Physicochem. Probl. Miner. Process., 54(2), 2018, 377-385

http://www.journalssystem.com/ppmp/

Physicochemical Problems of Mineral Processing

ISSN 1643-1049

Received March 9, 2017; reviewed; accepted August 21, 2017

Copper adsorption reaction rate and ion exchange ratio during the copper activation of sphalerite

Jian Liu [1,2], Deqiang Luo [2], Lingyun Huang [1], Yu Wang [2], Shuming Wen [1]

[1] State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China

[2] Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, China

Corresponding author: vacation2008@126.com (Jian Liu)

Abstract: A theoretical analysis method of the solution chemistry characteristic of Cu(II) at various pH values was developed. Using such method, the existence form of Cu species and their proportions in aqueous solution can be clearly determined. After that, the copper adsorption and ion exchange ratio (E) during the copper activation of sphalerite were investigated. The results indicated that the copper activation of sphalerite can be divided into two stages, i.e., the fast activation stage ($t \leq 4$ min) and slow activation stage ($t > 4$ min). The general form of the copper adsorption rate was determined as $\Gamma_{Cu}=K_1\ln(t)+\Gamma_1$, which is confirmed by the data fitting of the fast activation stage. The lower activation pH results in higher ion exchange efficiency for Cu substituting Zn. For a strong acid pH of 4.1, the E maintains about 1:1 in the entire activation time range and is not dependent on the activation time. However, the value of E is greater than 1 under weak acidic (pH=6.2) and alkaline (pH=9.1) pH conditions and it significantly depends on the activation time. For such conditions, E decreases with increase in the activation time, which supports the ion exchange mechanism, but within short activation time, it is not a 1:1 ion exchange process.

Keywords: *sphalerite, copper activation, solution chemistry, ion exchange ratio, reaction rate*

1. Introduction

Sphalerite (ZnS) is the most abundant Zn-bearing mineral, which accounts for more than 90% of the zinc output in industry. Compared with other sulphide ores, sphalerite has an inferior natural floatability. It does not respond well to short chain xanthate collectors, such as ethyl xanthogenate, due to the high solubility of zinc-xanthate in water. Thus, additional activators are generally added to treat the sphalerite surface to enhance the adsorption of collector molecules. Copper sulfate ($CuSO_4$) is the most widely used activator in sphalerite flotation. It is generally accepted that the copper activation of sphalerite at acidic condition follows an ion exchange mechanism (Chandra and Gerson, 2009; Finkelstein, 1999; Gerson et al., 1999) where the uptake of Cu^{2+} ions results in approximately 1:1 release of Zn^{2+} ions into the solution.

Numerous experimental studies involving the copper activation and xanthate adsorption in sphalerite flotation have been conducted, most of which focused on the effects of surface oxidation (Buckley et al., 1989; Fornasiero and Ralston, 2006), iron impurity in natural sphalerite (Boulton et al., 2005; Chen et al., 2012; Harmer et al., 2008), concentration of activators and collectors (Leppinen, 1990; Persson, 1994; Popov and Vučinić, 1990), conditioning time (Lascelles et al., 2001), solution pH (Fuerstenau et al., 1974; Popov and Vučinić, 1990), and the temperature onto flotation performance (Albrecht et al., 2016). Aside from these experimental studies, density functional theory (DFT) simulation is also widely used for investigating the fundamental aspects of copper activation and xanthate adsorption in sphalerite flotation. Chen et al. (2012) studied the effect of lattice defects on surface properties and copper activation of sphalerite using DFT, and found that Fe and Mn

http://dx.doi.org/10.5277/ppmp1832

impurities cannot be replaced by Cu atom, which reduces the exchange sites (Zn) for Cu atom. Thus, the Fe and Mn-bearing sphalerites are hard to be activated by copper. Long et al. (2016) studied the water molecule effect on the ethyl xanthate adsorption on unactivated and Cu-activated ZnS (110) surface using DFT; it was shown that the adsorption of water molecules decreases the reactivity of surface Zn atoms with xanthate, but has little influence on the properties of Cu-activated ZnS surface. In our previous work, it was found that the adsorption of Cu on S sites of sphalerite surface can also result in the activation of sphalerite (Liu et al., 2013), and the Cu adsorbed on S sites can spontaneously migrate to the Zn vacancy on sphalerite surface (Liu et al., 2016). Moreover, the DFT simulation (Liu et al., 2014) of the interaction among sphalerite (110) surface, copper and ethyl xanthate (EX) revealed that four types of stable interaction models exist among sphalerite surface, copper and EX, i.e., EX interacts with the Cu substituted for Zn, Cu adsorbed on the top site of S, Cu adsorbed on the bridge site of S and $Cu(OH)_2$ adsorbed on the sphalerite surface. The four interaction models can result in the activation flotation of sphalerite.

