Behavior of surface action between ethyl thiourea and chalcopyrite[①]

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[Abstract] The behavior of surface action between ethyl thiourea (ETU) and chalcopyrite was studied by means of measurement of adsorptive amount , IR and XPS . The adsorption behavior of ETU on chalcopyrite corresponds to Freundlich adsorption isothermal equation , which is $\Gamma = 6.31 \times 10^{-5} c^{0.31}$ mol/ g . The adsorption is a covalent bond type of chemical one composed of two σ type bonds and a back donation π type , mainly occurs between sulfur and nitrogen atom in ETU and copper atoms on the surface of chalcopyrite . For the two σ type bonds , one is formed by transferring a pair of electrons from sulfur atom in ETU to copper atoms on the surface of chalcopyrite , the other is from nitrogen atom . And the π type bond is caused by transfer of electrons from copper atoms on the surface of chalcopyrite to unoccupied π type orbit of C—S group in ETU . Theoretical index predicts that ETU can be an excellent kind of chelating collector for copper flotation .

[Key words] ethyl thiourea ; chalcopyrite ; surface action ; adsorption characteristic ; flotation reagents

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1　INTRODUCTION

It is well known that the adsorption characteristic of flotation reagent on mineral is a decisive factor to flotation . Usually , physical adsorption caused by van der Walls force or electrostatic force is weak with no or little selectivity , and exists among all kinds of reagents and minerals . The chemical bonds formed by chemical adsorption or surface chemical reaction is strong , and occurs selectively among certain reagents and minerals , which is what people desire in developing new flotation reagents .

As a typical kind of polar organic compound , alkyl thiourea possesses structural characteristic of collector . A series of thiourea with alkyl group were synthesized[1~3] , and some of them were investigated in flotation of gold ore and displayed high activities on gold ore flotation[4] . Judged from theoretical parameters such as connectivity index of polar group[5] , electronegativity of group[6] and energy criterion[7] , alkyl thiourea can strongly bond to chalcopyrite in the form of chemical adsorption . In order to determine whether such a performance exists or not , researches are done by means of measurement of adsorptive amount , IR technique and XPS technique .

2　EXPERIMENTAL

ETU was synthesized according to Ref .[1] , the purity analyzed by high performance liquid chromatography was more than 98 % . High pure sample of chalcopyrite was picked out from a kind of natural

ore , in which the mass fraction of copper , ferrous and sulfur was 32 .27 % , 29 .16 % and 34 .23 % , respectively (Theoretical content is 34 .63 % , 30 .43 % and 34 . 94 % , respectively) . The sample with particle size of 38 ~ 76 μm was used to measure adsorptive amount , and the particle size below 5 μm was utilized to prepare testing sample for IR and XPS .

The measurement method for adsorptive amount of ETU on the surface of chalcopyrite was as follows :

2 g chalcopyrite was transferred to a beaker , 100 mL solution of ETU with concentration of c_1 was added , and stirred for 15 min with a magnetron covered Teflon under 25 ℃ . After stopping stirring , part of the solution was scooped out , and the residual concentration (c_2) of ETU was measured on Shimadzu UV-3000 ultraviolet and visible spectrophotometer under a wavelength of 270 nm . Then a value of adsorptive amount was calculated according to equation $\Gamma = 0.05(c_1 - c_2)$.

In order to identify the adsorptive characteristics of ETU on the surface of chalcopyrite , FTIR 740 infrared ray spectrophotometer and Microlab MK Ⅱ XPS were used . The testing samples were processed as follows : 0 .1 g chalcopyrite in 50 mL redistilled water was radiated for 5 min in a ultrasonic bath , washed two times with 100 mL redistilled water , 50 mL solution of ETU with a concentration of 10^{-3} mol/ L was added , then stirred for 15 min with a magnetron covered Teflon under room temperature . After filtered and washed two times with 200 mL redistilled water , the sample was dried under room temperature and pressure of 0 .1 kPa . The operation

parameters for XPS were as below : monochromator of Alk_a , target voltage of 15 kV , emission current of 20 mA , voltage passed tube of 2 .9 kV , analyzer energy of 50 eV , and operation pressure less than 10^{-10} kPa .

