

Hydro-chemical conversion of galena in FeCl_3 -KCl solution

LONG Huai-zhong(龙怀忠)¹, CHAI Li-yuan(柴立元)¹, LIU Hui(刘辉)², QIN Wen-qing(覃文庆)²

1. School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China;

2. School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

Received 20 May 2009; accepted 10 August 2009

Abstract: The behaviours of complexation and dissolution of PbCl_2 on the surface of galena were investigated to explore the process of hydro-chemical conversion of galena (PbS) in chloride media. By means of solution chemistry calculation, the production and dissolution of the products PbCl_2 were studied. And the passivation of the galena was studied by Tafel curve. The results show that PbCl_4^{2-} is the main form of PbCl_2 presented in the saturated potassium chloride (KCl) solution. The PbCl_2 crystal is easy to precipitate when the total concentration of chloride ion ($[\text{Cl}^-]_{\text{T}}$) is equal to 0.92 mol/L, and it is inclined to dissolve when $[\text{Cl}^-]_{\text{T}}$ is more than 0.92 mol/L. The chloride complexing reaction rate strongly depends on the Fe^{3+} ion concentration when it is less than 6×10^{-4} mol/L, while passivation occurs on the surface of the electrode when Fe^{3+} concentration is larger than 6×10^{-4} mol/L. The reaction rate increases obviously when KCl is added, since the activity of Cl^- increases; thus accelerates the dissolution of PbCl_2 .

Key words: FeCl_3 -KCl solution; galena; complexation; solution chemistry

1 Introduction

At present, pyro-metallurgy is still a main method in plumburgy. However, traditional sintering technology as melting in the blast furnace, has many disadvantages, such as high energy consumption and serious environment pollution[1]. Recently, the basic study on a direct extract of Pb and preparation of material from original resource has been paid more attention to, with continuously increasing need of Pb and environment protection problem[2]. Chemistry extraction of Pb has attracted much attention because of its low energy consumption and friendly environment. Many methods have been reported in hydrometallurgy ways using FeCl_3 [3], $\text{Fe}_2(\text{SO}_4)_3$ [4–5], silicofluoric acid [6], HNO_3 [7] and EDTA [8]. The study on extraction technique using FeCl_3 , especially the thermodynamics and dynamics in the transformation process [9–18] was mostly performed because of its high transformation speed, efficiency and easy manipulation. However, there was less report about the complexation and dissolution behavior of reaction production on the surface of galena (PbS). In this study, the complexation and dissolution of chloride on the

surface of galena (PbS) in FeCl_3 -KCl media was investigated by means of solution chemistry calculation and corrosion electrochemistry.

2 Experimental

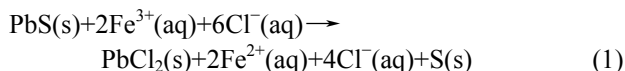
The galena used in this study consists of 82.20% Fe, 16.20% S and 1.6% SiO_2 , and was taken from Fankou Mine of Guangdong Province in China. Section cut out from the highly mineralized galena was fashioned into the form of electrodes for electrochemical measurement. The cut section of the mineral was mounted on the tip of a perspex tubule of $d7$ mm using epoxy resin and the exposed outer surface was well polished. The exposed surface area of the electrode was about 1 cm^2 . $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and KCl were analytical reagents. A conventional three-electrode system was used, including a Ag/AgCl reference electrode, a platinum plate as the counter electrode and galena (PbS) as working electrode. An EG&GPARC Model 273 bi-potentiostat and 686 rotating disk electrode were used for electrochemistry experiments. The Tafel experiment was performed at room temperature (298 K) and normal atmosphere with a rotating speed of 500 r/min. The potentials throughout

this study were referenced to standard hydrogen electrode(SCE).