Despite the valuable information that have been collected from these studies, the precise interpretation for the copper adsorption and ion exchange during the copper activation of sphalerite is still a contentious issue (Wang et al., 2013), especially for alkaline pH conditions. Some experimental phenomena cannot be fully interpreted by simple ion exchange mechanism, due to the hydroxylation of Cu^{2+} in solution. In addition, the DFT calculating result in our previous work, namely, the adsorption activation of Cu on the S sites of sphalerite surface, is lack of experimental verification. If such adsorption activation exists, the ion exchange ratio for Cu substituting Zn is most likely not 1:1. To further illuminate these issues, the solution chemistry characteristic of Cu(II) at various pH values was firstly theoretically calculated, which is an important foundation for understanding the interaction mechanism between copper species and sphalerite surface. Then, the copper adsorption reaction rate and ion exchange ratio for Cu substituting Zn during copper activation of sphalerite were fully investigated and discussed in the present investigation.

2. Experimental

2.1 Characterization of material

The material used for the present study is a natural pure sphalerite from southwest Yunnan province of China. It has a yellow-brown color and an average particle size around of 10 mm. The material was soaked in a 1% concentration of hydrochloric acid solution for 1 hour, cleaned with ultrasonic and then air-dried. After that, the dry material was hand-ground in a mortar and pestle, to obtain a fraction with particle size range of 40-75 μm by dry sieving. The chemical composition of the material was analyzed by atomic absorption spectrometry (AAS) with the result shown in Table 1.

Table 1. Chemical composition of sphalerite

Element	Zn	S	Fe	Pb	SiO_2
Content (wt.%)	64.84	32.81	0.19	0.014	1.21

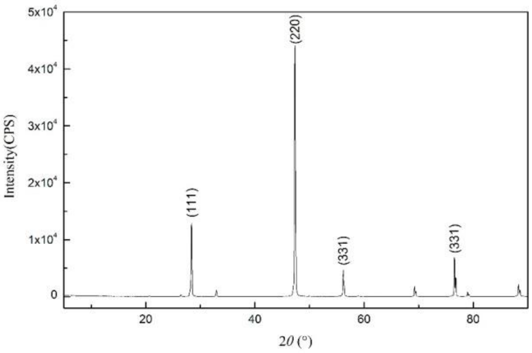

Fig. 1. XRD pattern of sphalerite

According to Table 1, this material contains 64.84% Zn and 32.81% S; thus, it reaches a theoretical purity of 96.76%, with only minor impurities of Fe, Pb and SiO_2. In addition, X-ray diffraction (XRD) (D/Max 2200, Rigaku, Japan) was used to further analyze the composition and crystalline structure of the material, with the result shown in Fig. 1.

In Fig. 1, four strong peaks at 2θ value of 28.56, 47.52, 56.29 and 76.81 were observed, which correspond to the crystalline phases of sphalerite (111), (220), (331) and (331), respectively. The XRD results confirm that it is a cubic structure sphalerite (β-ZnS) with no apparent impurities.

2.1 Experimental methods

The experiments of copper activation sphalerite were performed in a digital magnetic stirrer (DF-101S, Gongyi, China). For each experiment, 0.5 g of material with 20 cm^3 of diluted copper ion solution at desired concentration (1×10^{-4} mol/dm^3) and pH was added to a glass reactor 50 cm^3 in capacity, and followed by rapid magnetic stirring (1000 rpm) for appointed activation time. When an activation experiment was finished, the mixture was separated by a centrifugation (801, Jintan, China). The separated liquid was stored in sealed vial and analyzed in order to estimate the concentrations of zinc and copper using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (ICPS-1000 Ⅱ, Shimadzu, Japan). To eliminate zinc, released by the dissolution of sphalerite, blank test was also performed. For the blank test, 0.5 g material with 20 cm^3 of deionized water at desired pH was added to the glass reactor. The rest of the experimental procedure was the same as during activation procedure.

All the chemicals used in the experiments were purchased from Kunming Chemical Reagents Company with chemical purity. Copper nitrate was used as activator. Hydrochloric acid and sodium hydroxide were used for pH adjustment of acidic and alkaline solutions, respectively. Purely deionized water, with a resistivity of 18 MΩ produced by Mill-Q5O (made in USA) was used throughout the experiments.

