

Acid leaching kinetics of zinc plant purification residue

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Abstract: The leaching processes of zinc plant purification residue in sulfuric acid solution were investigated with respect to the effects of sulfuric acid concentration, reaction temperature, and particle size. A particle size of 75–80 μm was required to leach 99.8% cobalt and 91.97% zinc at 70 °C for 20 min when the sulfuric acid concentration was 100 g/L and the ratio of liquid to solid was 50:1 (mL/g). The leaching kinetics of zinc plant purification residue in sulfuric acid solution system conformed well to the shrinking core model, and the dissolution rates of cobalt and zinc were found to be controlled by diffusion through a porous product layer. The apparent activation energy values of cobalt and zinc reaction were calculated to be 11.6931 kJ/mol and 6.6894 kJ/mol, respectively, according to the Arrhenius formula equation. The results show that diffusion through the inert particle pores is the leaching kinetics rate-controlling step.

Key words: cobalt; zinc; acid leaching; leaching kinetics

1 Introduction

The gradually increasing demand for cobalt results in shortage of resources because cobalt is produced mainly as a byproduct of the mining and processing of copper and nickel ores [1]. Cobalt is presented in zinc concentrates with low concentration (0.001%–0.005%). Cobalt purification filtercake, which mainly consists of cobalt, manganese and zinc during the purification of zinc sulfate electrolyte, is considered a good resource of cobalt extraction [2,3]. The current research reported an effective hydrometallurgical process for the recovery of cobalt from cobalt purification filtercake [4]. Overall experimental approach used was to leach the cobalt after sulfation roasting, as well as purification of cobalt using different techniques including precipitation, anion-exchange and solvent extraction [5].

However, few papers have been published on the leaching kinetics of cobalt from zinc plant purification residues. Leaching kinetics zinc [6,7] and cadmium [8] from zinc plant purification residue have been studied by some researchers. SAFARZADEH et al [9] investigated the reductive dissolution of cobalt and manganese from zinc plant purification residues in sulfuric acid solution.

HUBLI et al [10] studied the kinetics of the reduction–dissolution of cobalt oxide in acid media. Some researchers studied the leaching kinetics of cobalt from spent cobalt catalyst [11], cemented carbide scrap [12] and other waste residue [13], while rarely reported the leaching kinetics of cobalt and zinc from zinc plant purification residue.

This paper presents the results of leaching kinetics of cobalt and zinc from zinc plant purification residue with sulfuric acid. In the leaching experiment, the effects of sulfuric acid concentration, reaction temperature, and particle size on cobalt and zinc extraction were investigated.

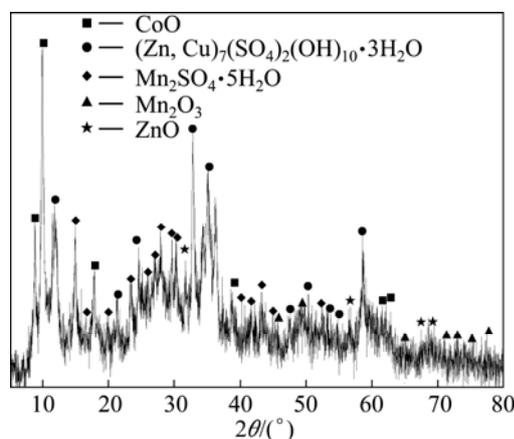
2 Experimental

2.1 Materials

The raw material was zinc plant purification residue. The chemical composition and XRD pattern of the cobalt residue are shown in Table 1 and Fig. 1, respectively. The chemical and mineralogical compositions of the cobalt residue were very complex, containing a great quantity of Zn, Co, Cd, Cu, and Pb, and a little Ni, Fe and Mn. The mineralogical compositions of cobalt and zinc are CoO and ZnO, respectively.

Table 1 Chemical composition of zinc plant purification residue (mass fraction, %)

Zn	Cd	Cu	Pb	Co	Ni	Fe	Mn	O
28.90	10.90	7.10	6.01	4.50	0.84	0.67	0.11	Bal.

**Fig. 1** XRD pattern of zinc plant purification residue

2.2 Experimental apparatus

The experiment was performed in a round-bottom three-necked flask of 1000 mL. The reaction temperature was maintained constant controlled by a constant temperature magnetic stirrer. The agitate rate did not significantly influence the leaching rate of cobalt, which increased by less than 4% when the stirring speed increased from 200 to 400 r/min. Further increase of the agitate rate had little effect on leaching cobalt. To eliminate the influence of the external diffusion and make the leaching agent homogeneously, the agitate rate was chosen to be 400 r/min.

