E−pH diagram of ZnS-H$_2$O system during high pressure leaching of zinc sulfide

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Abstract: The values of $G^\ominus$, $E^\ominus$ or pH from 110 to 160 °C were calculated and the relevant potential expressions were obtained. E−pH diagrams of ZnS-H$_2$O system at oxygen partial pressure of 0.8 MPa, ionic activity of 1.0 and different temperatures were drawn through thermodynamical calculation. With the temperature increasing, the stable regions of S and Zn(II) in the E−pH diagrams become gradually larger, but the amplification decreases over 150 °C. The impacts of leaching parameters, such as temperature, liquid to solid ratio, initial acidic concentration, leaching time, oxygen partial pressure and stirring speed on the leaching rate of Zn (II) and conversion rate of S in the single factor of high pressure leaching experiment of ZnS in autoclave, were studied. The leaching residue was examined by X-ray fluorescence (XRF) chemical composition identification and X-ray diffraction (XRD) phase identification, and the content of the leaching solution was tested by inductively coupled plasma-atomic emission spectrometry (ICP). The experimental results indicate that the leaching rate of zinc increases from 60.05% to 97.85% and the conversion rate of sulfur increases from 38.90% to 80.92% with the temperature increasing from 110 °C to 150 °C, 5:1 of liquid-to-solid ratio, 150 g/L of initial acidic concentration, 120 min of leaching time, 0.8 MPa of oxygen partial pressure, and 480 r/min of stirring speed, which tend to be stable over 150 °C. The experimental results correspond with theoretical calculation.

Key words: zinc sulfide; high pressure leaching; ZnS-H$_2$O system; E−pH diagram

1 Introduction

Sulfides (sphalerite, marmatite) are predominant sources of zinc in the earth crust[1]. In the production of zinc from the ores, it can be used by pyrometallurgical method and hydrometallurgical method. Hydrometallurgical method is more advantageous than pyrometallurgical method[2], but it has been reported that zinc metal produced from the concentrate was used by roast-leach-electrowinning process (RLE)[3]. The process involves a roasting step, which evolves toxic SO$_2$ gas and requires a sulfuric acid plant to be set up in the smelter[4]. The prevention of SO$_2$ emission from RLE and marketing of sulphuric acid are challenging the future of this technology[5]. As an environmental and economical technology, high pressure leaching is alternative to the traditional RLE route. In the latter, levels of SO$_2$ emissions unacceptable for release to the environment have necessitated expensive gas cleaning equipment and production of sulfuric acid. However, in the high pressure leaching process, the sulfides are oxidized to elemental sulfur, which is recovered and stockpiled[6].

Leaching of zinc sulfide is based on the oxidation of zinc sulphide in an acidic environment[7]. In the high pressure leaching of ZnS, oxygen acts as an oxidant in the dissolution. The amount of oxygen in the solution has an important effect on the kinetics of the whole process[8]. High pressure leaching of ZnS is expressed by a simply basic reaction as follows:

$$ZnS + H_2SO_4 + 1/2O_2 = ZnSO_4 + S^0 + H_2O \qquad (1)$$

E−pH diagram is a very important basis for thermodynamics of the high pressure leaching process. It also shows relations of the thermodynamic reactions and

gives the reasonable conditions in the solution. But currently, it has few references about E−pH diagram of sulfide and water system at atmospheric pressure and room temperature (25 °C, 0.1 MPa), and the research at high temperature and pressure was rarely reported. WANG et al[9−10] only studied E−pH diagram of high iron sphalerite at 150 °C.

In this work, E−pH diagrams of ZnS system were drawn from 110 to 150 °C at oxygen partial pressure of 0.8 MPa and ionic activity of 1.0. Single factor experiments were performed to assess the influence of the parameters such as temperature, initial acidic concentration, oxygen partial pressure, liquid to solid ratio, leaching time and stirring speed.

