

On the Critical Flotation Condition of a Sulfide Mineral Having Two Kinds of Positive Sites for the Anionic Collector and Depressant Adsorption

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Abstract

The critical flotation condition for the sulfide mineral having two kinds of positive sites was discussed from the viewpoint of the competitive adsorption of anionic collectors and depressants by means of statistical mechanics and chemical thermodynamics.

On the basis of the statistical mechanics as to the collector-depressant equilibria, the familiar Barsky relation was derived for the double positive site mineral. The Barsky constant can be dependent on all of the collector and depressant adsorptions for each kind of reaction site on the mineral surface according to their adsorption property.

In the chemical thermodynamics investigation, the chalcopyrite (CuFeS_2)-xanthate-hydroxyl ion system was considered. The chemical affinities of the xanthate ion and the hydroxyl ion onto the positive sites of CuS and FeS , respectively, were calculated, using thermodynamical data for the system. Consequently, it was ascertained that the depressing action of the hydroxyl ion for chalcopyrite was mainly connected with the adsorption of the hydroxyl ion onto the positive site due to FeS , while the collecting mechanism of the xanthate ion for the same mineral is closely related to the adsorption of the xanthate ion onto the positive site due to CuS . The chalcopyrite(CuFeS_2)-xanthate-cyanide ion and hydroxyl ion system was also considered in a similar manner. The flotation-non-flotation condition of chalcopyrite was able to be determined by considering the xanthate adsorption on the positive site due to CuS and the cyanide ion adsorption on the one due to FeS .

1. Introduction

In general there is a group of sulfide minerals of the binary form, composed of a sulfur atom and a kind of metal atom such as galena (PbS), cinnabar (HgS), sphalerite (ZnS), and the like. Furthermore, there is another group of sulfide minerals consisting of sulfur element and two or more kinds of metal elements such as chalcopyrite (CuFeS_2), arsenopyrite (FeAsS), and so on.

In the selective flotation of sulfide minerals, dialkyl-dithiophosphates or alkylxanthates have been used as anionic collectors and hydroxyl ions, cyanide

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ions, sulfite ions, hydrosulfide ions, sulfide ions, etc., have been used as anionic depressants. Their collecting and depressing action has been considered to be mainly due to the chemical affinity of the reaction between collector or depressant anions and metal atoms (positive sites) on the mineral surface. Generally, it is considered that the flotation characteristics of the sulfide minerals having two kinds of positive sites is intermediate between those of two simple sulfide minerals having a single positive site. According to the result of the flotation, for instance, pure chalcopyrite (CuFeS_2) tends to float better than pyrite (FeS_2), while it floats a little less than covellite (CuS). In spite of this interesting phenomenon, the fundamental study of the collector-depressant equilibria as well as the reaction mechanism of collectors and depressants onto the surface of a sulfide mineral having two kinds of positive sites has seldom been investigated so far. Accordingly, the critical flotation condition for the sulfide mineral will be discussed in this paper from the viewpoint of the competitive adsorption of collectors and depressants by means of statistical mechanics and chemical thermodynamics.

2. Discussions from statistical mechanics

The previous paper¹⁾ dealt with the relation between the adsorption amount of a collector onto the surface of a mineral and the floatability of the mineral, using galena as a typical sulfide mineral having a single positive site. As a result, it was concluded that collector or depressant molecules might probably react on a mineral surface as an ionic form. Therefore, assuming that collectors and depressants behave as an ionic form in their adsorption process, the critical flotation condition for the sulfide mineral having two kinds of positive sites is discussed.

Let a collector ion and a depressant one be denoted as X^- and D^- , respectively. If the probability of adsorption for collector ions on a kind of positive site of the mineral surface is written as θ_x , the following equation is obtained:

$$\frac{\theta_0}{\theta_x} q_x = \frac{Q_x}{N_x}, \quad (1)$$

where θ_0 , q_x , Q_x , and N_x represent the probability for a vacant reaction site, the Boltzman factor of the reversible adsorption work of X^- onto a vacant site, the partition function of X^- , and the concentration of X^- , respectively. Now, put $q_x/Q_x = K_x$, and then Eq. (1) becomes,

$$K_x = \theta_x/\theta_0 N_x. \quad (2)$$

The above equation corresponds to the adsorption equilibrium equation by Cook et al²⁾ and the constant, K_x , is regarded as a measure indicating the adsorption

property of X^- on a mineral surface.

