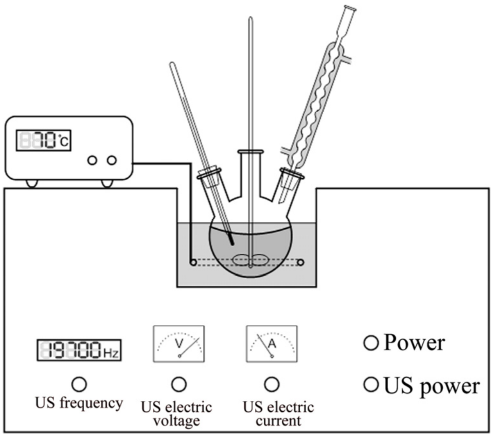

**Fig. 2** Experimental devices for ultrasonic extraction (US: ultrasound)

### 2.2 Kinetic equations and mechanism

Generally, from the viewpoints of chemistry reaction dynamics, two principal objectives are common to the vast majority of kinetic studies. One is the determination of the reaction rate equation that satisfactorily describes the extent of conversion of reactant or formation of product with time as reaction proceeds, usually, but not necessarily, at constant temperature. The other is to determine the influence of temperature on the reaction rate. Therefore, it is necessary for us to estimate the traditional kinetic triplets, i.e., activation energy, frequency factor and kinetic equation.

For this extraction system, the extraction reaction of scheelite in sodium carbonate can be expressed as Reaction (1). Generally, in this solid−liquid system of hydrometallurgy, the process can be described by an unreacted shrinking core model. And this model considers that the leaching process is controlled either by the diffusion of reactant through the solution boundary (external diffusion control), or through a solid product layer (internal diffusion control), or by the surface chemical reaction rate (chemical reaction control).

$$CaWO_4(s)+Na_2CO_3(aq)=CaCO_3(s)+Na_2WO_4(aq) \quad (1)$$

For the external diffusion control, it can be explicitly eliminated by intensive stirring of the reaction mixture. So, assuming that scheelite particles have a spherical geometry and the surface chemical reaction is the rate determining step, Eq. (2) can be used to describe the leaching kinetics:

$$1-(1-\alpha)^{1/3}=K_\mathrm{s}t,\quad K_\mathrm{s}=\frac{kc_\mathrm{s}^n}{\rho r_0} \tag{2}$$

where $\alpha$ is the fraction of extraction rate (%), $K_\mathrm{s}$ is the apparent rate constant of reaction ($\mathrm{s}^{-1}$), $t$ is the reaction time (s), $c_\mathrm{s}$ is the concentration of leaching reagent on the surface of the scheelite concentrate (mol/kg), $n$ is the reaction order, $r_0$ is the initial radius of the solid particles (μm), and $\rho$ is the density of mineral particle ($\mathrm{g/cm^3}$).

Langmuir equation can be used to evaluate $c_\mathrm{s}$ [18], and the equation is given by

$$\theta=\frac{K_\mathrm{a}c}{1+K_\mathrm{a}c}=\frac{c_\mathrm{s}}{c_\mathrm{sm}} \tag{3}$$

where $K_\mathrm{a}$ is the equilibrium constant of the adsorption reaction, $c$ is the concentration of leaching reagent (mol/kg), $c_\mathrm{sm}$ is the maximum concentration of leaching reagent on the surface of the scheelite concentrate (mol/kg), and $\theta$ is the fraction of surface sites occupied by leaching reagent.

Substituting Eq. (3) into Eq. (2), Eq. (4) can be obtained:

$$1-(1-\alpha)^{1/3}=\frac{k}{\rho r_0}\left(\frac{K_\mathrm{a}c}{1+K_\mathrm{a}c}\right)^n c_\mathrm{sm}^n t \tag{4}$$

where $k$ is the rate constant for surface reaction ($\mathrm{s}^{-1}$).

If the reaction is controlled by diffusion through the product layer, it will have an integrated rate equation as follows:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=K_\mathrm{d}t,\quad K_\mathrm{d}=\frac{2Dc_\mathrm{s}^n}{\rho r_0^2} \tag{5}$$

where $D$ is the diffusion coefficient in the porous product layer ($\mathrm{m^2/s}$).

