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Effects of copper ions on dissolution mechanism of marmatite

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Abstract: The dissolution mechanism of marmatite in the presence of Cu^{2+} was intensively studied by experiments and density functional theory (DFT) calculations. Leaching experiments showed that Cu^{2+} accelerated marmatite dissolution at high temperatures (above 55 °C), but the trend was reversed at low temperatures (below 45 °C), which may be because the reaction mechanism between Cu^{2+} and marmatite changed from surface adsorption to bulk substitution with increasing temperature. The substitution reaction caused more zinc atoms in the marmatite crystal lattice to be released and enhanced the electrochemical reactivity, while the adsorption of copper ions at low temperatures would passivate marmatite, thus inhibiting the reaction process. DFT calculations showed that the energy of the substitution reaction was more negative than that of the adsorption reaction at high temperatures, which further verified the proposed mechanism. **Key words:** dissolution mechanism; sphalerite; marmatite; copper ion

1 Introduction

Zinc is demanded for multiple industry fields, such as batteries, corrosion prevention, and dielectric materials; therefore, it plays a vital role in social and economic development [1]. Sphalerite is the most abundant Zn-bearing mineral, whereas the chemical composition of natural sphalerite varies considerably with the ore deposits due to the substitution of other impurities in the mineral lattice. Iron (Fe) is the most common impurity that occurs in the lattice [2,3]; in this case, marmatite $(Zn_xFe_{1-x}S)$ is defined as the content of iron in sphalerite exceeding 6 wt.% [4]. Sphalerite/ marmatite has an inferior natural floatability and responds not well to xanthate collectors, whereby additional activators, usually copper sulfate (CuSO₄) [4,5], are required to activate the mineral surface to enhance the adsorption of collector molecules. Hence, a considerable amount of copper ion is enriched into the concentrate along with marmatite. Deep separation of copper-zinc ore has long been a challenge in the mining industry, namely, copper ions present in marmatite concentrate are unavoidable.

Roasting-leaching-electrowinning (RLE) is a common zinc extraction method, wherein the leaching efficiency of sphalerite/marmatite directly affects zinc recovery [6,7]. In the research conducted earlier, the effect of metal ions on the dissolution of sulfide minerals was reported [8–10]. A few researchers have proposed that copper ions accelerate the dissolution of marmatite and realgar [9,10], but the specific mechanism remains unclear. Voluminous literature has investigated the surface product as copper ions activate marmatite during flotation, which is usually carried out under alkaline conditions [11,12], but the surface product and mechanism under acidic environments have

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rarely been reported.

In addition, environmental problems caused by the mining industry have attracted much attention. Marmatite mining and smelting activities pose potential risks to the environment [13]. For instance, the dissolution of sphalerite/marmatite in tailings and waste is one of the contributors to generate acid mine drainage (AMD), releasing large amounts of heavy metal ions into surroundings [14-16]. In general, tailing ponds usually consist of varieties of minerals, including marmatite and Cu-bearing minerals. Therefore, the effect of copper ions on marmatite dissolution also has a profound impact on the prevention of AMD. Tailings and wastes are usually stored in the mining area in the forms of ore heaps. Current literature indicates that sulfides in the heap could produce enough energy to maintain a high temperature and form gradients in different parts of the heap [17,18], and marmatite dissolution is a process which is affected by temperature [19,20]. Therefore, the effect of copper dissolution at ions on marmatite different temperatures and the corresponding reaction mechanism should be explained. However, little research has been reported on the precise mechanism responsible for the role of copper ions in marmatite dissolution and its discrepancy at different temperatures.

In this work, different dissolution behaviors and mechanisms of marmatite in the presence of copper ions at different temperatures were studied by leaching experiments, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM/EDS) and electrochemical tests. Additionally, density functional theory (DFT) methods were used to explore the underlying mechanism at an atomic level. The obtained results of the present work contribute not only to research on the (bio)hydrometallurgy of sphalerite/marmatite but also to the corresponding environmental issues.