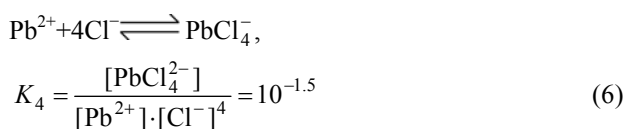
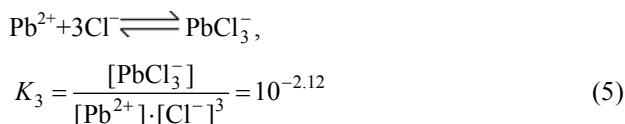
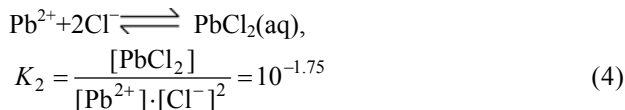
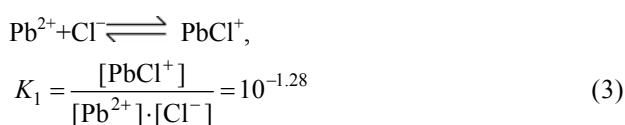
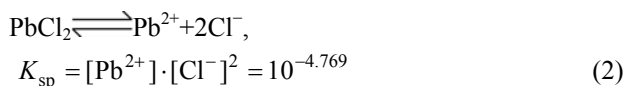
3 Results and discussion

3.1 Solution chemistry on surface of galena in chloride medium

In FeCl₃-KCl system, the surface of galena contacts with Fe³⁺ by the following reaction:



The strong oxidation capability of PbCl⁺ and Fe³⁺ facilitates the fracture of Pb—S bond on the surface of galena. S²⁻ is oxidized to S solid, and Pb(II) combines with Cl⁻ to form PbCl₂ crystal adhering on the surface of galena. The following complexing equilibriums of PbCl₂ crystal exist on the surface of galena in chloride medium:



Associating with Eqs.(2)–(6), the concentration of each component can be calculated by the following equations:

$$\lg[\text{Pb}^{2+}] = -4.769 - 2\lg[\text{Cl}^{-}] \quad (7)$$

$$\lg[\text{PbCl}^{+}] = -6.076 - \lg[\text{Cl}^{-}] \quad (8)$$

$$\lg[\text{PbCl}_2] = 6.546 \quad (9)$$

$$\lg[\text{PbCl}_3^{-}] = -6.916 + \lg[\text{Cl}^{-}] \quad (10)$$

$$\lg[\text{PbCl}_4^{2-}] = -6.926 + \lg[\text{Cl}^{-}] \quad (11)$$

According to Eqs.(7)–(11), the logarithmic solubility curve of PbCl₂ is drawn as shown in Fig.1. It

can be seen that the decrease of Cl⁻ concentration facilitates the dissolution of PbCl₂. As a result, the concentration of Pb²⁺ increases, but the probability of Pb²⁺ complexation with Cl⁻ to form high-coordination anion PbCl₄²⁻ decreases because of the low concentration of Cl⁻. Until the concentrations of Pb²⁺ and PbCl₄²⁻ are equal, the system reaches the balance. On the contrary, if the concentration of Cl⁻ increases, so that of Pb²⁺ decreases, and the complexation reaction takes place easily, resulting in high concentration of PbCl₄²⁻. As a result, PbCl₄²⁻ is in a dominant position when the concentration of Cl⁻ is high in the solution. So, in the FeCl₃-KCl system with saturated KCl medium, PbCl₂ exists as a form of complex PbCl₄²⁻.

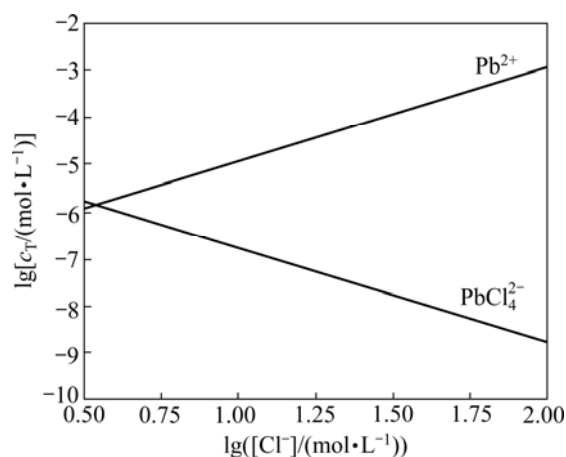


Fig.1 Logarithmic solubility diagram of lead chloride at 25 °C

In order to study the formation and dissolution of PbCl₂ in KCl medium, the total concentrations of Pb²⁺ ([Pb²⁺]_T) and Cl⁻ ([Cl⁻]_T) were calculated by the following equations that depended on -lg[Cl⁻].