2.3 Experimental method

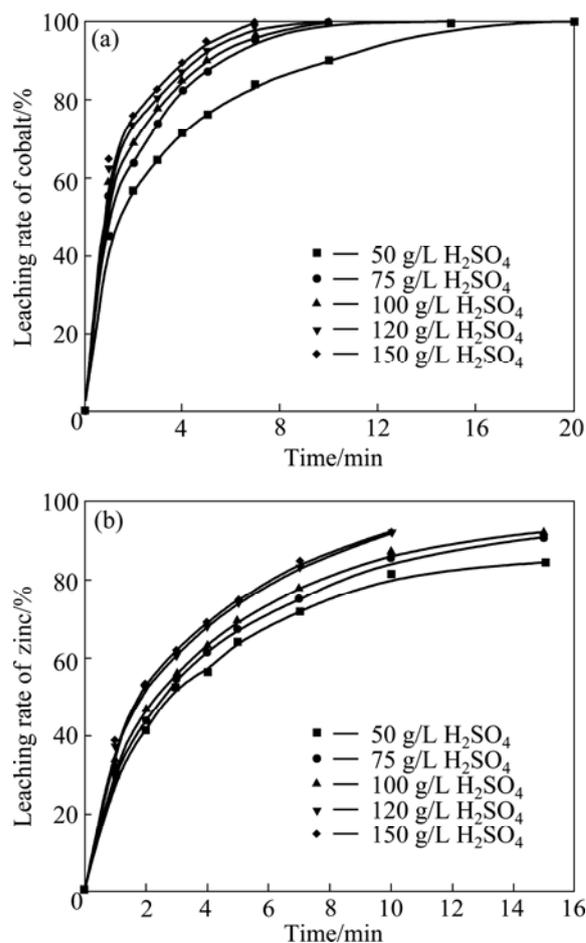
A solution of 500 mL sulfuric acid was put into the reactor. When the solution reached the required temperature, 10 g zinc plant purification residue with required size was added. At selected time intervals, a solution sample of about 1 mL was taken out using a syringe filter. The cobalt concentration of the sample was measured by ICP-AES (Intrepid 11 XSP).

3 Results and discussion

3.1 Effects of reactant concentration on leaching rate of cobalt and zinc

The effects of the concentration of sulfuric acid on the leaching rates of cobalt and zinc were studied under the conditions that fine residue particle size was 75–80 μm , the leaching temperature was 55 $^\circ\text{C}$, the leaching time was 20 min, and the ratio of liquid to solid was 50:1 (mL/g). The results are shown in Fig. 2. It is obvious that the concentration of sulfuric acid has a significant effect

on the dissolution of cobalt by varying to 50, 75, 100, 120 and 150 g/L. In general, the leaching rate increases with increasing concentration of reagent, but only up to a certain maximum level. It can be seen from Fig. 2 that the dissolution level of the process increases with the increase in the concentration of sulfuric acid until about 100 g/L both for cobalt and zinc. Substituting the results, the relationship between $1-3(1-x)^{2/3}+2(1-x)$ and leaching time at different concentrations of leaching agent is shown in Fig. 3.

**Fig. 2** Effects of sulfuric acid concentration on leaching rates of cobalt (a) and zinc (b)

As shown in Fig. 3, there are also linear relationships between leaching time and the diffusion model both for cobalt and zinc. This proves that the leaching kinetics can be described by the diffusion model.

3.2 Effects of reaction temperature on leaching rate of cobalt and zinc

The effects of reaction temperature on the leaching rate of cobalt and zinc were studied under the conditions that residue particle size was 75–80 μm and sulfuric acid concentration was 100 g/L, the leaching time was 20 min, and the ratio of liquid to solid was 50:1 (mL/g). The results are shown in Fig. 4. It shows that the reaction

temperature has an unnoticeable effect on the dissolution of cobalt and zinc. When the reaction temperature increases from 25 to 70 °C, the leaching efficiency of cobalt only increases by 3.9% (from 95.9% to 99.8%) and the leaching efficiency of zinc only increases by 2.1% (from 87.3% to 89.4%), which indicates that the leaching process of cobalt and zinc from zinc plant purification residue seems not to be controlled by the chemical reaction [14].