2 Experimental

2.1 Materials

In this work, marmatite samples were taken from Anhui Province of China. The high purity marmatite used in the test was sieved to obtain a particle size less than 74 μ m. Chemical analysis showed that the main elemental composition (mass fraction) of the sample was 51.45% Zn, 12.28% Fe, and 32.82% S. Copper sulfate (CuSO₄), as the source of copper ions, was supplied by Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all experiments, and all reagents were analytical grade.

2.2 Dissolution experiments

Erlenmeyer flasks (250 mL) were used as the leaching reactor and placed in a shaking incubator. The temperature gradient (25-75 °C) of the leaching solution in the reactor was provided by a constant temperature shaker (LYZ-2102-C, Shanghai Long-Yue Instruments Co., Ltd.). In the dissolution experiments, 2 g marmatite was suspended in 100 mL leaching solution (pulp density 2%, w/v), and sulfuric acid (H₂SO₄) was used to maintain the solution pH at 2.5. The stirring speed was kept at 170 r/min. Copper ions (100 or 2500 mg/L) were added to each Erlenmeyer flask. The pH and redox potential were measured by a pH/ORP meter (BPP-920, Bell Analytical Instruments Co., Ltd.). The liquid volume was kept constant with deionized water. Dissolution experiments were performed for 336 h, and then the sample was filtered. Supernatant samples (100 µL) were periodically (every 2 d) extracted during the dissolution experiments for solution analysis. Then, the concentrations of Cu, Fe and Zn were analyzed via inductively coupled plasma-optical emission spectrometry (ICP-OES) (ICAP 7400, Thermo Fisher Scientific Co.)

2.3 Electrochemical experiments

The electrochemical TAB (CHI700E, CH employed Instruments, Ins.) was for the electrochemical investigation. Dilute sulfuric acid (pH 2.5) was used as the electrolyte. Open circuit potential (OCP), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Tafel measurements were performed in a three-electrode cell system. The counter electrode was a couple of graphite rods, and the reference electrode was an Ag/AgCl (3 mol/L KCl) electrode. The working electrode was a single piece that was a mixture of 0.7 g marmatite, 0.2 g graphite and 0.1 g paraffin. The working electrodes were pretreated with different Cu^{2+} ions (0 and 2500 mg/L) at different temperatures (25 and 75 °C). To ensure the accuracy of the test, the working electrode was equilibrated at the OCP before EIS, Tafel and CV measurements. Frequency Response Analysis (Zivew-2.0) software was used to fit the EIS data.

2.4 XRD, Raman and SEM-EDS analyses

Dissolution residues were filtered and vacuum dried for the characterization of X-ray diffraction spectroscopy and (XRD), Raman scanning electron microscopy (SEM/EDS). The samples were analyzed by an Advance D8/Bruker X-ray diffractometer (XRD) with Cu K_a radiation at 2θ from 15° to 80°. In Raman spectroscopy test, a Renishaw Via spectrograph was used. A scanning electron microscope (JSM-6490LV/JEOL) equipped with an energy dispersive spectrometer (Neptune XM 4/EDAX) was used to determine the element content on the residue surface. Prior to all tests, all samples were washed with deionized water and then vacuum dried.

2.5 DFT calculations

For sphalerite, the (110) surface with the lowest surface energy is the most commonly exposed surface [21]. Therefore, the sphalerite (110) surface was used for the simulation study. The sphalerite (110) surface was designed as the substrate with two layers of atoms, which was simulated using the slab model, and the vacuum distance between the slabs was set to be 10 Å. Three Zn atoms on the sphalerite (110) surface were randomly replaced by Fe atoms to simulate the chemical formula of the original mineral sample. Then, we investigated the reaction behavior of Cu on this surface, and the energy changes during the reaction process were examined. Finally, four initial systems were constructed in the same cubic simulation lattice built with dimensions of x=16.22 Å, y=11.47 Å, and z=11.91 Å. All atoms were fully released in the optimization process.