$$\begin{aligned} [\text{Pb}^{2+}]_{\text{T}} &= K_{\text{sp}} \cdot 10^{-2\lg[\text{Cl}^{-}]} \alpha, \\ [\text{Cl}^{-}]_{\text{T}} &= [\text{Cl}^{-}] + [\text{Pb}^{2+}]_{\text{T}} \cdot \frac{\beta}{\alpha} \end{aligned} \quad (12)$$

where

$$\begin{aligned} \alpha &= 1 + 10^{-\lg K_1 + \lg[\text{Cl}^{-}]} + 10^{-\lg K_2 + 2\lg[\text{Cl}^{-}]} + 10^{-\lg K_3 + 3\lg[\text{Cl}^{-}]} + \dots + 10^{-\lg K_n + n\lg[\text{Cl}^{-}]} \\ \beta &= 1 + 10^{-\lg K_1 + \lg[\text{Pb}^{2+}]} + 10^{-\lg K_2 + 2\lg[\text{Pb}^{2+}]} + 10^{-\lg K_3 + 3\lg[\text{Pb}^{2+}]} + \dots + 10^{-\lg K_n + n\lg[\text{Pb}^{2+}]} \end{aligned} \quad (13)$$

If $n=4$, the total concentration of Pb²⁺ can be calculated from the following equation:

$$[\text{Pb}^{2+}]_{\text{T}} = K_{\text{sp}} [10^{-2\lg[\text{Cl}^{-}]} + 10^{-\lg K_1 - \lg[\text{Cl}^{-}]} + 10^{-\lg K_2} + 10^{-\lg K_3 + \lg[\text{Cl}^{-}]} + 10^{-\lg K_4 + 2\lg[\text{Cl}^{-}]}] \quad (14)$$

The best point for producing PbCl₂ is estimated by

differentiating Eq.(14). Assuming $\frac{d[\text{Pb}^{2+}]}{d(\lg[\text{Cl}^-])} = 0$, we

have

$$2 \times 10^{-\lg[\text{Cl}^-]} + 10^{-\lg K_1 - \lg[\text{Cl}^-]} = 10^{-\lg K_3 + \lg[\text{Cl}^-]} + 2 \times 10^{-\lg K_4 + 2\lg[\text{Cl}^-]}$$

Approximately, it can be written as

$$10^{-\lg K_1 - \lg[\text{Cl}^-]} = 10^{-\lg K_3 + \lg[\text{Cl}^-]}$$

$$\text{As a result, } \lg[\text{Cl}^-] = \frac{\lg K_1 - \lg K_3}{2}.$$

The solubility of PbCl_2 at different values of $\lg[\text{Cl}^-]$ could be calculated by Eqs.(12) and (13), and the results are listed in Table 1.

As a result, the relationship of $\lg[\text{Pb}^{2+}]$ and $\lg[\text{Cl}^-]$ with $\lg[\text{Cl}^-]$ is shown in Fig.2.

Table 1 Calculation results of solubility of PbCl_2

$\lg([\text{Cl}^-]/(\text{mol} \cdot \text{L}^{-1}))$	$\lg([\text{Pb}^{2+}]/(\text{mol} \cdot \text{L}^{-1}))$	$\lg([\text{Cl}^-]/(\text{mol} \cdot \text{L}^{-1}))$
-1.50	-1.440	-1.280
-1.00	-2.142	-0.987
-0.04	-2.565	-0.036
0.20	-2.434	0.224
0.60	-1.976	0.622

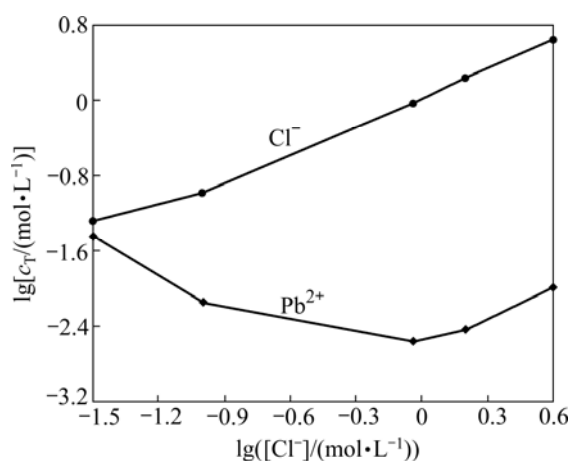


Fig.2 Relationship of $\lg[\text{Pb}^{2+}]_T$ and $\lg[\text{Cl}^-]_T$ with $\lg[\text{Cl}^-]$ at 25 °C