Additionally, the temperature dependence of the reaction rate constant ($K$) can be calculated using Arrhenius equation:

$$K=A\exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{6}$$

where $A$ is the frequency factor, $E_\mathrm{a}$ is the apparent activation energy (J/mol), $R$ is the mole gas constant (8.314 J/(K·mol)), and $T$ is the reaction temperature (K).

## 3 Results

### 3.1 Effect of reaction temperature

The effect of temperature on the decomposition of scheelite is shown in Fig. 3 under the conditions of $\mathrm{Na_2CO_3}$ concentration of 5/3 mol/kg and particle size of 45−58 μm. Obviously, the extraction of tungsten increases with the increase of reaction temperature and leaching time. Additionally, it can be seen that the extraction process is intensified with ultrasound, i.e., ultrasound has a positive effect on the leaching rate.

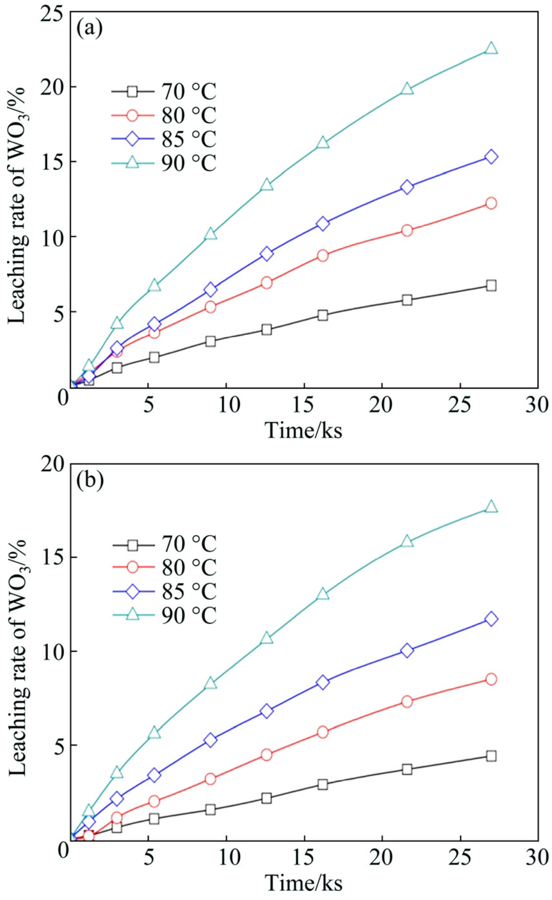

**Fig. 3** Effect of temperature on leaching rate of $\mathrm{WO_3}$ with (a) and without (b) ultrasound (5/3 mol/kg $\mathrm{Na_2CO_3}$, particle size 45−58 μm)

To calculate the traditional kinetic triplets and obtain the kinetic controlling step, the data of Fig. 3 are used to perform linear fitting via Eqs. (2) and (5), and the results are presented in Figs. 4 and 5, respectively. The comparison results reveal that the fitting coefficients of chemical reaction control shrinking core models ($R^2$=0.97−0.99) are higher than those fitted via internal diffusion control model ($R^2$=0.92−0.96). That is, chemical reaction control shrinking core model fits much better than the internal diffusion control model. It is worth noting that whether with or without the ultrasound, the mechanism of the leaching process has not been converted. In other words, the effect of the $\mathrm{CaCO_3}$ product layer on the reaction rate can be ignored. Hence, it can be concluded that at all leaching temperatures the process is controlled by the rate of chemical reaction.