All DFT calculations in this study were performed using the DMol³ program package in Materials Studio. The exchange and correlation terms were determined using the generalized gradient approximation (GGA) in the form proposed by PERDEW et al (PBE) [22]. The core DFT semicore pseudopotential (DSPP) method was utilized to calculate the core treatment of metal elements (Cu, Zn and Fe); for other elements, the all-electron method was applied [23]. Solvation effects were incorporated by the COSMO solvation model for all the systems with water as the solvent. The cut-off was set as 4.5 Å and a 0.005 Hartree smearing was used to facilitate the self-consistent field (SCF) convergence. The thresholds of energy, force, and displacement are 1×10^{-5} Hartree, 2×10^{-3} Hartree/atom, and 5×10^{-3} Å, respectively.

The interaction energies (E_{inter}) of the four systems mentioned above were calculated by Eq. (1):

$$E_{\text{inter}} = E_{\text{Cu/substrate}} - (E_{\text{Cu}} + E_{\text{substrate}})$$
(1)

where $E_{\text{substrate}}$ and E_{Cu} represent the energies of the substrate (including modified substrates) and the Cu atom, respectively, and $E_{\text{Cu/substrate}}$ is the total energy of the interacting (Cu⁺ substrate) system. According to Eq. (1), a negative value of E_{inter} indicates that the process is an exothermic reaction, and a high negative value corresponds to a stronger interaction, which indicates more heat release and a more stable product.

3 Results

3.1 Dissolution behaviors

Figure 1 compares the dissolution behavior of marmatite in the absence and in the presence of copper ions at different temperatures (25-75 °C). The effect of copper ions on marmatite dissolution was dramatically different with temperature change. Copper ions hindered marmatite dissolution at 25-45 °C but accelerated it when the temperature exceeded 55 °C. Meanwhile, the consumption of copper ions increased with increasing temperature, and the consumption rate was proportional to the temperature (Fig. 1). Compared with the final zinc concentration in the absence of copper ions, it increased approximately 60% in the presence of copper ions as the temperature was at least 65 °C (Figs. 1(e) and (f)). Meanwhile, copper ion consumption was proportional to the concentration of zinc dissolved from marmatite. The redox potential significantly decreased in the presence of copper ions when the temperature exceeded 65 °C (Fig. 2). In general, the dissolution of sulfide minerals would theoretically be accelerated by increasing the redox potential [24,25]. The decrease in redox potential indicated that the oxidation environment was not the main factor accelerating marmatite dissolution. In view of the difference in copper ion consumption, it was considered that the



Fig. 1 Dissolution behaviors of marmatite and Cu^{2+} consumption at different Cu^{2+} concentrations (0, 100 and 2500 mg/L) and different temperatures: (a) 25 °C; (b) 35 °C; (c) 45 °C; (d) 55 °C; (e) 65 °C; (f) 75 °C



Fig. 2 Redox potentials of dissolution process of marmatite at different temperatures: (a) Dissolution without Cu^{2+} ; (b) Dissolution with 2500 mg/L Cu^{2+}

reaction mechanism between marmatite and copper ions might change from the surface reaction to the bulk substitution reaction as the temperature increased, and the substitution reaction may be based on Reaction (2) [26]:

$$ZnS_{(s)} + Cu_{(aq)}^{2+} \rightarrow CuS_{(s)} + Zn_{(aq)}^{2+}$$
 (2)

3.2 Kinetics

The dissolution process of sulfide minerals has been described by many reaction models in the previous literature. A common model used for the kinetic analysis of acid leaching processes is the shrinking core model (SCM). It has been reported that the dissolution process is controlled either by the diffusion of leaching agents or by surface chemical reactions. If the reaction rate is controlled by diffusion through the product layer, its kinetics can be expressed as follows [27]:

$$1 - 2/3\alpha - (1 - \alpha)^{2/3} = k_{\rm d}t \tag{3}$$

where α is the leaching rate of metal, k_d is the diffusion rate constant, and *t* is the time. If the reaction is controlled by the surface reaction step,

its kinetics can be expressed as [28]

$$1 - (1 - \alpha)^{1/3} = k_{\rm r} t \tag{4}$$

where k_r is the rate constant of the surface reaction. The diffusion-controlled process was not sensitive to temperature, while the chemically controlled process was the opposite. A linear relationship was usually found between the diffusion coefficient and temperature, while the reaction coefficient controlled by the chemical reaction changed exponentially with temperature.