The copper uptake (Γ_{Cu}) by sphalerite surface during the activation of sphalerite at different activation pH and time can be defined as (Eq. 1):

$$\Gamma_{\mathrm{Cu}} = \frac{(C_{\mathrm{Cu}}^{\mathrm{initial}} - C_{\mathrm{Cu}}^{\mathrm{residual}}) \times V}{m}, \quad (1)$$

where, Γ_{Cu} is the amount of copper uptake by sphalerite from solution, V is the volume of sphalerite solution, and m is the mass of sphalerite.

The ion exchange ratio for Cu substituting Zn, as function of activation time was defined as (Ralston and Healy, 1980) (Eq. 2):

$$E = \frac{C_{\mathrm{Cu}}^{\mathrm{initial}} - C_{\mathrm{Cu}}^{\mathrm{residual}}}{C_{\mathrm{Zn}}^{\mathrm{total}} - C_{\mathrm{Zn}}^{\mathrm{blank}}}, \quad (2)$$

where $C_{\mathrm{Cu}}^{\mathrm{initial}}$ and $C_{\mathrm{Cu}}^{\mathrm{residual}}$ are the initial and residual concentrations of copper in the sphalerite solution after copper activation at desired time, respectively; $C_{\mathrm{Zn}}^{\mathrm{total}}$ is the zinc concentration in the sphalerite solution after copper activation at desired time and $C_{\mathrm{Zn}}^{\mathrm{blank}}$ is the concentration of zinc in the blank test.

3. Result and discussion

3.1 Solution chemistry characteristic of Cu(II) at various pH values

The solution chemistry characteristic of Cu(II) at various pH values, namely the existence form of Cu species and their proportions, is an important foundation for understanding the mechanism of copper activation of sphalerite. Thereby, a theoretical analysis method of the solution chemistry was firstly developed. Four copper hydroxyl complexes can be present in the system of Cu^{2+}-H_2O, i.e., $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, $Cu(OH)_4^-$, and the relevant chemical equilibrium reactions as well as their equilibrium constants (Albrecht et al., 2016; Wang and Hu, 1998) are as follows (Eqs. 3-6):

$$Cu^{2+} + OH^- = Cu(OH)^+,\ \beta_1 = \frac{C_{\mathrm{Cu(OH)^+}}}{C_{\mathrm{Cu^{2+}}}C_{\mathrm{OH^-}}} = 10^{6.3}, \tag{3}$$

$$Cu^{2+} + 2OH^- = Cu(OH)_2,\ \beta_2 = \frac{C_{\mathrm{Cu(OH)_2}}}{C_{\mathrm{Cu^{2+}}}C^2_{\mathrm{OH^-}}} = 10^{12.8}, \tag{4}$$

$$Cu^{2+} + 3OH^- = Cu(OH)_3^-,\ \beta_3 = \frac{C_{\mathrm{Cu(OH)_3^-}}}{C_{\mathrm{Cu^{2+}}}C^3_{\mathrm{OH^-}}} = 10^{14.5}, \tag{5}$$

$$Cu^{2+} + 4OH^- = Cu(OH)_4^{2-},\ \beta_4 = \frac{C_{\mathrm{Cu(OH)_4^{2-}}}}{C_{\mathrm{Cu^{2+}}}C^4_{\mathrm{OH^-}}} = 10^{16.4}, \tag{6}$$

where β_1, β_2, β_3 and β_4 are the dimensionless values of the standard equilibrium constant for Eqs. 3-6 at 25 °C, respectively; C is the concentration of the four copper hydroxyl complexes.

The total Cu concentration in the solution can be defined as follows (Eq. 7):

$$C_{\mathrm{Cu_T}} = C_{\mathrm{Cu^{2+}}} + C_{\mathrm{Cu(OH)^+}} + C_{\mathrm{Cu(OH)_2}} + C_{\mathrm{Cu(OH)_3^-}} + C_{\mathrm{Cu(OH)_4^{2-}}}, \tag{7}$$

where $C_{\mathrm{Cu_T}}$ is the total concentration of Cu in the system of Cu^{2+}-H_2O. Then, combining Eqs. 3-6 into Eq. 7, it is written:

$$C_{\mathrm{Cu_T}} = C_{\mathrm{Cu^{2+}}}(1 + \beta_1 C_{\mathrm{OH^-}} + \beta_2 C^2_{\mathrm{OH^-}} + \beta_3 C^3_{\mathrm{OH^-}} + \beta_4 C^4_{\mathrm{OH^-}}), \tag{8}$$

$$\text{and } C_{\mathrm{OH^-}} = \frac{10^{-14}}{C_{\mathrm{H^+}}}. \tag{9}$$

Combing Eq. 9 into Eq. 8, it is written:

$$C_{\mathrm{Cu_T}} = C_{\mathrm{Cu^{2+}}}(1 + \frac{\beta_1 10^{-14}}{C_{\mathrm{H^+}}} + \frac{\beta_2 10^{-28}}{C^2_{\mathrm{H^+}}} + \frac{\beta_3 10^{-42}}{C^3_{\mathrm{H^+}}} + \frac{\beta_4 10^{-56}}{C^4_{\mathrm{H^+}}}). \tag{10}$$