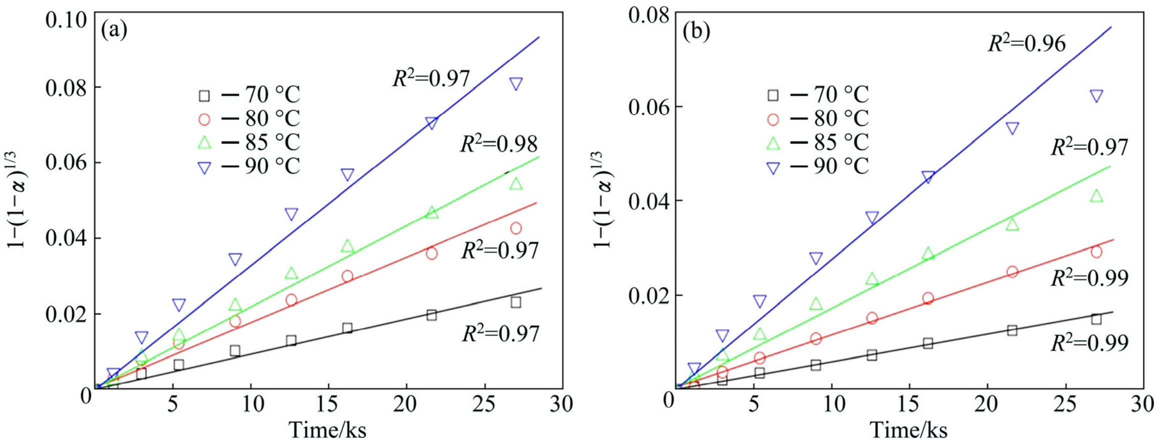

**Fig. 4** Relationship between $1-(1-\alpha)^{1/3}$ and leaching time for $WO_3$ extraction with (a) and without (b) ultrasound

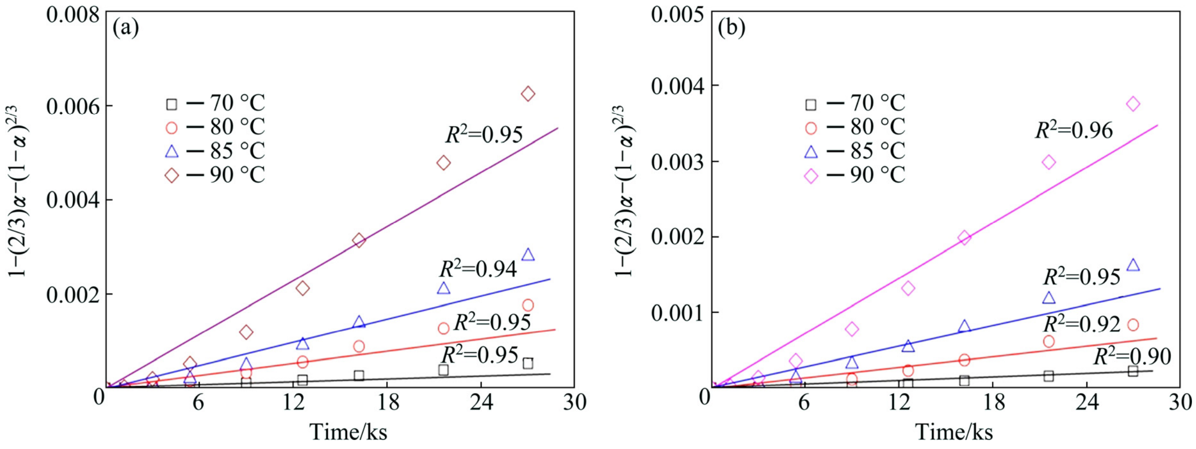

**Fig. 5** Relationship between $1-(2/3)\alpha-(1-\alpha)^{2/3}$ and leaching time for $WO_3$ extraction with (a) and without (b) ultrasound

According to Eq. (4), the slopes of the lines in Fig. 4 are the values of the apparent rate constant of the reactions ($K$). Combining Eqs. (2), (6) and the slope values obtained from Fig. 5, the apparent activation energies for the leaching process are evaluated from the plot of ln $K$ versus $1/T$ shown in Fig. 6. The goodness of the fit of the experimental data with the Arrehenius equation can be evidenced from Fig. 6. And the apparent activation energy for both situations with or without ultrasound is the same 72 kJ/mol, which further evidences that both of the leaching processes are controlled by the surface chemical reaction.

### 3.2 Effect of sodium carbonate concentration

Figure 7 shows the effect of sodium carbonate concentration on the tungsten dissolution under the conditions of 80 °C, particle size 45−58 μm, with or without ultrasound. Similar to the results obtained from Fig. 3, ultrasound can accelerate the extraction process. However, for the effect of sodium carbonate concentration itself, the tungsten extraction rate increases at first and decreases subsequently in the used concentration range, whether with or without ultrasound.