Based on the experimental data in Fig. 4, the relationship between $1-3(1-x)^{2/3}+2(1-x)$ and time is given in Fig. 5. Figures 4 and 5 show that about 95.2% of cobalt in the residue sample is extracted at 40 °C for 7 min, similarly, about 75.9% of zinc is extracted under the condition. When leaching time increases from 7 to 12 min, the leaching efficiency of cobalt increases slowly to 99.8%, but the leaching rate of zinc increases quickly from 75.9% to 90.97%. When the reaction time increases

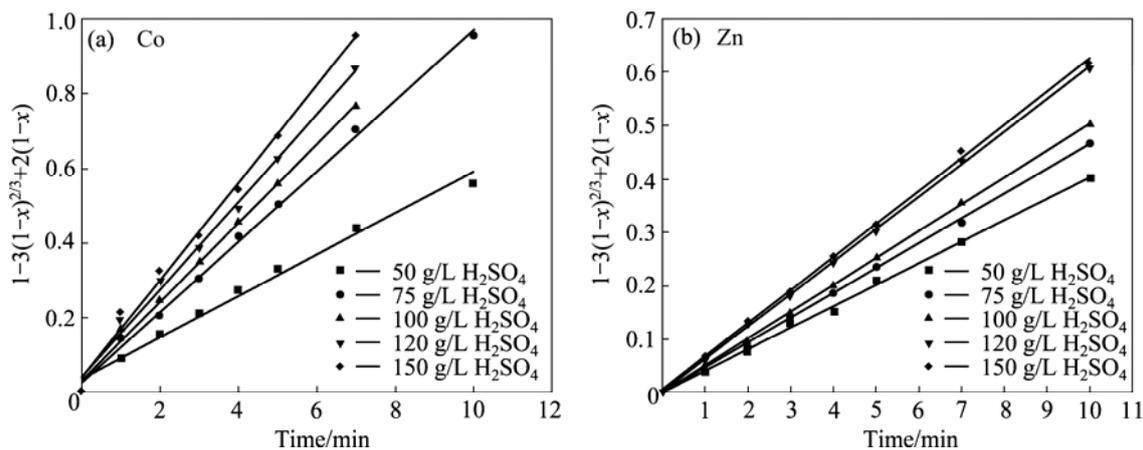


Fig. 3 $1-3(1-x)^{2/3}+2(1-x)$ vs time curves at different concentrations of leaching agent

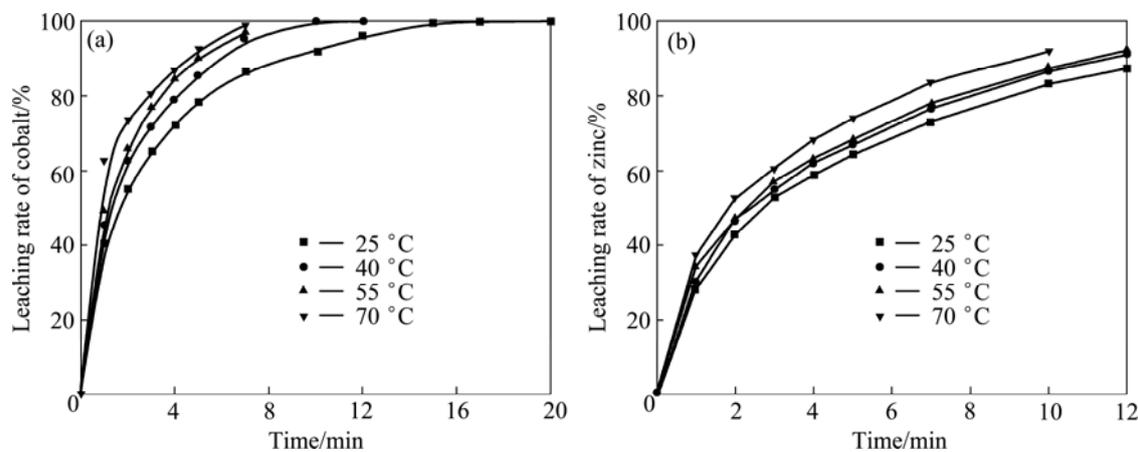


Fig. 4 Effect of temperature on leaching rates of cobalt (a) and zinc (b)