As can be seen in Fig.2, the total concentration of Cl^- increases with increasing $\lg[\text{Cl}^-]$, while that of Pb^{2+} decreases. When the value of $\lg([\text{Cl}^-]/(\text{mol} \cdot \text{L}^{-1}))$ is -0.04 and the total concentration of Cl^- is 0.92 mol/L, the concentration of Pb^{2+} reaches the minimal value of 0.002 8 mol/L, then the equilibrium point of production and dissolution occurs. When the value of $\lg([\text{Cl}^-]/(\text{mol} \cdot \text{L}^{-1}))$ is lower than -0.04, the dissolution rate of PbCl_2 is less than that of production, so the

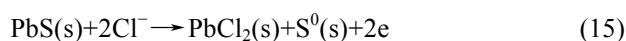
production reaction is dominant. When the value of $\lg([\text{Cl}^-]/(\text{mol} \cdot \text{L}^{-1}))$ is larger than -0.04, the dissolution rate of PbCl_2 is more than that of production, indicating that at a high concentration of Cl^- , the complexation reaction of Pb^{2+} with Cl^- is dominant, and the dissolution rate of PbCl_2 becomes rapid. As a result, the surface of galena can contact with Fe^{3+} and dissolve continuously.

3.2 Corrosion electrochemistry on surface of galena in chloride medium

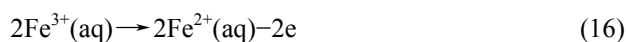
Galena has the character of semiconductor. Actually in chloride medium, galena (PbS) reacts with Fe^{3+} as a corrosion primary cell. In this study, the corrosion electrochemistry technique, Tafel curve was used to investigate the corrosion and dissolution behavior of galena in chloride medium.

On the surface of electrode in FeCl_3 -KCl solution system, the following reactions occur:

Anode



Cathode



The Tafel curve test was carried out with the M352 software using 686 rotating electrode. The rotating speed of the electrode was 400 r/min, the scanning rate was 1.5 mV/s, and the step was 0.20 s. The pH value was adjusted to 3.0 at each time and pure N_2 was pumped into the solution to remove the oxygen before the measurement. The electrokinetic potential polarization curves of anode dissolution are shown in Fig.3 and Fig.4, from which the corrosion potential (ϕ_{corr}) and corrosion current density (J_{corr}) were calculated and the results are listed in Table 2.

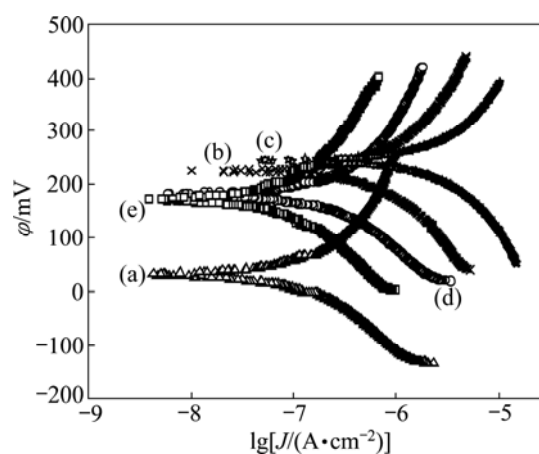


Fig.3 Tafel curves of lead sulfide electrode under different ferric chloride concentrations without KCl: (a) $[\text{FeCl}_3]=0$; (b) $[\text{FeCl}_3]=2 \times 10^{-4}$ mol/L; (c) $[\text{FeCl}_3]=5 \times 10^{-4}$ mol/L; (d) $[\text{FeCl}_3]=8 \times 10^{-4}$ mol/L; (e) $[\text{FeCl}_3]=1.0 \times 10^{-3}$ mol/L