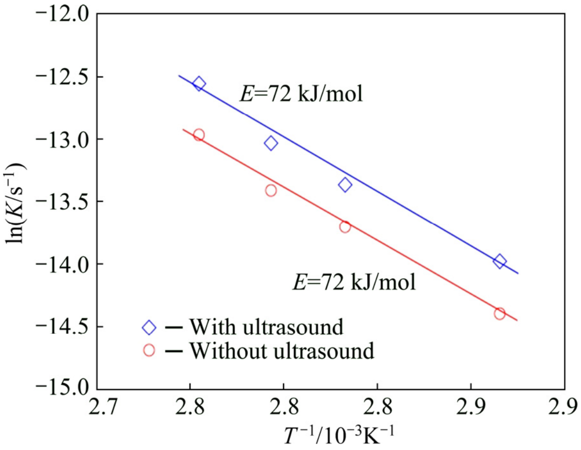

**Fig. 6** Arrhenius plots for apparent activation energy

And two main reasons can be used to explain this phenomenon. 1) When the $Na_2CO_3$ concentration is low, i.e., $K_a c \ll 1$, the right-hand side of Eq. (4) can be written as $kK_a^n c^n c_{sm}^n t/(\rho r_0)$. Conversely, when $Na_2CO_3$ concentration is high, i.e., $K_a c \gg 1$, the right-hand side of Eq. (4) can be written as $kc^0 c_{sm}^n t/(\rho r_0)$. This means that the apparent reaction order with respect to $c$ varies from $n$ to 0 as the $Na_2CO_3$ concentration increases.

Therefore, the growth rate of $K$ will decrease with increasing $Na_2CO_3$ concentration. 2) In addition, the solubility of $Na_2WO_4$ in $Na_2WO_4$−$Na_2CO_3$−$H_2O$ system decreases with increasing $Na_2CO_3$ concentration [19]. In other words, a too high $Na_2CO_3$ concentration corresponds to a low equilibrium concentration of $Na_2WO_4$. Therefore, when the $Na_2CO_3$ concentration is too high, it will inhibit the leaching reaction to produce $Na_2WO_4$, instead of improving the leaching process. This result is consistent with the researches by CHO [18]. That is why in the real practical production of $Na_2CO_3$ decomposition of scheelite, the initial concentration of $Na_2CO_3$ should be limited in the scope of 120−200 g/L, corresponding with the terminal $Na_2CO_3$ concentration of 80−130 g/L [20−22].