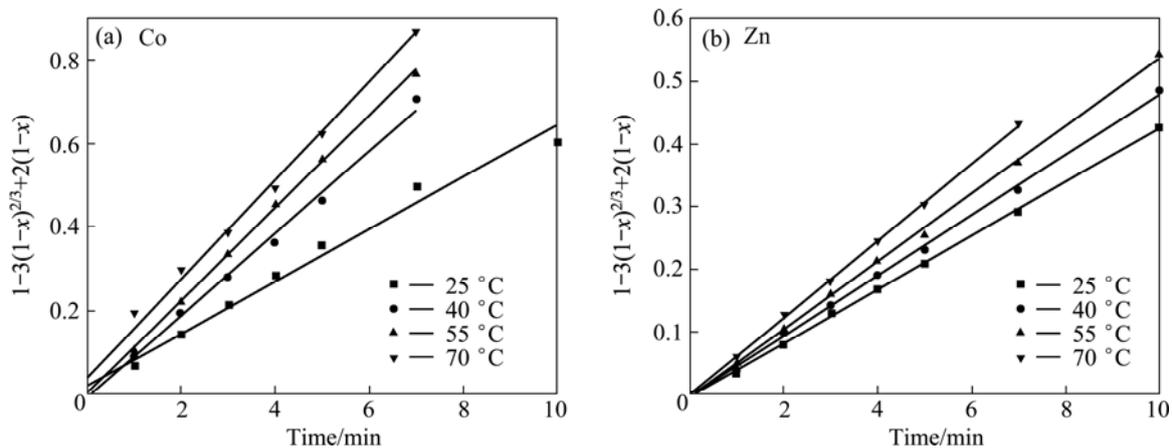


Fig. 5 $1-3(1-x)^{2/3}+2(1-x)$ vs time curves at different temperatures

from 12 to 20 min, the leaching efficiency of cobalt only increases from 95.9% to 99.8% at 25 °C. The leaching efficiency has reached the maximum. Thus, about 99.8% of cobalt and 91.97% of zinc are extracted at 70 °C. The plot in Fig. 5 is also linear, which indicates that the rate of the reaction is controlled by diffusion through the solid layer around the shrinking unreacted core.

3.3 Effects of particle size on leaching rate of cobalt and zinc

The effects of particle size on the leaching rates of cobalt and zinc were studied under the conditions that sulfuric acid concentration and leaching temperature were kept constant of 100 g/L and 70 °C, respectively, the leaching time was 20 min, and the ratio of liquid to solid was 50:1 (mL/g). The results are given in Fig. 6. The results show that about 99.8% of cobalt and 91.97% of zinc in the cobalt residue with particle size of 75–80 μm are extracted. When the initial particle size of the residue increases to 80–109 μm, the leaching rates of cobalt and zinc decrease to 95.9% and 83.5%, respectively. These indicate that the leaching velocity of cobalt increases as the particle size of the residue decreases. The smaller the particle size of the residue

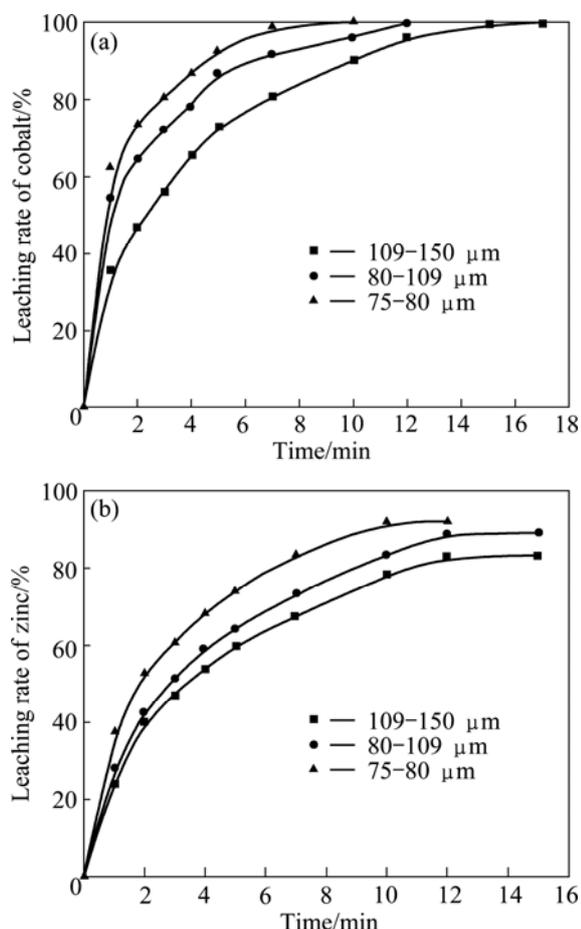


Fig. 6 Effects of particle size on leaching rates of cobalt (a) and zinc (b)