2 Thermodynamic calculation

2.1 Method of drawing E−pH diagram

All hydrometallurgy reactions are expressed as

$$a\mathrm{A}+m\mathrm{H}^+ +Z\mathrm{e}=b\mathrm{B}+c\mathrm{H_2O} \qquad (2)$$

According to Nernst isotherm equation, the equilibrium potential are expressed as

$$E_T = E_T^\Theta - [RT/(ZF)]\ln[(\alpha_B^b \cdot \alpha_{H_2O}^c)/(\alpha_A^a \cdot \alpha_{H^+}^m)] \qquad (3)$$

$$E_T = E_T^\Theta - 2.303(RTm/ZF)\mathrm{pH} - \\ 2.303[RT/(ZF)]\lg[\alpha_B^b / \alpha_A^a] \qquad (4)$$

According to Nernst equation, $\Delta G_T^\Theta = -RT\ln K = -ZFE_T^\Theta$, whichever value of ΔG_T^Θ, K or E_T^Θ is known, E−pH diagram is obtained at this temperature according to Eq.(4). This reaction could be expressed as a linear relation in the E−pH diagram, whose slope is $-2.303[RTm/(ZF)]$, intercept is $E_T^\Theta - 2.303[RT/(ZF)]\cdot\lg[\alpha_B^b / \alpha_A^a]$, and the value of abscissa and ordinate of horizontal line are pH and φ, respectively[11].

2.2 Method of calculating G_T^Θ of materials

The methods such as the average of thermal melting method and the ionic similar to linear thermal melting method were used to calculate the thermodynamic data of each material during the high pressure leaching process of ZnS, but they are complicated and would easily be miscalculated[12].

YI[13] studied As-H$_2$O system at high temperature. The following approximate calculation was obtained according to thermodynamics basic law as

$$G_T^\Theta = G_{298}^\Theta + \int_1^p V\mathrm{d}p + \int_{298}^T c_p \mathrm{d}T - \\ T\int_{298}^T c_p \mathrm{d}\ln T - (T-298)S_{298}^\Theta \qquad (5)$$

As the partial molar volume changes little below 300 °C, $\int_1^p V\mathrm{d}p$ could be neglected. When the change of temperature is not significant, c_p could be expressed as $c_p^\Theta\big|_{298}^T$ approximately, so the Eq.(5) could be expressed as

$$G_T^\Theta = G_{298}^\Theta + (T-298)c_p^\Theta\big|_{298}^T - \\ T\ln(T/298)c_p^\Theta\big|_{298}^T - (T-298)S_{298}^\Theta \qquad (6)$$

According to the Eq.(7), $c_p^\Theta\big|_{298}^T$ could be expressed as Eq.(8). Then Eq.(8) is substituted into Eq.(6), so the Eq.(9) is obtained:

$$\int_{298}^T c_p^\Theta \mathrm{d}T \approx \frac{(T-298)}{\ln(T/298)}\int_{298}^T (\frac{c_p^\Theta}{T})\mathrm{d}T \\ = \frac{(T-298)}{\ln(T-298)}(S_T^\Theta - S_{298}^\Theta) \qquad (7)$$

$$c_p^\Theta\big|_{298}^T \approx \frac{\int_{298}^T c_p^\Theta \mathrm{d}T}{\int_{298}^T \mathrm{d}T} \approx \frac{S_T^\Theta - S_{298}^\Theta}{\ln(T/298)} \qquad (8)$$

$$G_T^\Theta = G_{298}^\Theta - [TS_T^\Theta - 298S_{298}^\Theta] + \frac{(T-298)}{T/298}[S_T^\Theta - S_{298}^\Theta] \qquad (9)$$

S_T^Θ of ions is calculated at high temperature, according to "corresponding principle of entropy" proposed by CRISS and COBBLE[14] and empirical formula for calculating the absolute entropy proposed in Ref.[15], so Eq.(10) is obtained:

$$S_T^\Theta = a_T - d_T Z + c_T \overline{S_{298}^\Theta} \qquad (10)$$

where $a_T = A(T-298)$, $d_T = D(T-298)$ and $c_T = 1-0.002\ 24(T-298)$.

In Eq.(10), Z is the absolute value of ion charge number. Compared with "corresponding principle of entropy", this empirical formula adds $d_T Z$ to adjust the influence of ionic charge.