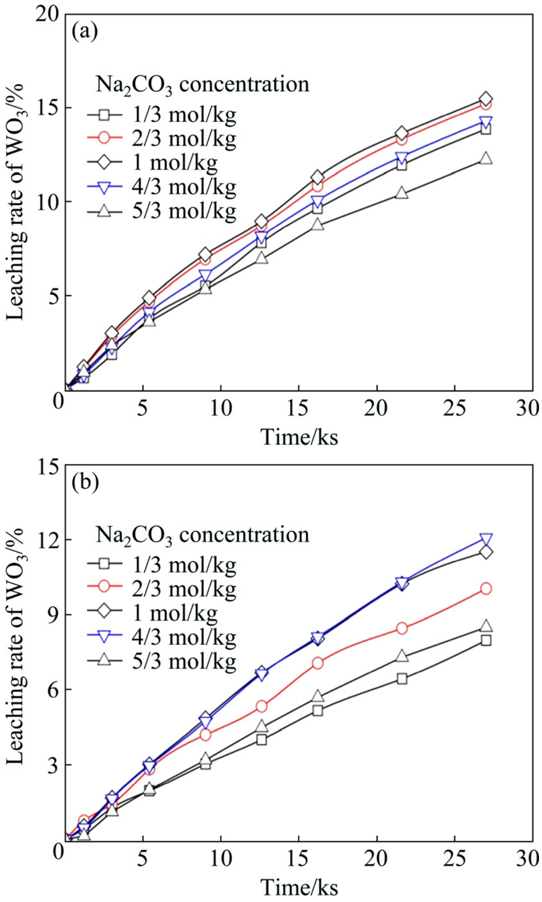

**Fig. 7** Effect of $Na_2CO_3$ concentration on leaching rate of $WO_3$ with (a) and without (b) ultrasound

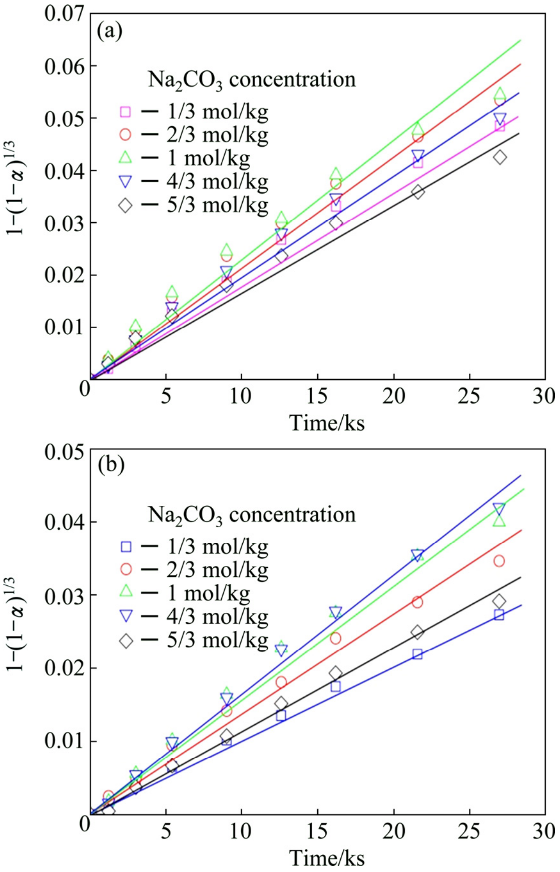

**Fig. 8** Linear plots according to surface reaction model for effect of $Na_2CO_3$ concentration on leaching rate with (a) and without (b) ultrasound

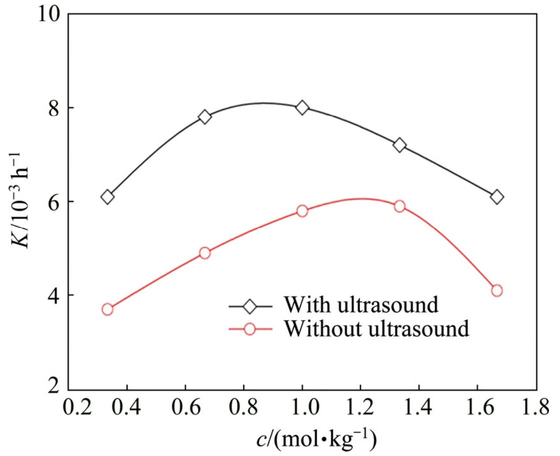

**Fig. 9** Variations of apparent rate constant $K$ with $Na_2CO_3$ concentration

In spite of this, the linear fitting results are also in good agreement with the experimental data according to the surface reaction model for the effect of $Na_2CO_3$ concentration, as shown in Fig. 8, and the linear correlation coefficient $R^2$ are all over 0.98. In addition, Fig. 9 presents the plot of apparent reaction rate $K$ vs $Na_2CO_3$ concentration. Just as the results of Fig. 7, the reaction rate increases at first and decreases subsequently with increasing $Na_2CO_3$ concentration, and the highest rate is obtained at 1 mol/kg $Na_2CO_3$. Because of the tendency of the reaction rate, it is impossible to obtain the reaction order, $n$, of $Na_2CO_3$ concentration. Even so, it will not hamper the investigation of the leaching kinetics.

### 3.3 Effect of particle size

The effect of the particle size of the scheelite concentrate on the $WO_3$ dissolution is shown in Fig. 10.

Obviously, the finer the granularity of the scheelite concentrate particles is, the higher the leaching rate and chemical reaction rate can be obtained, whether with or without ultrasound. And it can be contributed to the higher specific area of the finer particles.