3　RESULTS AND DISCUSSION

3 .1　Adsorption isothermal equation of ETU on surface of chalcopyrite

The measurement results of adsorptive amount of ETU on the surface of chalcopyrite are shown in Fig . 1 . The adsorptive amount increases with the concentration of ETU when the concentration is less than 3×10^{-3} mol/ L , but it no longer increases when the concentration of ETU is more than 3×10^{-3} mol/ L , which indicates that the adsorption of ETU on the surface of chalcopyrite gets saturated at the concentration of about 3×10^{-3} mol/ L .
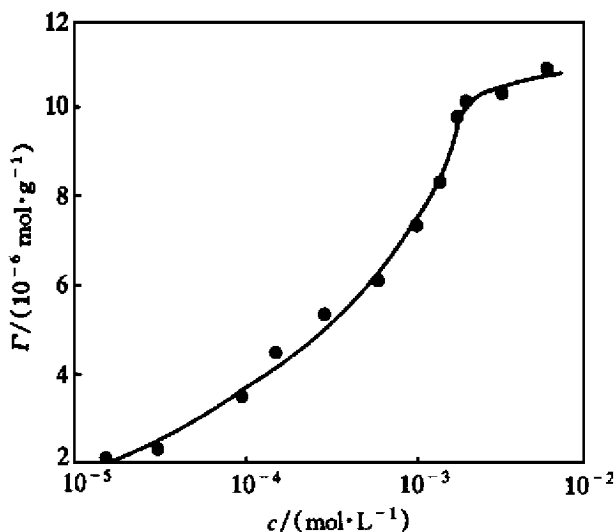
Fig .1　Adsorption isothermal curve of ETU on surface of chalcopyrite at 25 ℃

Processed the data of Fig .1 with several usual adsorption isothermal equations , it is found that there exists a perfect linear relationship between the logarithm of the adsorptive amount and the logarithm of the concentration of ETU (as shown in Fig .2) . Such a relationship indicates that the adsorption behavior of ETU on the surface of chalcopyrite corresponds to Frendlich adsorption isothermal equation , and performs an asymmetric one with more layers . From Fig .2 , we get

$$\lg \Gamma = - 4 .20 + 0 .31 \lg c \qquad (1)$$

Then

$$\Gamma = 6 .31 \times 10^{-5} c^{0 .31} \qquad (2)$$

where Γ is the adsorption amount of ETU on the surface of chalcopyrite , c is the concentration of ETU .

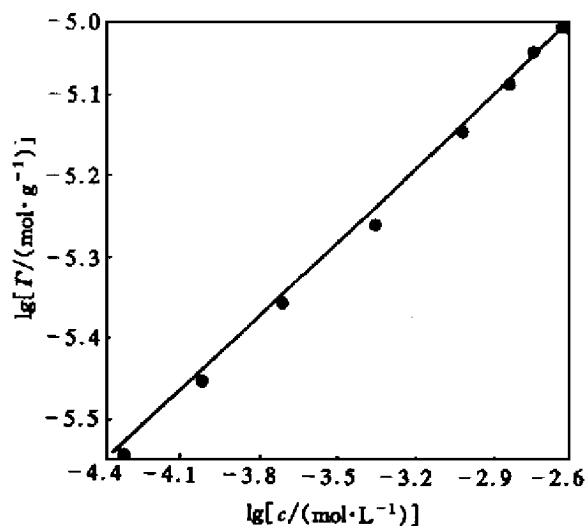### 3 .2　Adsorption characteristic of ETU on surface of chalcopyrite

Fig .2　Relationship between logarithm of adsorptive amount and logarithm of concentration of ETU

IR and XPS spectra of ETU acted with chalcopyrite are shown in Fig .3 and Fig .4 , respectively . In Fig .3 , the characteristic adsorption peaks of ETU appear on the surface of chalcopyrite treated with ETU , which suggests that a tight bonding takes place between them and the water can' t remove the adsorbed molecules of ETU from the surface of chalcopyrite . Comparing the position of characteristic adsorption peaks of ETU absorbed before and after , the wavenumber of C—S group shifts from 1 230 cm^{-1} to 1 218 cm^{-1} .

In Fig .4 , spectrum of N1s was observed in chalcopyrite treated with ETU besides spectra of S2s and S2p , in which , the spectrum of N1s is from ETU molecule adsorbed on the surface of chalcopyrite , while the spectra of S2s and S2p are from both ETU and chalcopyrite . The results of XPS also indicate
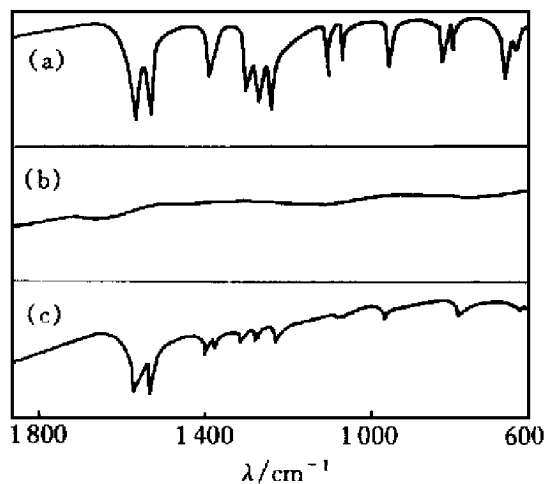
Fig .3　IR spectra of ETU before and after absorbed on chalcopyrite
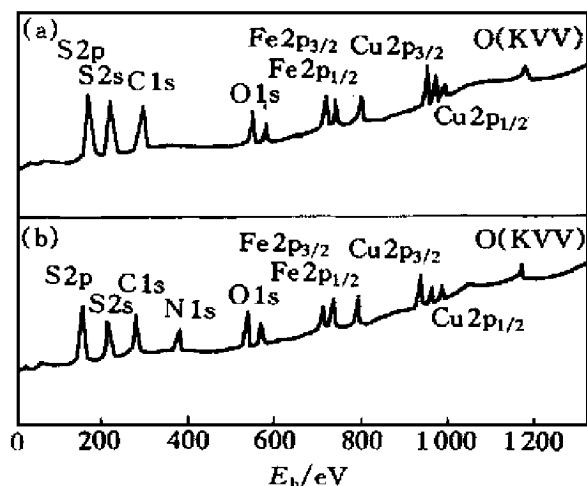(a) —ETU ; (b) —Chalcopyrite ;
(c) —ETU absorbed on chalcopyrite