In this work, the kinetic constants of the reaction between marmatite and copper ions were calculated using the SCM model. Figure 3 shows the linear fit results of the leaching data obtained under different conditions and their correlation constants (R^2). All the rate constants fitted via the SCM model are listed in Table 1. The activation energy was calculated by the Arrhenius equations (Eqs. (5) and (6)) [29,30]:

$$k = A \exp[-E_a/(RT)]$$
(5)

$$\ln k = \ln A - E_a/(RT) \tag{6}$$

where k, A, E_a and R are the reaction rate constant,



Fig. 3 Plots of $1-(1-\alpha)^{1/3}$ (a, b) and $1-2/3\alpha-(1-\alpha)^{2/3}$ (c, d) versus *t* at different temperatures, solid/liquid ratio of 2 g/L, stirring speed of 170 r/min and particle size of 75 µm: (a, c) 0 mg/L Cu²⁺; (b, d) 2500 mg/L Cu²⁺

different temperatures and Cu ²⁺ concentrations						
$\rho(\mathrm{Cu}^{2+})/T/$		Appare constant	ent rate $/10^{-5} d^{-1}$	Correlation coefficient, R^2		
(mg·L ¹) °C	<i>k</i> _d (Eq. (3))	$\frac{ CU^{2} ^{2} \operatorname{concer} }{\operatorname{nt rate}}$ $\frac{(10^{-5} \mathrm{d}^{-1})}{k_{\mathrm{r}}(\mathrm{Eq.}(4))}$ 9.83 9.64 16.9 9.01 8.06 14.7 6.11 5.14	Eq. (3)	Eq. (4)	
	25	0.19	9.83	0.981	0.973	
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9.64	0.963	0.987		
0	45	0.79	16.9	0.967	0.976	
	55	1.42	9.01	0.934	0.995	
	65	1.06	8.06	0.894	0.993	
	75	2.16	14.7	0.848	0.985	
	25	0.01	6.11	0.992	0.92	
	35	0.09	Apparent rate $nstant/10^{-5}d^{-1}$. (3)) k_r (Eq. (4)) 19 9.83 52 9.64 79 16.9 42 9.01 06 8.06 16 14.7 01 6.11 09 5.14 34 3.76 23 14.1 36 8.01 52 15.2	0.952	0.975	
2500	45	0.34	3.76	0.925	0.996	
	55	2.23	14.1	0.934	0.988	
	65	6.36	8.01	0.931	0.898	
	75	7.62	15.2	0.965	0.844	

Table 1 k_d , k_r and correlation coefficient values at different temperatures and Cu²⁺ concentrations

frequency factor, activation energy and molar gas constant (8.3145 J/(K·mol), respectively. The activation energy values (E_a) are listed in Table 2. Combining the results of Tables 1 and 2, the kinetic control step of marmatite dissolution shifted from surface reaction control to diffusion control with increasing temperature when copper ions were present. In this case, the change in the kinetic control step with increasing temperature provided support for the transformation of the reaction mechanism.