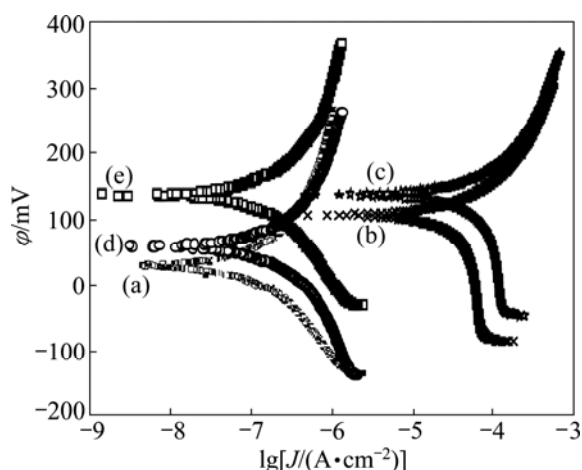


Fig.4 Tafel curves of lead sulfide electrode in saturated KCl solution under different ferric chloride concentrations: (a) $[\text{FeCl}_3]=0$; (b) $[\text{FeCl}_3]=2 \times 10^{-4}$ mol/L; (c) $[\text{FeCl}_3]=5 \times 10^{-4}$ mol/L; (d) $[\text{FeCl}_3]=8 \times 10^{-4}$ mol/L; (e) $[\text{FeCl}_3]=1 \times 10^{-3}$ mol/L

Table 2 Tafel parameters of lead sulfide electrode in saturated KCl solution and without KCl under different ferric chloride concentrations

$[\text{Fe}^{3+}]$ (mol·L ⁻¹)	Without KCl		Saturated KCl	
	$\varphi_{\text{corr}}/$ mV	$J_{\text{corr}}/$ ($\mu\text{A}\cdot\text{cm}^{-2}$)	$\varphi_{\text{corr}}/$ mV	$J_{\text{corr}}/$ ($\mu\text{A}\cdot\text{cm}^{-2}$)
0	28.99	0.222	28.84	0.212
2×10^{-4}	211.5	1.456	102.1	104.1
5×10^{-4}	235.4	16.89	134.9	255.7
8×10^{-4}	183.5	0.423	61.33	0.789
10×10^{-4}	170.2	0.143	135.7	0.309

It can be seen from Fig.3 and Table 2 that, when the concentration of Fe^{3+} ($[\text{Fe}^{3+}]$) is $0\text{--}5 \times 10^{-4}$ mol/L, φ_{corr} and J_{corr} increase with the increase of $[\text{Fe}^{3+}]$. While when $[\text{Fe}^{3+}]$ is more than 5×10^{-4} mol/L, the corrosion current density decreases with the increase of $[\text{Fe}^{3+}]$. It is illuminated that there is passivation reaction on the surface of galena. The electrochemistry reaction production PbCl_2 crystal agglomerates on the surface of electrode, resulting in the increase of resistance and decrease of current. At the open circuit voltage ($[\text{Fe}^{3+}]=0$), φ_{corr} and J_{corr} do not change any more with and without KCl addition, indicating that KCl has little effect on the rest potential. When $[\text{Fe}^{3+}]$ is 5×10^{-4} mol/L, J_{corr} reaches the maximum value.

From Fig.4 and Table 2, φ_{corr} and J_{corr} in saturated KCl system have the same trend of change as the in the system without KCl. That is, with the increase of $[\text{Fe}^{3+}]$, φ_{corr} and J_{corr} increase firstly. When $[\text{Fe}^{3+}]$ is more than 5×10^{-4} mol/L, φ_{corr} and J_{corr} decrease. The difference is

when $[\text{Fe}^{3+}]$ is equal to 5×10^{-4} mol/L, the current density increase abruptly. The reason is that with the addition of KCl, the concentration of Cl^- increases. The complexation reaction of Pb^{2+} with Cl^- accelerates, which facilitates the dissolution of PbCl_2 crystal on the surface of electrode. As a result, the electrode surface resistance decreases, and the current density increases.

In $\text{FeCl}_3\text{--KCl}$ system, when $[\text{Fe}^{3+}]$ is less than 5×10^{-4} mol/L, the corrosion rate depends on the existence of Fe^{3+} , and increases rapidly with increasing Fe^{3+} concentration. When $[\text{Fe}^{3+}]$ is more than 5×10^{-4} mol/L, passivation reaction takes place on the surface of galena. With the addition of KCl, the complexation reaction of Pb^{2+} and Cl^- facilitates the dissolution of PbCl_2 , so the electrode surface resistance decreases, and the corrosion current density increases.

4 Conclusions

1) In $\text{FeCl}_3\text{--KCl}$ system, the strong oxidation of Fe^{3+} facilitates the transformation of galena to PbCl_2 crystal, which is dissolved by complexation with Cl^- . This equilibrium state is verified by liquid chemistry calculation. PbCl_2 exists as complex compound PbCl_4^{2-} in saturated KCl solution.