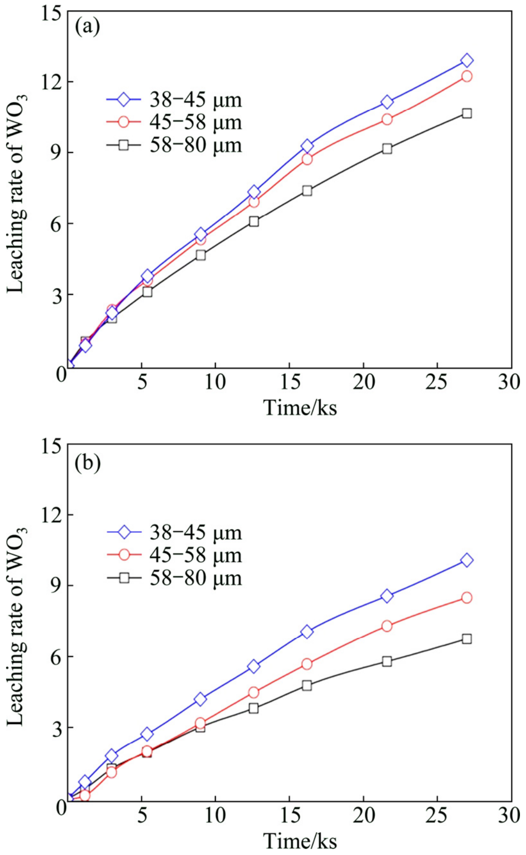

**Fig. 10** Effect of particle size on leaching rate of $WO_3$ with (a) and without (b) ultrasound

For unreacted shrinking core model, if the process is controlled by the surface chemical reaction, the relationship between apparent reaction rate ($K$) and reciprocal of particle initial radius ($1/r_0$) should be linear (Eq. (2)). Based on this consideration, the plot of $K$ and $1/r_0$ is drawn and the results are presented in Fig. 11. As expected, the value of $K$ is proportional to $1/r_0$, which proves again that the reaching process is controlled by the surface chemical reaction step.

### 3.4 Establishment of kinetic equations

Combining Eqs. (4) with (6), the kinetic equation could be expressed as

$$1-(1-\alpha)^{1/3}=\frac{c_{\mathrm{sm}}^n}{\rho r_0}\left(\frac{K_\mathrm{a}c}{1+K_\mathrm{a}c}\right)^n\cdot A\exp\left(\frac{E_\mathrm{a}}{RT}\right)t \tag{7}$$

For a certain $Na_2CO_3$ concentration of 5/3 mol/kg, the value of $\frac{c_{\mathrm{sm}}^n}{\rho}\left(\frac{K_\mathrm{a}c}{1+K_\mathrm{a}c}\right)^n$ can be considered as constant, and the relationship between $1-(1-\alpha)^{1/3}$ and $r_0^{-1}\cdot\exp[-E/(8.314T)]\cdot t$ is shown in Fig. 12. Although the points in the plot show a little scatter, a straight line could be fitted to the data with a correlation coefficient $R^2$ over 0.97 in both situations. And the value of

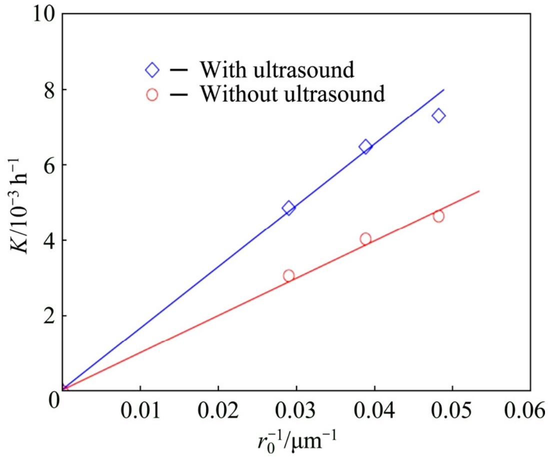

**Fig. 11** Plot of apparent rate constant, $K$, vs $1/r_0$ according to Eq. (2)

$$\frac{c_{\mathrm{sm}}^n}{\rho}\left(\frac{K_\mathrm{a}c}{1+K_\mathrm{a}c}\right)^n A$$ can be obtained as the slope of the lines in Fig. 12, corresponding to the values of $1.37\times10^3$ mm/s for the non-ultrasound experiments and $1.78\times10^3$ mm/s for the ultrasound experiments, respectively.