Table 2 Activation energy and correlation coefficientvalues at different temperatures and Cu^{2+} concentrations

$ ho(\mathrm{Cu}^{2+})/$ (mg·L ⁻¹)	Activatio (kJ·m	n energy/ 10l ⁻¹)	Correlation coefficient, <i>R</i> ²		
	Eq. (3)	Eq. (4)	Eq. (3)	Eq. (4)	
0	19.59	52.08	0.557	0.889	
2500	96.72	49.67	0.980	0.966	

3.3 Electrochemical properties

Electrochemical experiments were performed to investigate the impact of electrochemical activity after copper ions and marmatite reacted at different temperatures. Marmatite electrodes were pretreated for 24 h under different conditions, and each electrochemical test was conducted under the same experimental conditions. Figure 4(a) clearly shows that the open circuit potential (OCP) of the electrode pretreated with copper ions obviously increased, indicating that the intermediate product changed in the presence of copper ions.

Tafel measurements were used to obtain the corrosion behavior of marmatite pretreated under different conditions. The corrosion potential (φ_{corr}) was determined by the x-axis scale corresponding to the lower end of the curve. Compared with the condition without copper ions, it shifted to the right in the x-axis scale when the electrode was pretreated with copper ions. The corrosion current density (J_{corr}) (Fig. 4(b)) was calculated via the slope of the anodic and cathodic curves. Compared with the electrode pretreated at low temperatures, the corrosion current density obviously increased (from 1.382 to 43.83 μ A/cm²) at high temperatures. A higher corrosion current density indicated that the electron conduction on the marmatite surface was more active.

Figure 4(c) shows the voltammograms for marmatite electrodes pretreated at different temperatures in the presence and absence of copper ions. Cyclic voltammetry tests were performed in the potential range of -800 to 800 mV (vs Ag/AgCl). The measurement was initiated at the OCP. The redox peak intensity of the marmatite electrode pretreated with copper ions at high temperatures obviously increased, revealing the stronger liveness of the corresponding redox reactions. Moreover, the anodic current density of the marmatite electrode pretreated with copper ions at high temperatures was greater than that pretreated at low temperatures, which indicated that the oxidation of marmatite was faster.

Electrical impedance spectroscopy tests are often used to obtain information about the properties of systems, such as the reaction rate and charge transfer abilities. The corresponding equivalent circuit shown in Fig. 4(d) was used to fit the impedance spectra. R_{sol} was associated with the solution resistance, R_1 represented the obstacle to the transmission of electrons on the marmatite surface, and R_2 was connected to the passivation layer resistance. Table 3 shows the parameters (R_{sol} , R_1 and R_2) fitted via the equivalent circuit for the impedance spectra. It was found that the resistance of marmatite electrodes pretreated with copper ions at low temperature increased, especially the



Fig. 4 Electrochemical analysis results of marmatite electrodes pretreated under different conditions (25 and 75 °C): (a) Open circuit potential; (b) Tafel curves; (c) Cyclic voltammetry curves (20 mV/s); Electrochemical impedance spectroscopy: (d) Nyquist impedance spectra; (e, f) Bode plots

	$R_{ m sol}$ / $(\Omega^{\cdot} m cm^2)$	$\frac{R_1}{(\Omega \cdot \mathrm{cm}^2)}$ –	CPE ₁ /		$R_2/$	CPE ₂ /	
Condition			$(\mathbf{F}\cdot\mathbf{s}^n\cdot\mathbf{cm}^2)$			$(\mathbf{F}\cdot\mathbf{s}^n\cdot\mathbf{cm}^2)$	
			CPE ₁ -T	CPE ₁ -P	$(\Omega \cdot \mathrm{cm}^2)$	CPE ₂ -T	CPE ₂ -P
0 mg/L Cu ²⁺ , 25 °C	114.7	1500	1.11×10^{-5}	0.96262	13177	2.67×10^{-5}	0.7814
2500 mg/L Cu ²⁺ , 25 °C	14.98	1659	6.15×10^{-6}	0.88482	45468	1.08×10^{-4}	0.61987
2500 mg/L Cu ²⁺ , 75 °C	112.3	207.4	2.1×10^{-3}	0.72542	1984	4.68×10 ⁻³	0.65409

Table 3 Impedance parameters for equivalent circuit

passivation resistance (from 13177 to 45468 $\Omega \cdot \text{cm}^2$). However, it could be observed that the values of R_1 (from 1500 to 207.4 $\Omega \cdot \text{cm}^2$) and R_2 (from 13177 to 1984 $\Omega \cdot \text{cm}^2$) obviously decreased when marmatite electrodes were pretreated with copper ions at high temperatures. The reaction of copper ions and marmatite at different temperatures has an opposite effect on the electrochemical activity of the mineral, which is favorable evidence to prove the change in the reaction mechanism.