For the convenience of calculation, Eq.(10) is substituted into Eq.(9), and Eq.(11) is obtained:

The values of A, D, α, β and γ are listed in Table 1 and Table 2[13]. The values from Table 1 and Table 2 are substituted into Eq.(11), then G_T^Θ of main materials in ZnS-H$_2$O system is listed in Table 3.

$$\Delta G_T^\Theta = \Delta G_{298}^\Theta + \{(298 - \frac{T-298}{\ln(T/298)}) - (T - \frac{T-298}{\ln(T/298)}) \cdot \\ [1-0.002\ 24(T-298)]\}\overline{S}_{298,\text{absolute}}^\Theta - (T - \frac{T-298}{\ln(T/298)}) \cdot \qquad (11)$$

$$(T-298)A + (T - \frac{T-298}{\ln(T/298)})(T-298)DZ = \\ \Delta G_{298}^\Theta + \alpha\Delta S_{298}^\Theta - \beta + \gamma Z$$

$$\alpha = (T-298)\times[0.002\,24\times(T-\frac{T-298}{\ln(T/298)})-1] \quad (12)$$

$$\beta = [T-\frac{(T-298)}{\ln(T/298)}]\times(T-298)\times A \quad (13)$$

$$\gamma = [T-\frac{(T-298)}{\ln(T/298)}]\times(T-298)\times D \quad (14)$$

Table 1 A and D values for calculation of ΔG_T^{Θ}

Coefficient	Cation	Non-oxyacid, anion and dissolved gas	Oxyacid and anion
A	0.170 4	0.170 4	0.268 4
D	0.100 0	0.249 6	0.249 6

Table 2 α, β and γ values for calculation of ΔG_T^{Θ}

T/K	Cation			Non-oxyacid, anion and dissolved gas			Oxyacid and anion		
	α	β	γ	α	β	γ	α	β	γ
373	−68.465	497.15	291.76	−68.465	497.15	728.23	−68.465	783.08	728.23
383	−76.57	641.26	376.33	−76.570	641.26	939.32	−76.570	1 010.1	939.32
393	−84.427	804.32	472.02	−84.427	804.32	1 178.20	−84.427	1 266.9	1 178.20
403	−92.032	986.46	578.91	−92.032	986.46	1 445.00	−92.032	1 553.8	1 445.00
413	−99.384	1 187.90	691.13	−99.384	1 187.90	1740.00	−99.384	1 871.1	1 740.00
423	−106.48	1 408.80	826.74	−106.480	1 408.80	2 063.50	−106.480	2 219.0	2 063.50
433	−113.32	1 649.20	967.85	−113.320	1 649.20	2 415.70	−113.320	2 597.7	2 415.70
443	−119.90	1 909.40	1 120.5	−119.900	1 909.40	2 796.80	−113.320	2 597.7	2 415.70

Table 3 ΔG_T^{Θ} of main substances of ZnS-H$_2$O system at different temperatures

Material	G_{383}^{Θ}/(kJ·mol^{-1})	G_{393}^{Θ}/(kJ·mol^{-1})	G_{403}^{Θ}/(kJ·mol^{-1})	G_{413}^{Θ}/(kJ·mol^{-1})	G_{423}^{Θ}/(kJ·mol^{-1})	G_{433}^{Θ}/(kJ·mol^{-1})
ZnS	−227.826	−228.552	−229.289	−230.007	−230.659	−231.467
Zn^{2+}	−98.053	−97.926	−97.320	−96.705	−95.596	−95.495
Zn	−16.256	−16.775	−17.254	−17.421	−18.213	−18.749
Zn(OH)$_2$	−560.461	−559.276	−557.432	−554.769	−552.826	−550.995
ZnO$_2^{2-}$	−501.739	−499.728	−496.279	−493.067	−491.776	−491.071
ZnSO$_4$	−1 024.921	−1026.342	−1 027.785	−1 029.032	−1 030.001	−1 032.093
ZnSO$_4$·Zn(OH)$_2$	−2 736.540	−2743.300	−2 746.233	−2 749.264	−2 753.609	−2 758.149
S^0	−11.815	−11.932	−12.052	−12.169	−12.303	−12.403
S^{2-}	25.481	26.022	26.563	27.107	27.200	28.189
HS$^-$	−47.279	−47.388	−47.496	−47.605	−47.714	−47.850
H$_2$S	−100.702	−102.373	−104.542	−106.715	−108.723	−111.049
SO$_4^{2-}$	−928.433	−927.654	−926.876	−926.097	−925.652	−924.593
HSO$_4^-$	−945.777	−947.037	−948.297	−949.583	−952.233	−952.303
H$^+$	6.479	6.249	6.017	5.785	5.791	5.323
OH$^-$	−231.204	−230.675	−230.056	−229.347	−228.638	−227.750
O$_2$	−78.373	−80.822	−83.120	−85.266	−87.412	−89.575
H$_2$	−50.328	−51.707	−53.095	−54.494	−55.892	−57.306
H$_2$O	−313.368	−314.271	−315.174	−316.085	−316.875	−317.881