When a depressant ion, D^- , adsorbs onto the same kind of reaction site as X^- does, the following equation is also obtained:

$$K_D = \theta_D / \theta_0 N_D, \quad (3)$$

where the notation with index D gives the same meaning for the depressant as that with X for the collector.

An equation (4) is also derived from the probability relation,

$$\theta_0 + \theta_D + \theta_X = 1 \quad (4)$$

Combining Eqs. (2), (3), and (4), we get,

$$\frac{\theta_X}{1 - \theta_X - \theta_D} = K_X \cdot N_X, \quad (5)$$

$$\frac{\theta_D}{1 - \theta_X - \theta_D} = K_D \cdot N_D. \quad (6)$$

On the other hand, similar equations for another kind of reaction site on the same mineral surface can be obtained as follows;

$$\theta_0' + \theta_D' + \theta_{X'} = 1, \quad (4)'$$

$$\frac{\theta_{X'}}{1 - \theta_{X'} - \theta_D'} = K_X \cdot N_X, \quad (5)'$$

$$\frac{\theta_D'}{1 - \theta_{X'} - \theta_D'} = K_D \cdot N_D. \quad (6)'$$

where a prime sign means a different reaction site.

Sutherland³⁾ derived the theoretical equation of collector-depressant equilibrium for the critical flotation condition on the basis of the constant coverage ratio of collector ions to depressant ones on the surface of a mineral, thus finding the above assumption reasonable. The authors extend this idea to the collector-depressant equilibria on the mineral surface having two kinds of reaction sites. That is, the following relation for the critical flotation condition of the mineral is assumed:

$$\frac{\theta_X + \theta_{X'}}{\theta_D + \theta_D'} = C \quad (\text{constant}). \quad (7)$$

From Eqs. (5) and (6) the following equations can be obtained:

$$\theta_D = \frac{K_D N_D}{1 + K_X N_X + K_D N_D}, \quad (8)$$

$$\theta_X = \frac{K_X N_X}{1 + K_X N_X + K_D N_D}. \quad (9)$$

Similarly the following equations are derived from Eqs. (5)' and (6)',

$$\theta_{D'} = \frac{K_D' N_D}{1 + K_X' N_X + K_D' N_D}, \quad (8)'$$

$$\theta_{X'} = \frac{K_X' N_X}{1 + K_X' N_X + K_D' N_D}. \quad (9)'$$

Substituting these in Eq. (7), we obtain:

$$\frac{N_X}{N_D} \left\{ \frac{K_X(1 + K_X' N_X + K_D' N_D) + K_X'(1 + K_X N_X + K_D N_D)}{K_D(1 + K_X' N_X + K_D' N_D) + K_D'(1 + K_X N_X + K_D N_D)} \right\} = C. \quad (10)$$

Put

$$m = 1 + K_X N_X + K_D N_D,$$

$$n = 1 + K_X' N_X + K_D' N_D.$$

Then, Eq. (10) leads to,

$$\frac{N_X}{N_D} = C \left(\frac{nK_D + mK_D'}{nK_X + mK_X'} \right). \quad (11)$$

In both cases where the concentrations of collector or depressant ions are very dilute, and where n is nearly equal to m without regard to the concentration of collector or depressant, Eq. (11) is rewritten as

$$\frac{N_X}{N_D} = C \left(\frac{K_D + K_D'}{K_X + K_X'} \right). \quad (12)$$

The above equation indicates the well known Barsky relation.