2) When $[\text{Cl}^-]_{\text{T}}$ is equal to 0.92 mol/L, PbCl_2 precipitates in solid state. When $[\text{Cl}^-]_{\text{T}}$ is more than 0.92 mol/L, PbCl_2 dissolves because of complex reaction.

3) With the addition of KCl, the activity of Cl^- increases, and the complex reaction becomes stronger. Therefore, the electrode surface resistance decreases, and corrosion current density increases.

References

- [1] KHOLMOGOROV A, KONONOVAB O N. Recovery of lead from sulfide concentrate after mechanochemical activation using nitric acid [J]. Chinese J Chem Eng, 2005, 13(1): 91–95.
- [2] KHOLMOGOROV A, PASHKOV G, MIKHLINA E, MIKHLIN Y. Electrochemical aspects of the nitric acid leaching of lead sulfide concentrates: On the way to a highly effective method for Pb recovery [J]. ECS Transactions, Electrochemistry in Mineral and Metal Processing VII, 2006, 2(3): 221–230.
- [3] WANG S, FANG Z, WANG Y, CHEN Y. Electrogenative leaching of galena with ferric chloride [J]. Minerals Engineering, 2003, 16(9): 869–872.
- [4] DUTRIZAC J E. The leaching of sulphide minerals in chloride media [J]. Hydrometallurgy, 1992, 29(1/3): 1–45.
- [5] GABRIEL D S. Kinetics and mechanism of the bacterial and ferric sulphate oxidation of galena [J]. Hydrometallurgy, 2004, 75(1/4): 99–110.
- [6] ALAN A. The ferric fluosilicate leaching of lead concentrates [J]. Metallurgy Transactions B, 1994, 25: 473–478.
- [7] WRIGHT K, HILLIER I H, VAUGHAN D J, VINCENT M A.

- Cluster models of the dissociation of water on the surface of galena (PbS) [J]. Chemical Physics Letters, 1999, 299(6): 527–531.
- [8] ROGER S, GREET C. Diagnostic leaching of galena and its oxidation products with EDTA [J]. Minerals Engineering, 2002, 15(7): 515–522.
- [9] ZHANG Sheng, LI Jian-ping, WANG Yu-rong, HU Guang-qian. Dissolution kinetics of galena in acid NaCl solutions at 25–75 °C [J]. Applied Geochemistry, 2004, 19: 835–841.
- [10] AYDOĞANA S, ERDEMOĞLUB M, UÇARA G, ARASA A. Kinetics of galena dissolution in nitric acid solutions with hydrogen peroxide [J]. Hydrometallurgy, 2007, 88(1/4): 52–57.
- [11] DAI Zhong-xu, WANG Di-hua, ZOU Jin-yun. Studies on the behaviors of PbSO₄/Pb and PbO₂/PbSO₄ electrodes prepared from lead carbonate by powder microelectrode technique [J]. Wuhan University Journal of Natural Science, 2000, 5(4): 474–478. (in Chinese)
- [12] BALAZ P. Influence of solid state properties on ferric chloride leaching of mechanically activated galena [J]. Hydrometallurgy, 1996, 40(3): 359–368.
- [13] da SILVA G. Kinetics and mechanism of the bacterial and ferric sulphate oxidation of galena [J]. Hydrometallurgy, 2004, 75(1/4): 99–110.
- [14] PRITZKER M. Model for the ferric chloride leaching of galena [J]. Metallurgical Trans B, 1998, 29: 953–959.
- [15] GONG Qian, GONG Ya-jun. Oxidation of galena in ammonium carbonate solution and applied reactor [J]. Trans Nonferrous Met Soc China, 1995, 5(3): 41–44.
- [16] KOBAYASHI M, et al. A critical review of the ferric chloride leaching of galena [J]. Canadian Metallurgical Quarterly, 1990, 29(3): 201–211.
- [17] WANG Dian-zuo, HU Yue-hua. Flotation solution chemistry [M]. Changsha: Hunan Science and Technology Press, 1988.
- [18] LI Shu-tang. Elements of X-ray crystallography [M]. Beijing: Metallurgical Industry Press, 1990. (in Chinese)
- (Edited by YUAN Sai-qian)**