3 Drawing $E-$pH diagram of ZnS-H$_2$O system at high temperature and high pressures

The data used in thermodynamic calculation are from Refs.[16−17], and the calculating thermodynamic data refer to Table 3. According to the method above, ΔG_T^{Θ} is calculated by

$$\Delta G_T^{\Theta} = \sum G_{T,\,\text{product}}^{\Theta} - \sum G_{T,\,\text{reactant}}^{\Theta} \qquad (16)$$

Substituting ΔG_T^{Θ} into Nernst formula, then the expressions of E_{at}^{Θ} or pH_T^{Θ} are acquired at different temperatures. The expressions are listed in Table 4. Submitting them into Eq.(4), then the $E-$pH diagrams of ZnS-H$_2$O system (Fig.1) were drawn from 110 to 160 °C at oxygen partial pressure of 0.8 MPa and activity of 1.0.

Corresponding to the material of reactions (18) and (19), the pH value of stable region is beyond reaction (20), so the two reactions could not be expressed in Fig.1.

The stable region of Zn(II) and S is determined from the $E-$pH diagram of ZnS-H$_2$O system, and the leaching conditions are controlled to ensure that ZnS converts to zinc ionic and sulfide. In this work, $E-$pH diagrams of different temperatures are compared in the same activity and oxygen partial pressure, and how the stable region of zinc ion changes could be observed.

According to Fig.1 and Fig.2, with increasing the temperature, the stable region of S and Zn(II) does not change significantly while the deposition potential of corresponding reaction in stable region increases. But when the temperature is higher than 150 °C, the amplification becomes smaller. According to $E_T = -\Delta G_R(ZH)$, the improvement of deposition potential means that the value of ΔG_T is more negative. That is to say, the higher the temperature is, the more thoroughly the reaction proceeds. This shows that increasing temperature is beneficial to the process of leaching and the conditions of reaction kinetics are more favorable at high temperature.

Table 4 Calculated values of each reaction of E_T^{Θ} or pH_T^{Θ} of ZnS-H$_2$O system at different temperatures