3.4 Characterization of residue

The investigation results of XRD can be used to calculate the structure, particle size and lattice distortion of residue crystals. The distortion (ε) of the crystal lattice (presented as a percentage) and the crystallite size (D) were determined from the changes in the profile of the diffraction peaks.

Figures 5(a, c) show the XRD analysis results of the residues. Cu-containing phases were not detected at reaction temperatures below 45 °C. However, additional peaks assigned to the coppercontaining phase appeared when the reaction temperature was above 55 °C. Moreover, Raman spectroscopy was used to characterize and differentiate the reaction products of marmatite dissolution at different temperatures in the presence of copper ions, and it can identify the type of chemical bonding between atoms present as specific compounds. As shown in Figs. 5(b, d), two Raman peaks (approximately 300 and 330 cm⁻¹) assigned to Fe—S and Zn—S vibrations disappeared with increasing temperature, indicating that marmatite dissolved more thoroughly [31]. The sharp Raman peak (approximately 470 cm⁻¹) was attributed to the stretching modes from the covalent S-S bonds, which was a dominant feature of the Cu-S compounds [32]. Peaks appeared at approximately 137 and 266 cm⁻¹ as the temperature increased above 65 °C. Intense Raman peaks at approximately 475 cm⁻¹ and weaker bands at 140 and 265 cm⁻¹ were typically observed in the Raman spectra of covellite [33]. DALAPATI et al [34] reported that the Raman peak presented at approximately 475 cm⁻¹ may correspond to the $Cu_{2-x}S$ secondary phase. Moreover, Raman microscope images showed that the surface morphology of the residue changed significantly, which was obtained at different temperatures (Fig. 6).



Fig. 5 XRD (a, c) and Raman (b, d) spectra of leaching residues obtained under different conditions

XRD and Raman data revealed that the Cu–S compounds appeared in the residue leached at high temperature. The lattice distortion (ε) and crystallite size (D) of residue leached under different conditions are listed in Table 4. The lattice distortion and crystallite size showed no significant change with increasing temperature, indicating that the reaction between Cu²⁺ and marmatite did not significantly change the lattice structure of marmatite.



Fig. 6 Raman microscope images: (a) Original sample; (b, c) Residues obtained at 25 and 75 °C, respectively

Table 4 Crystal lattice distortion (ε) and crystallite size (*D*) at different temperatures

() 1		
Temperature/°C	<i>D</i> /nm	<i>ɛ</i> /%
25	217	0.049
35	113.1	-0.012
45	190.1	0.068
55	100.9	0.013
65	107.9	-0.015
75	103.9	0.002

The surface morphology and elemental contents of the residues collected under different conditions were further examined by SEM–EDS (Fig. 7). The surface of the residue leached at low temperatures was smooth (Figs. 7(a) and (b)). However, the surface of the residue was rough, and the surface flocculent phase was clear at high temperatures (Figs. 7(c) and (d)).

EDS analyses of the residues leached at low temperatures showed that almost no copper adhered to the surface of the residues. However, the copper content on the residue surface was very high at high temperatures, illustrating that copper compounds were enriched on the residue surface. Meanwhile, the zinc content on the residue surface was significantly reduced at high temperatures when compared with that at low temperatures, indicating that copper ions mainly replaced zinc sites in the marmatite crystal lattice. The results of residue analysis directly proved that the reaction between copper ions and marmatite was converted from a surface reaction to a bulk substitution reaction with increasing temperature.