sample, the faster the leaching velocity of cobalt, and the higher the leaching efficiency. The reason is that total quantum of residue sample is constant. The number of particles increases as the particle size of the residue decreases and then the reaction-surface area increases. The leaching velocity is in direct proportion to the reaction-surface area. So, the leaching velocity and the leaching rate of cobalt increase as the particle size of the cobalt residue sample decreases.

The relationship between $1-3(1-x)^{2/3}+2(1-x)$ and leaching time at different particle sizes is shown in Fig. 7. There is a good linear relationship between $1-3(1-x)^{2/3}+2(1-x)$ and leaching time. It is determined that leaching process is controlled by the step of diffusion through the solid layer around the shrinking unreacted core. So, the leaching kinetics can be described by the diffusion model.

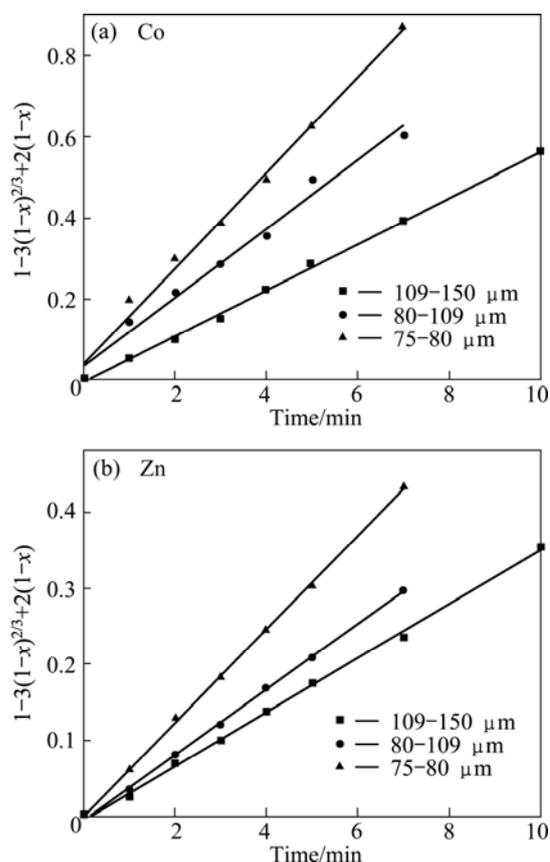


Fig. 7 $1-3(1-x)^{2/3}+2(1-x)$ vs time curves at different particle sizes

Under the acid leaching conditions that particle size is 75–80 μm, sulfuric acid concentration is 100 g/L, and the ratio of liquid to solid is 50:1 (mL/g) at 70 °C for 20 min, XRD pattern of leaching residue is shown in Fig. 8.

The main mineralogical composition of the leaching residue is $PbSO_4$. A great mass of cobalt and zinc are leached into solution. The leaching rates of cobalt and zinc prove this point.

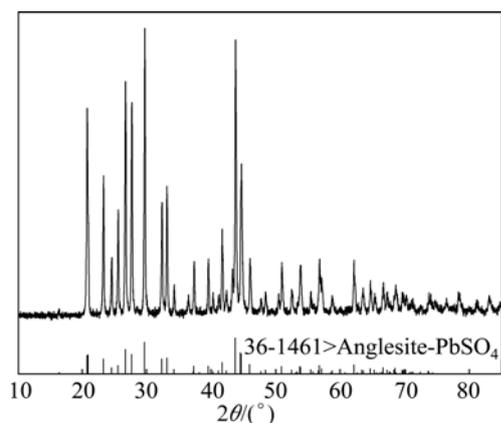


Fig. 8 XRD pattern of leaching residue

3.4 Kinetic model analysis

3.4.1 Diffusion control model

In the leaching process, solid particles almost remain unchanged in size during the heterogeneous reaction if the residue contains a large amount of gangues, which remain as a nonflaking residual so called solid layer [15]. If the reaction rate is controlled by chemical reaction, then the integral rate expression becomes

$$1-(1-x)^{1/3}=K_C t \quad (1)$$

where K_C is the surface chemical rate constant.