Reaction	E_T^{Θ} or pH_T^{Θ}					
	383 K	393 K	403 K	413 K	423 K	433 K
(1) Zn^{2+}+S+2e=ZnS	0.609	0.615	0.621	0.628	0.638	0.640
(2) ZnS+2H$^+$=Zn^{2+}+H$_2$S	−1.066	−1.046	−0.997	−0.950	−0.904	−0.860
(3) S+2H$^+$+2e=H$_2$S	0.528	0.533	0.542	0.550	0.563	0.567
(4) SO$_4^{2-}$+H$^+$= HSO$_4^-$	3.249	3.406	3.556	3.700	3.956	3.966
(5) HSO$_4^-$+7H$^+$+6e=S+4H$_2$O	0.630	0.632	0.634	0.635	0.635	0.637
(6) Zn^{2+}+HSO$_4^-$+7H$^+$+8e=ZnS+4H$_2$O	0.624	0.627	0.630	0.633	0.635	0.638
(7) Zn^{2+}+SO$_4^{2-}$+8H$^+$+8e=ZnS+4H$_2$O	0.656	0.661	0.666	0.671	0.677	0.681
(8) ZnSO$_4$·Zn(OH)$_2$ 2H$^+$=2Zn^{2+}+SO$_4^{2-}$+2H$_2$O	11.184	10.943	10.894	10.402	10.390	9.529
(9) ZnSO$_4$·Zn(OH)$_2$+SO$_4^{2-}$+18H$^+$+16e=2ZnS+10H$_2$O	0.026 5	0.026 8	0.029 5	0.032 1	0.035 4	0.035 5
(10) S^{2-}+H$^+$=HS$^-$	10.805	10.586	10.378	10.179	9.956	9.777
(11) ZnS+H$^+$+2e=Zn+HS$^-$	−0.817	−0.819	−0.821	−0.825	−0.823	−0.828
(12) H$^+$+HS$^-$=H$_2$S	8.168	8.138	8.173	8.250	8.253	8.301
(13) ZnS+2H$^+$+2e=Zn+H$_2$S	−0.507	−0.502	−0.495	−0.490	−0.476	−0.472
(14) ZnS+2e=Zn+S^{2-}	−1.228	−1.232	−1.235	−1.242	−1.241	−1.251
(15) Zn^{2+}+2e=Zn	−0.426	−0.420	−0.415	−0.411	−0.401	−0.398
(16) 2Zn(OH)$_2$+SO$_4^{2-}$+2H$^+$==ZnSO$_4$·Zn(OH)$_2$+2H$_2$O	14.507	15.055	15.068	15.120	15.125	15.132
(17) Zn(OH)$_2$+10H$^+$+SO$_4^{2-}$+8e=ZnS+6H$_2$O	0.894	0.895	0.902	0.911	0.921	0.928
(18) ZnO$_2^{2-}$+SO$_4^{2-}$+12H$^+$+8e=ZnS+6H$_2$O	0.979	0.988	0.997	1.013	1.014	1.023
(19) ZnO$_2^{2-}$+SO$_4^{2-}$+12H$^+$+10e=Zn+S^{2-}+6H$_2$O	0.537	0.543	0.550	0.587	0.563	0.569
(20) O$_2$+4H$^+$+4e=2H$_2$O	1.170	1.161	1.153	1.144	1.136	1.128
(21) 2H$^+$+2e=H$_2$	−0.075 9	−0.077 9	−0.079 9	−0.081 9	−0.083 9	−0.859

Fig.1 $E−$pH diagrams of ZnS-H_2O system at different temperatures with activity of 1.0 and oxygen pressure of 0.8 MPa: (a) 110 °C; (b) 120 °C; (c) 130 °C; (d) 140 °C; (e) 150 °C; (f) 160 °C

Fig.2 Comparison of S-quality regional at different temperatures and activity of 1.0 and oxygen pressure of 0.8 MPa ((b) is enlargement of (a))

4 Experimental

4.1 Material

The experimental material was ZnS (analytically pure), and the additive is calcium lignosulfonate, and leaching solution is H_2SO_4 (98%) diluted to a certain concentration.

4.2 Leaching experiment

The major equipment used in the experiment was a 2 L zirconium autoclave (KCFD2-10 type) consisting of a reactor chamber and a head assembly, both of which could be combined and tightened with a leak-proof closure. Heat was provided to the autoclave by an electrical heating mantle that was connected to a thermocouple and controlled by an external temperature controller. The autoclave was further equipped with a solid feeding device that allowed for convenient injection of zinc sulfide or sulphuric acid into the reactor chamber once the desired temperature had been reached. The autoclave was directly connected to an oxygen cylinder in order to reach the required oxygen partial pressure[18].

The experimental parameters are 110−160 °C of the leaching temperature, 0.2−1.0 MPa of oxygen partial pressure, 1:1−8:1 of liquid to solid ratio, 120−160 g/L of initial acidic concentration, 30−150 min of leaching time and 120−600 r/min of stirring speed.