The proportion of various Cu species in solution can be defined as follows:

$$\alpha_0 = \frac{C_{\mathrm{Cu^{2+}}}}{C_{\mathrm{CuT}}} = (1 + \frac{\beta_1 10^{-14}}{C_{\mathrm{H^+}}} + \frac{\beta_2 10^{-28}}{C^2_{\mathrm{H^+}}} + \frac{\beta_3 10^{-42}}{C^3_{\mathrm{H^+}}} + \frac{\beta_4 10^{-56}}{C^4_{\mathrm{H^+}}})^{-1}, \tag{11}$$

$$\alpha_1 = \frac{C_{\mathrm{Cu(OH)^+}}}{C_{\mathrm{CuT}}} = \frac{C_{\mathrm{Cu^{2+}}}}{C_{\mathrm{CuT}}} \times \frac{C_{\mathrm{Cu(OH)^+}}}{C_{\mathrm{Cu^{2+}}}} = \alpha_0 \frac{\beta_1 10^{-14}}{C_{\mathrm{H^+}}}, \tag{12}$$

$$\alpha_2 = \frac{C_{\mathrm{Cu(OH)_2}}}{C_{\mathrm{CuT}}} = \frac{C_{\mathrm{Cu^{2+}}}}{C_{\mathrm{CuT}}} \times \frac{C_{\mathrm{Cu(OH)_2}}}{C_{\mathrm{Cu^{2+}}}} = \alpha_0 \frac{\beta_2 10^{-28}}{C^2_{\mathrm{H^+}}}, \tag{13}$$

$$\alpha_3 = \frac{C_{\mathrm{Cu(OH)_3^-}}}{C_{\mathrm{CuT}}} = \frac{C_{\mathrm{Cu^{2+}}}}{C_{\mathrm{CuT}}} \times \frac{C_{\mathrm{Cu(OH)_3^-}}}{C_{\mathrm{Cu^{2+}}}} = \alpha_0 \frac{\beta_3 10^{-42}}{C^3_{\mathrm{H^+}}}, \tag{14}$$

$$\alpha_4 = \frac{C_{\mathrm{Cu(OH)_4^{2-}}}}{C_{\mathrm{CuT}}} = \frac{C_{\mathrm{Cu^{2+}}}}{C_{\mathrm{CuT}}} \times \frac{C_{\mathrm{Cu(OH)_4^{2-}}}}{C_{\mathrm{Cu^{2+}}}} = \alpha_0 \frac{\beta_4 10^{-56}}{C^4_{\mathrm{H^+}}}, \tag{15}$$

$$\alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 1, \tag{16}$$

where α_0 , α_1 , α_2 , α_3 and α_4 are the percentage contribution of Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2$, Cu $(OH)_3^-$ and Cu $(OH)_4^{2-}$ species in the solution, respectively.

According to Eqs. 11-16, MATLAB software (version 6.1) was used for constructing the relationship of various Cu species and pH values, with the results illustrated in Fig. 2.

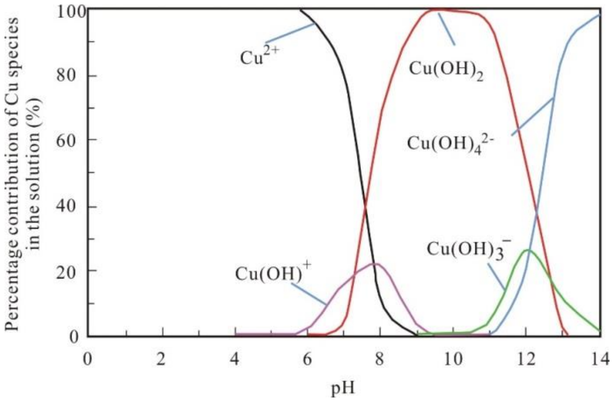

Fig. 2. Copper species and their percentage contribution in the solution vs. pH

As shown in Fig. 2, the solution of acidic pH（pH<7）contains mainly Cu^{2+} species, with a small occurrence of $Cu(OH)^+$ and $Cu(OH)_2$ ones. When the pH is less than 5.5, the copper exist only as Cu^{2+}. At pH range of 7-12.25, the copper species such as $Cu(OH)_2$ and a small quantity of Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ are mainly present in the solution. When the solution pH exceeds 12.25, there is only one copper species – mainly $Cu(OH)_4^{2-}$. For instance, the proportion of $Cu(OH)_4^{2-}$ in the solution is as high as 87% at pH=13. Define Cu species and their contribution at the exprimental pH values in presented investigations were calculated from Eqs. 11-16, with the results listed in Table 2.