If the rate of the reaction is controlled by the step of diffusion through solid layer consisting of insoluble part of the ore around the unreacted core, the integral rate equation is as follows:

$$1-3(1-x)^{2/3}+2(1-x)=K_D t \quad (2)$$

where x is the leaching rate of cobalt or zinc; K_D is the pore diffusion rate constant; t is the reaction time.

Based on Figs. 3, 5, 7 and the above analyses, it can be concluded that under the experimental conditions, the leaching kinetics can be described by diffusion model, and controlled by the step of diffusion through the solid residual layer around the shrinking unreacted core.

3.4.2 Calculation of activation energy

The reaction rate constant K_D is the function of temperature. The relationship between K_D and T can be expressed with the Arrhenius equation [16].

$$K_D=K_0 \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where K_0 is the frequency factor and E_a is the apparent activation energy. Integral representation of Eq. (3) is as follows:

$$\ln K_D=\ln K_0-\frac{E_a}{RT} \quad (4)$$

To calculate the activation energy, the Arrhenius plot of this leaching process is plotted using the values of $\ln K_D$ against $1000/T$ with the correlation coefficient $R^2=0.9279$ for cobalt and $R^2=0.9979$ for zinc in Fig. 9.

According to Arrhenius equation, the apparent activation energy values of cobalt and zinc reaction are calculated to be 11.6931 kJ/mol and 6.6894 kJ/mol, respectively. The energy value falls in the range of 4–12 kJ/mol for a typical inner diffusion controlled process, further confirming that the leaching process is inner diffusion controlled [17,18].

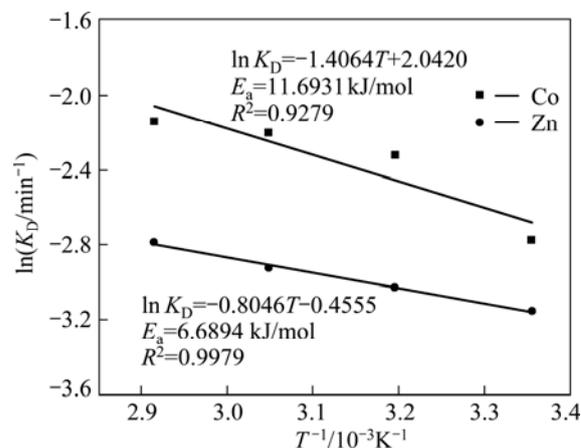


Fig. 9 Arrhenius plots for activation energy

4 Conclusions

1) Cobalt and zinc in the zinc plant purification residue can be leached in the sulfuric acid system. Leaching rates of cobalt and zinc are 99.8% and 91.97%, respectively, under the conditions that particle size is 75–80 μm , sulfuric acid concentration is 100 g/L, and the ratio of liquid to solid is 50:1 (mL/g) at 70 $^{\circ}\text{C}$ for 20 min.

2) Leaching process is controlled by the diffusion step through the solid residual layer around the shrinking unreacted core. Leaching velocity can be described by the shrinking core model. The apparent activation energy values of cobalt and zinc reaction are calculated to be 11.6931 kJ/mol and 6.6894 kJ/mol, respectively.

3) Increasing the concentration of leaching agent properly, raising reaction temperature and decreasing the particle size of the zinc plant purification residue can increase the leaching rates of cobalt and zinc.

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湿法炼锌净化渣酸浸的动力学

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摘要: 对湿法炼锌净化渣的浸出动力学进行了研究, 并探讨了硫酸浓度、反应温度、粒度等对钴、锌浸出率的影响规律。从动力学的角度分析了整个浸出过程, 得到优化条件: 液固比 50:1(mL/g), 硫酸浓度 100 g/L, 反应温度 70 °C, 粒度 75~80 μm, 反应时间 20 min。在此优化条件下钴的浸出率为 99.8%, 锌的浸出率为 91.97%。结果表明: 在硫酸体系中钴的浸出符合不生成固体产物层的“未反应收缩核”模型。通过 Arrhenius 经验公式求得钴和锌表观反应活化能分别为 11.693 kJ/mol 和 6.6894 kJ/mol, 这表明浸出过程受边界层扩散控制。

关键词: 钴; 锌; 酸浸出; 浸出动力学

(Edited by Hua YANG)