4.3 Analysis

The Prodigy XP type inductively coupled plasma-atomic emission spectrometry (ICP) of American Leeman Lab was used to test the Zn^{2+} content of leaching solution. The chemical composition identication of leach residue was analyzed by ZSX 100e X-ray fluorescence spectrometer (XRF) and phase identication was analyzed by PW3040/60 X-ray diffraction (XRD) of Dutch Panalytical Company, and the diffraction angle (2θ) was from 5° to 90°, and scanning rate was 7(°)/s.

5 Results and discussion

The E−pH diagrams of ZnS-H_2O system are used to guide the single factor experiment of ZnS high pressure leaching. The XRD pattern of leaching residue is shown in Fig.3 and the experimental results are shown in Fig.4.

According to E−pH diagram, temperature is the most important factor in the process of leaching. In the temperature range from 110 to 150 °C, the leaching rate of zinc increases from 60.05% to 97.85% and the conversion rate of sulfur increases from 38.90% to

80.92% when other conditions are 5:1 of liquid-to-solid ratio, 150 g/L of initial acidic concentration, 120 min of leaching time, 0.8 MPa of oxygen partial pressure, and 480 r/min of stirring speed. The experimental results tend to be stable over 150 °C. With the temperature increasing from 110 to 150 °C, the leaching of Zn(II) and the conversion of S proceed more thoroughly. It is favorable for kinetics condition at high temperature, and temperature has an important effect on decreasing the kinetics resistance.
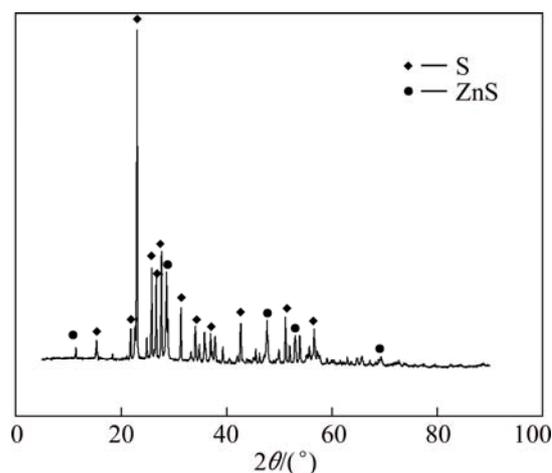
Fig.3 XRD pattern of leaching slag

In the process of ZnS high pressure leaching, oxygen acts as an oxidant in the dissolution, passes through gas/liquid interphase firstly and is adsorbed on the surface of solid particles. Then, the oxygen molecule which is adsorbed cracks into oxygen atom, and it is the key link of the whole oxidation process. However, this cracking reaction needs high activation energy. Consequently, temperature has a significant influence on promoting the oxygen bond fracture and making the oxygen molecule dissoluted crack into oxygen atom. Meanwhile, effect of temperature could be expressed by reaction rate constant. According to Arrhenius formula $K=A\exp[−E/(RT)]$, the value of K increases and the motion of ion aggravates with increasing the temperature, which is beneficial to improving the reaction rate. In conclusion, the experimental results correspond with theoretical calculation.