Table 2. Cu species and their percentage contribution at exprimental pH values

Solution pH	Cu species (%)				
	Cu^{2+}	$Cu(OH)^+$	$Cu(OH)_2$	$Cu(OH)_3^-$	$Cu(OH)_4^{2-}$
4.1	99.97	0.03	---	---	---
6.2	96.79	3.06	0.15	---	---
9.1	0.10	2.45	97.39	0.06	---

3.2 Copper adsorption rate

To investigate the adsorption regularity of copper on sphalerite surface, the theoretical derivation of copper adsorption rate equation was performed. It is assumed that Cu species in solution is state A, and then Cu species migration from solution to the sphalerite surface is state B. According to the transition state theory (Galwey and Brown, 2002; Mott, 1947), the transition rate of atom from A to B can be defined as (Eq. 17):

$$K_{A\rightarrow B}=\nu\exp(-\frac{\Delta E}{kT}), \tag{17}$$

where v is the ion vibration frequency, ΔE is the barrier height or activation energy, k is the Boltzmann constant, and T is the absolute temperature.

During the process of copper activation, the copper species are firstly adsorbed onto the sphalerite surface and then exchange with the surface Zn atom. Thus, the copper uptake (Γ_{Cu}) is one of key parameters which directly affects the activation performance. In addition, the activation energy of many gases adsorption increases with surface coverage, which is positive correlation with adsorption (Somorjai and Klerer, 1972). If the activation energy for copper activation of sphalerite increases with the increase of copper adsorption, like gases adsorption, the ΔE can be defined as Eq. 18 (Ralston and Healy, 1980):

$$\Delta E = a_0 N_A \Gamma_{\text{Cu}}, \tag{18}$$

where, a_0 and N_A are the adsorption constant and Avogadro's number, respectively.

Then, combing Eq. 18 into Eq. 17, the adsorption rate expressed in the form of Cu adsorption can be written:

$$\frac{d\Gamma_{\mathrm{Cu}}}{dt} = K_{A\to B} = \nu \exp\left(-\frac{a_0 N_A \Gamma_{\mathrm{Cu}}}{kT}\right), \tag{19}$$

from Eq. 19:

$$\exp\left(\frac{a_0 N_A \Gamma_{\mathrm{Cu}}}{kT}\right) d\Gamma_{\mathrm{Cu}} = \nu dt. \tag{20}$$

Integrating over the limits (t=0, t=t) and (Γ_{Cu} =0, $\Gamma_{\mathrm{Cu}} = \Gamma_{\mathrm{Cu}}$) and taking logarithms yields:

$$\Gamma_{\mathrm{Cu}} = \frac{kT}{a_0 N_A}\ln\left(t + \frac{kT}{\nu a_0 N_A}\right) + \frac{kT}{a_0 N_A}\ln\left(\frac{\nu a_0 N_A}{kT}\right). \tag{21}$$

If the activation time $t >> \frac{kT}{\nu a_0 N_A}$, Eq. 21 reduces to:

$$\Gamma_{\mathrm{Cu}} = \frac{kT}{a_0 N_A}\ln(t) + \frac{kT}{a_0 N_A}\ln\left(\frac{\nu a_0 N_A}{kT}\right). \tag{22}$$

According to Eq. 22, the general form of the adsorption reaction rate of copper activation of sphalerite can be written:

$$\Gamma_{\mathrm{Cu}} = K_1 \ln(t) + \Gamma_1, \tag{23}$$

where $K_1 = \frac{kT}{a_0 N_A}$, $\Gamma_1 = K_1 \ln\left(\frac{\nu a_0 N_A}{kT}\right)$.

According to Eq. 23, the K_1 is related to the activation temperature and adsorption constant. Aside from the activation temperature and adsorption constant, Γ_1 is related to the ionic vibration frequency of activation atom.

3.3. Determination of copper uptake and ion exchange ratio

To further investigate the process of copper adsorption and verify the theoretical copper adsorption rate equation, the copper uptake during copper activation of sphalerite at various pH and time was determined, with the result illustrated in Table 3.