Fig .4   XPS spectra of chalcopyrite before and
after treated with ETU

(a) —Chalcopyrite ; (b) —Chalcopyrite treated with ETU

Fig .5   BE in Chalcopyrite before and
after treated by ETU

(a) —$Cu\,2p_{3/2}$ before treatment ; (b) —$Cu\,2p_{3/2}$ after treatment ;
(b) —$Fe\,2p_{3/2}$ before treatment ; (d) —$Fe\,2p_{3/2}$ after treatment

Fig .6   BE in ETU before and after
adsorption on Chalcopyrite

(a) —$S\,2p_{3/2}$ before adsorption ; (b) —$S\,2p_{3/2}$ after adsorption ;
(c) —N1s before adsorption ; (d) —N1s after adsorption

that the molecules of ETU adsorbed on the surface of chalcopyrite are difficult to desorb .

The analysis of IR and XPS shows that there exists a kind of intensive chemical adsorption between ETU and chalcopyrite . According to ionic percentage suggested by Hanney[8] , the one between ETU and chalcopyrite is 22 % , which indicates that such a kind of adsorption is mainly chemical one of covalent bond type .

3 .3   Essence of adsorption bond between ETU and chalcopyrite

It can be found that there occurs a chemical shift of orbital electronic binding energy (BE) in the high resolution XPS . Fig .5 shows BE of $Cu\,2p_{3/2}$ and $Fe\,2p_{3/2}$ in chalcopyrite before and after treated with ETU , while Fig .6 shows BE of $S\,2p_{3/2}$ and N1s in ETU before and after adsorbed on chalcopyrite .

In Fig .5 , BE of $Cu\,2p_{3/2}$ decreases 0 .2 eV towards lower energy after chalcopyrite was treated with ETU , which indicates that copper atoms on the surface of chalcopyrite obtain electrons from ETU and result in the increase of electronic densities of outer layer . However , BE of $Fe\,2p_{3/2}$ does not change , which indicates that the electricity of ferric atoms does not alter , showing that ferric atoms on the surface of chalcopyrite does not participate in bonding with ETU .