6 Conclusions

1) E−pH diagrams of ZnS-H_2O system were drawn by thermodynamic calculation method under the condition of oxygen partial pressure of 0.8 MPa, ionic activity of 1.0 and different temperatures from 110 to 160 °C.
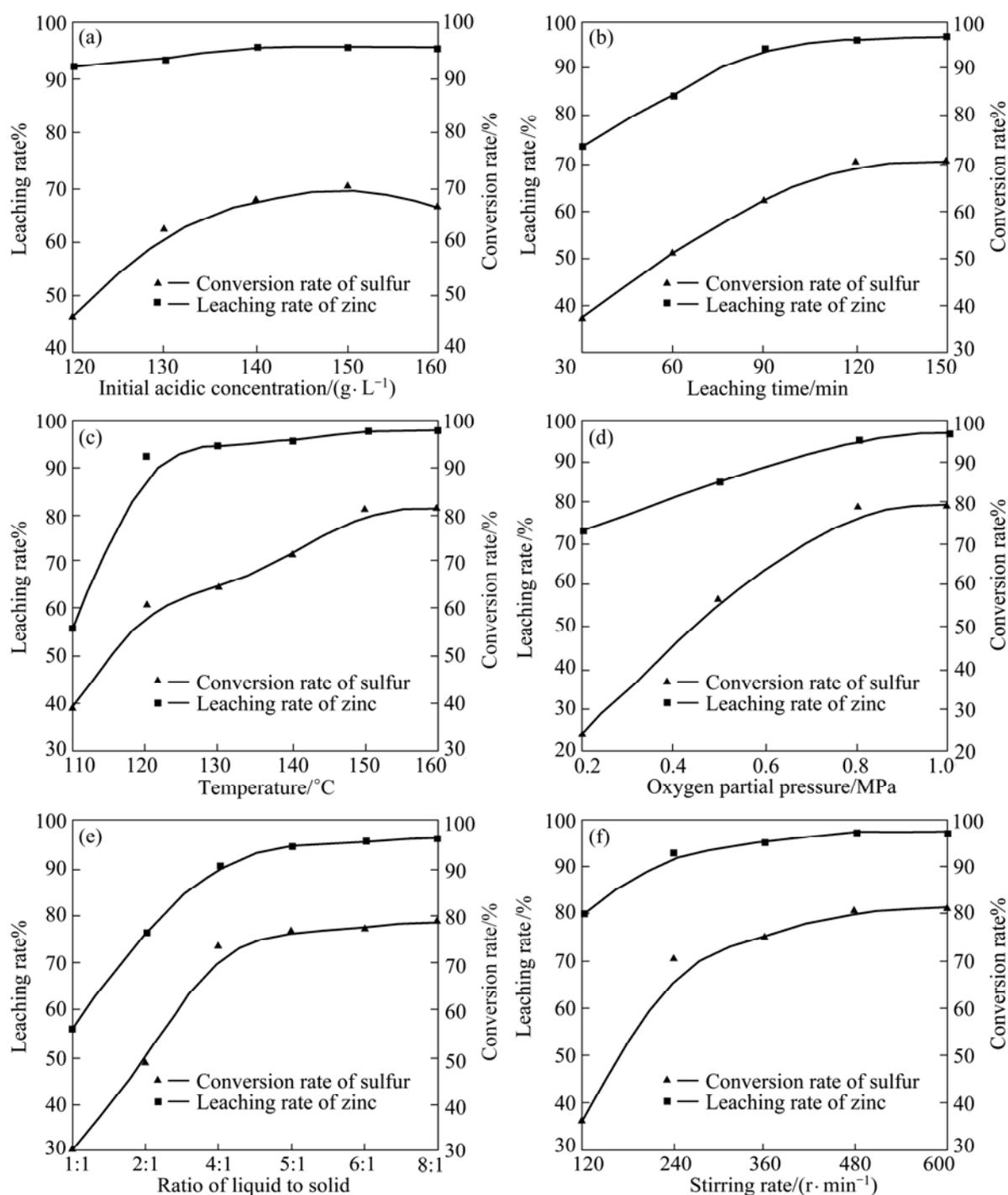
Fig.4 Single factor experimental results of ZnS high pressure leaching

2) By comparing the change trend of the stable region of S and Zn(II) from 110 to 160 °C, it is shown that with increasing the temperature, ΔG_T of reactions corresponding to S and Zn(II) stable regions in the E−pH diagrams are more negative, and the values of pH increase. But, when the temperature is higher than 150 °C, the amplification is smaller. Thus, how temperature influences the stable region is clear, and E−pH diagram provides thermodynamics basis for ZnS high pressure leaching.

3) The experimental results show that with increasing the temperature from 110 to 150 °C, while other parameters are 5:1 of liquid to-solid-ratio, 150 g/L of initial acidic concentration, 120 min of leaching time, 0.8 MPa of oxygen partial pressure, and 480 r/min of stirring speed, the leaching rate of zinc increases from 60.05% to 97.85% and the conversion rate of sulfur increases from 38.90% to 80.92%, which tend to be stable over 150 °C. The experimental results of ZnS high pressure leaching justify the guiding significance of

E−pH diagram.

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