Table 3. Copper uptake during copper activation of sphalerite at various pH and time

Activation time (min)	Γ_{Cu}, $\times10^{-6}$ (mol/g)		
	pH=4.1	pH=6.2	pH=9.1
0.5	3.92	3.89	4.12
1	4.07	4.04	4.19
2	4.17	4.22	4.26
4	4.30	4.30	4.32
6	4.32	4.32	4.33
8	4.33	4.33	4.33
10	4.34	4.33	4.34
60	4.36	4.33	4.34

As shown in Table 3, the Cu uptake remarkably increases with the increase of activation time when the time was less than or equal to 4 minutes. However, the Cu uptake increases inconsiderably when the activation time exceeds 4 minutes. The maximum uptake is about 4.30×10^{-6} mol/g. It can be clearly seen from Table 3 that copper activation of sphalerite can be divided into two stages, i.e., the fast activation stage (t≤4 min) and slow activation stage (t>4 min). Such a result is in agreement with Ralston and Healy (1980). Compared with the copper uptake at acidic pH, its uptake at alkaline pH is obviously greater. It means that Cu adsorption rate at alkaline pH is faster than at acidic pH values. The high Cu adsorption rate at alkaline pH can be attributed to electrostatic interactions between the electric neutrality of $Cu(OH)_2$ and positive $Cu(OH)^+$ with the negatively charged sphalerite surface. The reasons may be explained as follows.

The surface charge of adsorbent is usually characterized by a point of zero charge or pH_{zpc}; it is positive at $pH < pH_{zpc}$ and negative for $pH > pH_{zpc}$ (Alkan et al., 2008). The pH_{zpc} of the sphalerite in the present study was determined at pH=6.5. Combining the analysis of the solution chemistry characteristic of Cu(II) in Table 2, it was concluded that there is an electrostatic repulsion between sphalerite surface and Cu(II) at acidic pH values, but an electrostatic attraction at alkaline pH value. Aside from the electrostatic interaction, the main driving force for the copper adsorption onto sphalerite surface is chemical affinity, especially for the acidic pH conditions.

The data fitting between the Cu uptake (Γ_{Cu}) and activation time ($t \leq 4$), as shown in Table 3, was performed to verify the theoretical copper adsorption rate equation, with the result illustrated in Fig. 3.

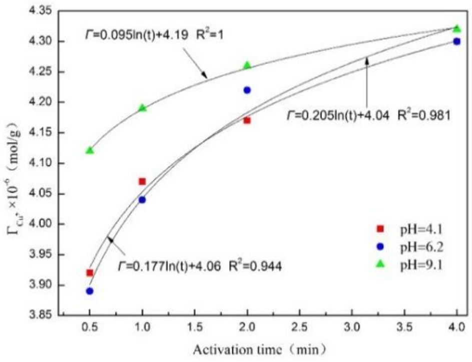

Fig. 3. Data fitting of the Cu uptake vs. activation time (t≤ 4)

It can be seen (Fig. 3) that the form of fitting equations is in good agreement with that of the general form of the copper adsorption reaction rate equation shown as Eq. 23, with a high dependent coefficient (R^2) exceeding 0.94. It was indicated that the general form of the reaction rate equation has well representativeness for the fast activation stage. Further analyzing the data presented in Table 3 and Fig. 3, it was found that Γ_1 in Eq. 23 is just about the copper uptake of sphalerite at 1 minute activation time.

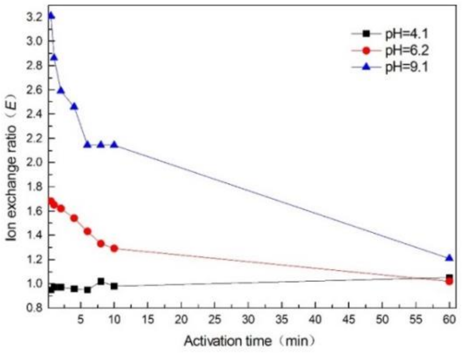

Fig. 4. Ion exchange ratio during copper activation of sphalerite at various pH and time

Aside from copper uptake, the ion exchange ratio (E) for Cu substituting Zn is another key parameter affecting copper activation performance of sphalerite. The ion exchange ratio (E) at various pH values and activation time during copper activation of sphalerite is shown in Fig. 4.

As shown in Fig. 4, the pH has an important influence on the ion exchange ratio. The E of a lower activation pH is obviously less than that of higher pH value, which indicates that the lower activation pH results in higher ion exchange efficiency for Cu substituting Zn. For a strong acidic pH of 4.1, the E maintains about 1:1 in the entire activation time range and is not dependent on the activation time. It was indicated that the copper activation of sphalerite follows an ion exchange mechanism where the uptake of Cu^{2+} ions results in approximately 1:1 release of Zn^{2+} ions into the solution.