3.5 DFT calculations

To validate the experimental observations at the atomic scale, DFT calculations were further utilized to investigate the changes in the reaction mechanism between copper ions and marmatite. To simulate the structure of an actual mineral sample, three Fe atoms are introduced to the optimized geometric structure of sphalerite. Since Fe exerted considerable influence on the surface properties of sphalerite [35,36], the site of S connected to Fe and Zn simultaneously was selected as the adsorption/ substitution sites of Cu. The dissolution process is performed in a water environment, so the calculation is carried out in a solution environment to make the computer simulation closer to the real reaction environment. Figure 8 shows the adsorption reaction of copper ions with unsaturated sulfur. The adsorption energy is significantly negative (-1.71 eV), indicating that the adsorption reaction of copper ions easily occurs on the marmatite surface under normal conditions.

In general, partial Zn - S bonds on the marmatite surface would break under the action of high temperatures. Thereby, a fractured Zn-S bond is added to the optimized structure of marmatite to simulate the reaction mechanism between copper

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Fig. 7 SEM micrographs (a, c) and EDS microanalysis results (b, d) of residues obtained at different temperatures (Normal pressure, pH 2.5, 2500 mg/L Cu²⁺, 170 r/min, 336 h): (a, b) 25 °C; (c, d) 75 °C



Fig. 8 DFT-optimized geometries for adsorption of Cu²⁺ ions on sphalerite (110) surface at low temperatures

ions and marmatite at high temperatures. Figure 9 shows the interaction energies as copper ions react with the marmatite surface via two different reaction mechanisms. Route 1 shows that Cu replaces the Zn site on the sphalerite (110) surface, and the substitution energy (ΔE_{sub}) is -4.56 eV. Route 2 denotes that copper ions still perform the adsorption reaction with unsaturated sulfur bonds, and the calculated energy ΔE_{ads} is -2.83 eV. Compared with the adsorption energy under normal conditions, it became more negative (from -1.71 to -2.83 eV) but still exceeded the substitution energy as the fractured Zn—S bond was introduced. A high negative value of reaction energy corresponds to a

stronger interaction, which indicates more heat releasing and a more stable product. Thereby, the reaction between copper ions and marmatite proceeds preferentially according to Route 1 at high temperatures.

4 Discussion

The role of copper ions in marmatite dissolution was obviously affected by temperature. Dissolution experiments (Fig. 1) suggested that marmatite dissolution can be obviously accelerated via copper ions at high temperatures (above 55 °C), while it was hindered at low temperatures (below



Fig. 9 Illustration of transformation of reaction mechanism between copper ions and marmatite at high temperatures

45 °C). In addition, the acceleration effect of copper ions was strengthened as the temperature increased, and the discrepancy in final Zn concentrations reached up to 60% in the presence and absence of copper ions. Meanwhile, the consumption of copper ions increased with increasing temperature and was proportional to the leaching concentration of Zn^{2+} . The kinetic control step of marmatite dissolution shifted from surface reaction control to diffusion control with increasing temperature when copper ions existed (Fig. 3). Combined the results of the experiment and kinetic analysis, we considered that the reaction mechanism transformed from surface reaction to bulk substitution as the temperature increased.

The Cu-containing mineralogical phase was observed in the residue dissolved at high temperatures according to the XRD and Raman results (peaks at 475, 140 and 265 cm^{-1}), but it was not detected at low temperatures (Fig. 5). It was found that the surface of residues was smooth at low temperatures, and copper was not detected via SEM-EDS. In contrast, it was covered with flocculent products at high temperatures, and the copper content was high in the flocculent products (Fig. 7). The analysis results of the residue verified the hypothesis that a small amount of copper ions were involved in the surface reaction with marmatite at low temperatures; therefore, the Cu-containing mineralogical phase was not detected in the residue. Thereafter, the mechanism between copper ions and marmatite varied to bulk substitution at high temperatures, and almost all copper ions participated in the reaction, whereby copper was discovered in the residue.