In summary, the kinetic equation of $Na_2CO_3$ leaching of scheelite with and without ultrasound can be expressed concretely as Eqs. (8) and (9), respectively.

With ultrasound:

$$1-(1-\alpha)^{1/3}=1.78\times10^3 r_0^{-1}\exp\left(\frac{-72000}{8.314T}\right)t \tag{8}$$

Without ultrasound:

$$1-(1-\alpha)^{1/3}=1.37\times10^3 r_0^{-1}\exp\left(\frac{-72000}{8.314T}\right)t \tag{9}$$

## 4 Discussion

Undoubtedly, ultrasound as auxiliary energy is a powerful tool for accelerating leaching processes, and the accelerating mechanisms were studied systematically [23−25]. Although the mechanical effects of ultrasound on the reaction (such as increasing the surface area between the reactants, accelerating dissolution, and renewing the surface of a solid reactant) for a special leaching process are similar to each other, the transformation of the kinetics may be different.

Table 2 lists the leaching kinetic equations of scheelite via NaOH, $Na_3PO_4$, and $Na_2CO_3$ methods with

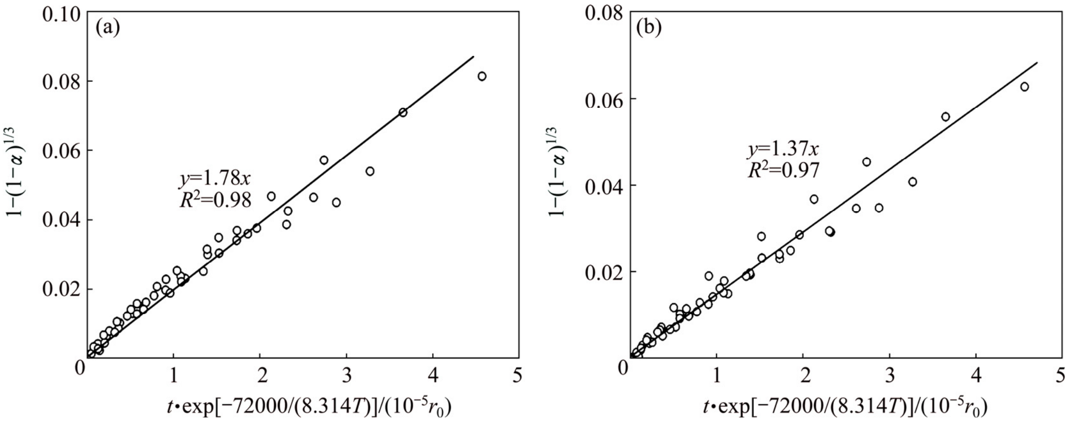

**Fig. 12** Relationship between $1-(1-\alpha)^{1/3}$ and $r_0^{-1}$•exp[−72000/(8.314$T$)]•$t$ with (a) and without (b) ultrasound

**Table 2** Leaching kinetics of scheelite via different methods with or without ultrasound

| Method | Ultrasound | Kinetic equation | Ref. |
|---|---|---|---|
| NaOH leaching | Without | $1-(1-\alpha)^{1/3}=10.03\times10^3[\mathrm{NaOH}]^{1.3}r_0^{-1}\exp\left(\frac{-80000}{8.314T}\right)t$ | [16] |
|  | With | $1-(1-\alpha)^{1/3}=96.85\times10^3[\mathrm{NaOH}]^{0.8}r_0^{-1}\exp\left(\frac{-80000}{8.314T}\right)t$ |  |
| $Na_3PO_4$ leaching | Without | $1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=92.19[\mathrm{Na_3PO_4}]^{0.39}[\mathrm{NaOH}]^{0.34}r_0^{-2}\exp\left(\frac{-78000}{8.314T}\right)t$ | [17] |
|  | With | $1-(1-\alpha)^{1/3}=6.20[\mathrm{NaOH}]^{0.07}r_0^{-1}\exp\left(\frac{-50000}{8.314T}\right)t$ |  |
| $Na_2CO_3$ leaching | Without | $1-(1-\alpha)^{1/3}=1.37\times10^3r_0^{-1}\exp\left(\frac{-72000}{8.314T}\right)t$ | This work |
|  | With | $1-(1-\alpha)^{1/3}=1.78\times10^3r_0^{-1}\exp\left(\frac{-72000}{8.314T}\right)t$ |  |