Compared with the strong acidic pH condition, the ion exchange ratio of copper activation at weak acidic (pH=6.2) and alkaline pH (pH=9.1) conditions significantly depends on the activation time. The *E* decreases with an increase in the activation time, which supports the ion exchange mechanism; but within short activation time, it is not a 1:1 ion exchange process. The *E* is greater than 1 for weak acidic and alkaline pH conditions, which indicates that the adsorption of copper species can not immediately result in a 1:1 ion exchange as the strong acidic pH condition. For example, the *E* is as high as 1.4 and 2.1 for pH=6.2 and pH=9.1 after 5 minutes activation, respectively. Such phenomenon suggests that the activation mechanism at weak acidic and alkaline pH conditions most likely involves both ion exchange activation mechanism and the adsorption activation mechanism, especially in a short activation time. In case of adsorption activation mechanism (Liu et al., 2013, 2014, 2016), the copper species can be adsorbed onto S-sites of sphalerite surface, which also results in the activation of sphalerite.

It is interesting that it has almost the same proportion of Cu^{2+} in solution at pH=4.1 (99.97%) and pH=6.2 (96.79%) as shown in Table 2, but results in a vast difference of ion exchange ratio as presented in Fig. 4. It was suggested that the H^+ ions present in the solution play an important role in the reaction rate of Cu substituting Zn. This may be due to the dissolving action of H^+ on sphalerite surface, which weakens the bond of Zn-S and accelerates the release of Zn^{2+} ions into the solution. In addition, under the alkaline pH condition, it was noted that the ion exchange ratio can't reach a 1:1 even at a long activation time of 60 minutes. Such phenomenon is due to the hydroxylation of Cu(II) ions in the solution. As illustrated in Table 2, the vast majority of the Cu species (97.39%) exists in the form of $Cu(OH)_2$.The release of Cu^{2+} from the $Cu(OH)_2$ molecule may need more activation time.

4. Conclusions

A theoretical analysis method of the solution chemistry characteristic of Cu(II) at various pH values was developed. Using such method, the existence form of Cu species and their contribution at various pH values can be clearly determined.

It was proved that copper activation of sphalerite can be divided into two stages, i.e., the fast activation stage ($t \le 4$ min) and slow activation stage ($t > 4$ min). The general form of the copper adsorption rate was determined as $\Gamma_{\mathrm{Cu}} = K_1 \ln(t) + \Gamma_1$. It was found that the Γ_1 is just about the copper uptake of sphalerite after 1 minute activation time.

The lower activation pH results in higher ion exchange efficiency for Cu substituting Zn. For a strong acid pH of 4.1, the ion exchange ratio maintains about 1:1 in the entire activation time range and is not dependent on the activation time. However, the ion exchange ratio of copper activation at weak acidic (pH=6.2) and alkaline pH (pH=9.1) conditions significantly depends on the activation time. For such conditions, the *E* decreases with increase in the activation time, which supports the ion exchange mechanism; but within short activation time, it is not a 1:1 ion exchange process. The activation mechanism at weak acidic and alkaline pH conditions most likely involves both ion exchange activation mechanism and adsorption activation mechanism.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (Grant nos. 51764037 and 51704035), the University-Enterprise Cooperation Fund from Yunnan Copper Group (Grant No. KKZ4201521003) and the Scholar Development Project of Yunnan Province (Grant no.KKSY201421110) are sincerely appreciated.

References

ALBRECHT, T. W. J, ADDAI-MENSAH, J., FORNASIERO, D., 2016. *Critical copper concentration in sphalerite flotation: Effect of temperature and collector*. Int. J. Miner. Process., 146, 15-22.

ALKAN, M., KALAY, B., DOĞAN, M., DEMIRBAS, O., 2008. *Removal of copper ions from aqueous solutions by kaolinite and batch design*. J. Hazard. Mater., 153, 867-876.

BOULTON, A., FORNASIERO, D., RALSTON, J., 2005. *Effect of iron content in sphalerite on flotation.* Miner. Eng., 18, 1120-1122.

BUCKLEY, A., WOODS, R., WOUTERLOOD, H., 1989. *An XPS investigation of the surface of natural sphalerites under flotation-related conditions*. Int. J. Miner. Process., 26, 29-49.

CHANDRA, A. P., GERSON, A. R., 2009. *A review of the fundamental studies of the copper activation mechanisms for selective flotation of the sulfide minerals, sphalerite and pyrite*. Adv. Colloid Interface Sci., 145, 97-110.