DFT calculations further revealed the transformation of the reaction mechanism at the atomic scale. The results suggested that copper ions would be easily adsorbed on the marmatite surface to form Cu-S bonds at low temperatures, and the E_{ads} was approximately -1.71 eV (Fig. 8). Broken Zn-S bonds were added to the marmatite structure to simulate the reaction between copper ions and marmatite at high temperatures. The reaction energy at which Cureplaced the Zn site in marmatite (E_{sub}) was -4.56 eV, which was more negative than that of Cu adsorption (E_{ads} =-2.83 eV) when the broken Zn—S bond existed (Fig. 9). The results of the DFT calculations proved that the priority of the reaction (absorption/substitution) between copper ions and marmatite changed at different temperatures. The substitution reaction occurred prior to the absorption reaction at high temperatures, proving the feasibility of the mechanism transformation in theory.

Electrochemical analysis showed that the reaction of copper ions and marmatite has different effects on the electrochemical activity of marmatite at different temperatures. The adsorption products of copper ions on the marmatite surface had a negative effect on the electrochemical activity at low temperatures (higher passivation layer resistance of 45468 $\Omega \cdot cm^2$ and charge transfer resistance of 1659 $\Omega \cdot cm^2$), as shown in Fig. 4 and



Fig. 10 Mechanism model for interpreting role of copper ions in marmatite dissolution at different temperatures

Table 3. However, the electrochemical reactivity of the marmatite electrode pretreated at high temperatures was enhanced (obvious redox peaks and smaller resistance). Combining the above conclusions, we considered that the reaction between copper ions and marmatite converted from surface adsorption to bulk substitution with increasing temperature. Copper ions replaced zinc sites in marmatite lattices and accelerated further dissolution of zinc. According to the present results and discussion, one mechanism model of this work is shown in Fig. 10.

5 Conclusions

(1) Marmatite dissolution in the presence of copper ions was obviously dependent on temperature. Cu^{2+} accelerated marmatite dissolution at high temperatures (above 55 °C), but the trend was reversed at low temperatures (below 45 °C), and the consumption rate of copper ions was proportional to the temperature. This phenomenon might be because the reaction mechanism between Cu^{2+} and marmatite shifted from surface adsorption to bulk substitution with increasing temperature. Meanwhile, the kinetic regimes shifted from surface reaction to diffusion control as the temperature increased.

(2) Electrochemical measurements and residue analysis indicated that copper ions accelerated marmatite dissolution at high temperatures from two aspects: the substitution reaction between Cu^{2+} ions and marmatite causes more Zn^{2+} in the marmatite crystal lattice to be released; the substituted products enhanced the electrochemical activity of marmatite. However, the adsorption of copper ions at low temperatures would passivate marmatite and impede the electrochemical reaction.

(3) DFT calculations showed that the energy of the substitution reaction was more negative than that of the adsorption reaction at high temperatures, indicating that the reaction priority of the former was higher than that of the latter, which further verified the proposed mechanism.

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铜离子对铁闪锌矿溶解机制的影响

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摘 要:通过实验和密度泛函理论(DFT)模拟计算研究铜离子存在下铁闪锌矿的溶解机制。浸出实验结果表明, 铜离子在高温条件下(高于 55 ℃)加速铁闪锌矿的溶解,但在低温条件下(低于 45 ℃)抑制其溶解。导致该现象的 原因可能是铜离子与铁闪锌矿间的反应机制随反应温度的升高从表面吸附反应转变为体相取代反应。体相取代反 应使铁闪锌矿晶格中更多的锌原子被释放,并且取代反应产物,增强铁闪锌矿表面的电化学反应活性;然而,低 温条件下铜离子的吸附会使铁闪锌矿表面钝化,从而阻碍电化学反应的进行。DFT 模拟计算表明,高温条件下取 代反应的反应能比表面吸附反应能更负,进一步验证了所提出的反应机制。 关键词:溶解机制;闪锌矿;铁闪锌矿;铜离子

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