All of experiments used the same batch of scheelite concentrate and ultrasonic instrument

or without ultrasound. It can be found that for the NaOH and $Na_2CO_3$ decomposition method, whether with or without ultrasound, the apparent activation energies for them are the same, 80 kJ/mol and 72 kJ/mol, corresponding to the same surface chemical reaction control mechanism. And the improvement of the reaction rate mainly reflects in the increase of frequency factor. But for the $Na_3PO_4$ decomposition process, the diffusion through the solid film is the rate limitation step for the leaching of scheelite in the absence of ultrasound. While in the presence of ultrasound, the controlling step changes from the internal diffusion to the surface chemical reaction rate. And the apparent activation energy decreases from 78 kJ/mol in the absence of ultrasound to 50 kJ/mol in the presence of ultrasound.

The reason for different transformation kinetics of different decomposition methods mainly depends on the densification degree of the solid product layer. For the solid product $Ca(OH)_{(s)}$ and $CaCO_3$, the density of them is low, and the formed product layer is loose and porous [1]. Therefore, the diffusion of the reactant NaOH or $Na_2CO_3$ is high-efficient. Conversely, the solid product layer of $Ca_3(PO_4)_2$ is compact, so it is difficult for $Na_3PO_4$ to diffuse through it. With the assistance of ultrasound, the surface of a solid reactant can be renewed, and the surface area between the reactants increases, so the controlling step changes from the internal diffusion to the surface chemical reaction rate.

## 5 Conclusions

1) The comparative kinetic analysis of conventional and ultrasound-assisted leaching of scheelite with sodium carbonate was performed. The shrinking core model with surface chemical reaction control fits the experimental results very well, and the apparent activation energy is the same, 72 kJ/mol for both cases of with or without ultrasound.

2) For $Na_2CO_3$ decomposition of scheelite, the effect of ultrasound for reaction acceleration is mainly focused on the pre-exponential factor, which embraces the collision factor.

3) Through a comprehensive comparison of the relative researches on scheelite leaching, it can be seen

that for the process with the formation of a compact product layer, the intensification of the tungsten extraction with ultrasound mainly reflects in the elimination of product layer, and the kinetic controlling step will be transformed, corresponding to the reduction of apparent activation energy. But for the one with a loose and porous product layer, the intensification mainly embodies in the increase of frequency factor, and the apparent activation energy of the reaction always remains constant.

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# 超声场中白钨矿苏打浸出动力学对比

杨金洪，何利华，刘旭恒，丁文涛，宋云峰，赵中伟

中南大学 冶金与环境学院，长沙 410083

**摘　要**：为进一步了解超声波对浸出反应的强化机理，对有无超声波作用下白钨矿的苏打浸出过程动力学进行对比研究，并建立相应的反应动力学方程。结果表明，有无超声作用情况下所得浸出反应的表观活化能均为 72 kJ/mol，并且反应过程均为表面化学反应控制。通过对比超声场作用下 $Na_2CO_3$、NaOH 和 $Na_3PO_4$ 分解白钨矿的动力学分析发现，当浸出过程有致密产物膜形成时，超声强化主要体现在对产物膜的剥离和消除，浸出动力学会从无超声波作用下的扩散控制转变为超声场作用下的动力学控制，且反应活化能降低。当浸出过程无致密产物层或产物层为疏松多孔结构时，超声强化白钨矿浸出过程主要体现在指前因子的增加，浸出过程控制步骤以及反应表观活化能维持不变。

**关键词**：白钨矿；动力学；超声波；超声化学；活化能

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