CHEN, J., YE, C., LI, Y., 2010. *Quantum-mechanical study of effect of lattice defects on surface properties and copper activation of sphalerite surface*. Trans. Nonferrous Met. Soc. China, 20, 1121-1130.

CHEN, Y., CHEN, J., LAN, L., YANG, M., 2012. *The influence of the impurities on the flotation behaviors of synthetic ZnS*. Miner. Eng., 27, 65-71.

FINKELSTEIN, N.P., 1999. *The activation of sulphide minerals for flotation: a review*. Int. J. Miner. Process., 55, 283-286.

FORNASIERO, D., RALSTON, J., 2006. *Effect of surface oxide/hydroxide products on the collectorless flotation. of copper-activated sphalerite*. Int. J. Miner. Process., 78, 231-237.

FUERSTENAU, M., CLIFFORD, K., KUHN, M., 1974. *The role of zinc-xanthate precipitation in sphalerite flotation*. Int. J. Miner. Process., 1, 307-318.

GALWEY, A. K., BROWN, M. E., 2002. *Application of the Arrhenius equation to solid state kinetics: can this be justified?*. Thermochim. Acta., 386(1), 91-98.

GERSON, A. R., LANGE, A. G., PRINCE, K. E., SMART, R. S., 1999. *The mechanism of copper activation of sphalerite*. Appl. Surf. Sci., 137, 207-223.

HARMER, S. L., MIERCZYNSKA-VASILEV, A., BEATTIE, D. A., SHAPTER, J. G., 2008. *The effect of bulk iron concentration and heterogeneities on the copper activation of sphalerite*. Miner. Eng., 21, 1005-1012.

LASCELLES, D., SUI, C. C., FINCH, J. A., BUTLER, I. S., 2001. *Copper ion mobility in sphalerite activation*. Colloids Surf. A., 186, 163-172.

LEPPINEN, J., 1990. *FTIR and flotation investigation of the adsorption of ethyl xanthate on activated and non-activated sulfide minerals.* Int. J. Miner. Process., 30, 245-263.

LIU, J., WEN, S. M., CHEN, X. M., BAI, S. J., LIU, D., CAO, Q. B, 2013. *DFT computation of Cu adsorption on the S atoms of sphalerite (110) surface*. Miner. Eng., 46-47, 1-5.

LIU, J., WEN S. M., DENG, J. S., CHEN, X. M., FENG, Q. C., 2014. *DFT study of ethyl xanthate interaction with sphalerite (110) surface in the absence and presence of copper*. Appl. Surf. Sci., 311, 258-263.

LIU, J., WEN, S. M., WANG, Y. J, DENG, J. S., CHEN X. M., 2016. *Transition state search study on the migration of Cu absorbed on the S sites of sphalerite (110) surface.* Int. J. Miner. Process., 147, 28-30.

LONG, X., CHEN, J., CHEN. Y., 2016. *Adsorption of ethyl xanthate on ZnS (110) surface in the presence of water molecules: A DFT study*. Appl. Surf. Sci., 370, 11-18.

MOTT, N. F., 1947. *The theory of the formation of protective oxide films on metals.-III.* Trans. Faraday. Soc., 43, 429-434.

PERSSON, I., 1994. *Review: Adsorption of ions and molecules to solid surfaces in connection with flotation of sulphide minerals*. J. Coord. Chem., 32, 261-342.

POPOV, S. R., VUČINIĆ, D., 1990. *The ethylxanthate adsorption on copper-activated sphalerite under flotation-related conditions in alkaline media*. Int. J. Miner. Process., 30, 229-244.

RALSTON, J., HEALY, T., 1980. *Activation of zinc sulphide with Cu* ^{II}*, Cd* ^{II} *and Pb* ^{II}*: I. Activation in weakly acidic media*. Int. J. Miner. Process., 7, 175-201.

RALSTON, J., HEALY, T., 1980. *Activation of zinc sulphide with Cu* ^{II}*, Cd* ^{II} *and Pb* ^{II}*: II. Activation in neutral and weakly alkaline media*. Int. J. Miner. Process., 7, 203-217.

SOMORJAI, G. A., KLERER, J., 1972. *Principles of surface chemistry*. J. Electrochem. Soc., 119, 279C-279C.

WANG, D. Z., HU, Y. H., 1998. *Solution chemistry of flotation*. Hunan Science and Technology Press, Changsha, China (In Chinese).

WANG, J., LIU, Q., ZENG, H., 2013. *Understanding Copper Activation and Xanthate Adsorption on Sphalerite by ToF-SIMS, XPS and in-situ SECM*. J. Phys. Chem. C, 117, 20089-20097.