In Fig .6 , there exists two values of BE of $S\,2p_{3/2}$ after the molecules of ETU adsorbed on the surface of chalcopyrite , which stands for two sulfur bearing compounds in different circumstances . The value of 161 .2 eV is the same as that of $S\,2p_{3/2}$ in chalcopyrite , coming from sulfur atoms on the surface of chalcopyrite . While the value of 162 .4 eV is caused by sulfur atoms in ETU , and increases 0 .3 eV towards high energy when compared with that of
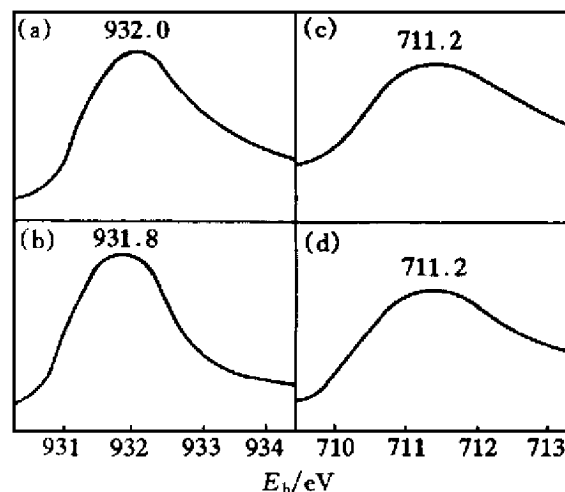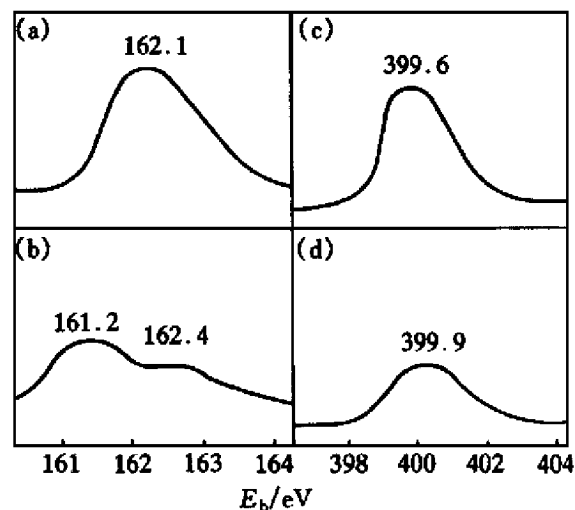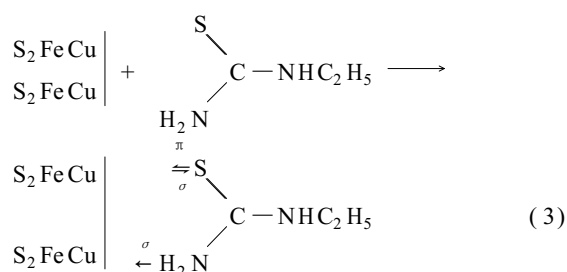
$S\,2p_{3/2}$ before adsorption , which indicates that sulfur atom of ETU supplies electrons to chalcopyrite and results in decrease of electronic densities of outer layer . Moreover , BE of N1s transfers from 399 .6 eV to 399 .9 eV , there also occurs a chemical shift of 0 .3 eV . Obviously , nitrogen atoms of ETU also offer electrons for the bonding between ETU and chalcopyrite .

Because of the increase of electronic densities of outer layer in copper atoms and the decrease of that in sulfur atoms and nitrogen atoms , the essence of the adsorption of ETU on the surface of chalcopyrite may be the formation of σ type bond , which is caused by the transfer of the two pairs of non-bonding electrons provided by sulfur atom and nitrogen one in molecule

of ETU to the outer layer empty orbits of copper atoms on the surface of chalcopyrite . Furthermore , concluded by the shift of the characteristic peak of C—S group towards low wavenumber mentioned above , back donation π-type bond may form via electrons transfer from 3d orbit of copper atoms on the surface of chalcopyrite to the unoccupied π-type orbit of C—S in ETU . The reason is that the transfer of electrons to non-bonding π-type orbits makes the intensity of C—S bond lower . Therefore , the adsorption of ETU on the surface of chalcopyrite can be expressed as

$$
\begin{array}{c}
\left.\begin{array}{c} S_2FeCu \\ S_2FeCu \end{array}\right| + \begin{array}{c} S \\ \diagdown \\ C-NHC_2H_5 \\ \diagup \\ H_2N \end{array} \longrightarrow
\end{array}
$$

$$
\left.\begin{array}{c} S_2FeCu \\ \\ S_2FeCu \end{array}\right| \begin{array}{c} \overset{\pi}{\rightleftharpoons} S \\ \overset{\sigma}{\diagdown} \\ C-NHC_2H_5 \\ \diagup \\ \overset{\sigma}{\leftarrow} H_2N \end{array} \qquad (3)
$$

3 .4 Prediction of collectability of ETU for chalcopyrite flotation

The performance of flotation reagent is associated with three structural factors[6] . As a kind of collector for mineral flotation , it must possess two conditions such as bond factor and hydrophile-hydrophobe balance in the meanwhile[8] . According to the calculation formula of hydrophile-hydrophobe balance for flotation systems[9] , the optimal carbon chain of thiourea for chalcopyrite flotation is ethyl . On account of both the intensive chemical adsorption of ETU on the surface of chalcopyrite and the suitable condition of non-polar group for hydrophile-hydrophobe balance , ETU may possess a high collectability to chalcopyrite flotation .

In the molecule of ETU , either sulfur atom or nitrogen one can provide electrons to participate in chemical adsorption on the surface of chalcopyrite , which indicates that ETU performs a kind of chelating collectors for chalcopyrite flotation .

4 CONCLUSIONS

1) The behavior of ETU on the surface of chal-copyrite is a kind of chemical adsorption of covalent bond type , which corresponds to Freundlich adsorption isothermal equation , as expressed as $\Gamma = 6 .31 \times 10^{-5} c^{0.31}$ mol/ g .

2) The adsorption bond of ETU on the surface of chalcopyrite is composed of two σ-type bond and a back donation π-type one . The former is caused by two pairs of electrons transfer from sulfur and nitrogen atom of ETU to outer layer empty orbit of copper atoms on the surface of chalcopyrite , and the latter is from 3d orbit of copper atoms on the surface of chalcopyrite to unoccupied π-type orbit of C—S group in the molecule of ETU .

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