Considering a depressant ion, D^- , as a hydroxyl ion, OH^- , and then using the ion product of water, K_W ;

$$N_{OH} \cdot N_H = K_W,$$

equation (12) can be expressed in the following form;

$$\log N_X = \log C \left(\frac{K_{OH} + K_{OH}'}{K_X + K_X'} \right) K_W + \text{pH} = \log A + \text{pH}, \quad (13)$$

where

$$A = C \left(\frac{K_{OH} + K_{OH}'}{K_X + K_X'} \right) K_W.$$

The critical flotation condition represented by the logarithm of the collector concentration against the pH value gives a linear line whose location depends on the magnitude of A in Eq. (13). It shifts to a more alkaline range as the value of A becomes smaller; while it shifts to a more acidic range as the value of A becomes larger. As can be understood from Eq. (12) the value of A is dependent on all values of K_X , K_X' , K_D , and K_D' . As mentioned in the earlier part of this section,

K_X and K_X' show the adsorption property of the collector ion, X^- , onto two kinds of positive sites, respectively. Similarly, either K_D or K_D' indicates the adsorption property of the depressant ion, D^- , onto each adsorption site of the two kinds. The adsorbability of the collector or the depressant ion onto the adsorption site of a mineral is not necessarily the same in all processes, since it depends on the nature of the mineral.

If the value of A is governed by either K_X and K_D or K_X' and K_D' , the collector and depressant ions adsorb competitively onto the same kind of reaction site; and consequently the competitive adsorption determines the critical flotation condition for the mineral. On the other hand, if the value of A is mainly governed by either K_X and K_D' or K_X' and K_D , the collector and depressant adsorption onto the separate kinds of reaction sites leads to the determination of the critical flotation condition.

Accordingly, in order to discuss the critical flotation condition of a mineral having two kinds of reaction sites, it is very important to know the reaction site with which collector ions or depressant ions predominantly react.

3. Considerations from the chemical affinities between mineral surface and collector or depressant ions

In the previous section, the collector-depressant equilibrium for the mineral composed of two kinds of reaction sites was discussed by means of statistical mechanics. As a consequence, it is important for the determination of the critical flotation condition to know with which reaction site the collector and depressant ions predominantly have a strong affinity. Also it should be known that the collector and depressant adsorption influential for the flotation condition may occur either at the same kind of reaction sites in one case or at the separate kinds of reaction sites in another case.

The authors already demonstrated that the critical flotation curves for some sulfide minerals having one kind of positive site (MS) coincided very well with those obtained from the chemical affinity of the reaction between a collector ion or a depressant ion and a sulfide mineral⁴⁾.

This idea can be extended to a mineral having two kinds of positive sites. Accordingly, this kind of critical flotation condition is investigated in this section by the thermodynamical viewpoint of the chemical affinity of the reaction between a xanthate ion, X^- , or a hydroxyl ion, OH^- , and a metal atom (positive site) on the mineral surface.

Chalcopyrite ($CuFeS_2$) was chosen as a typical sulfide mineral of double positive sites. Assume that the two kinds of positive sites on the chalcopyrite

surface are those originated from CuS and FeS. Each chemical affinity of a xanthate ion and a hydroxyl ion to CuS and FeS is calculated by Eqs. (14) and (15), as it was described in the previous paper.

The chemical affinity of a xanthate ion to the positive site, ΔF_{MX_2} , is:

$$\Delta F_{MX_2} = RT \ln 10 \{ \log L_{MX_2} - \log [M^{++}] - 2 \log [X^-] \}; \quad (14)$$

and the chemical affinity of a hydroxyl ion to the same site, $\Delta F_{M(OH)_2}$, is;

$$\Delta F_{M(OH)_2} = RT \ln 10 \{ \log L_{M(OH)_2} - \log [M^{++}] - 2 \log [OH^-] \}, \quad (15)$$

where L_{MX_2} and $L_{M(OH)_2}$ are solubility products of metal xanthate and metal hydroxide, respectively, each value being 6.3×10^{-25} ⁵⁾ and 1.6×10^{-19} ⁶⁾ for Cu^{++} and 8×10^{-8} ⁷⁾ and 1.8×10^{-15} ⁶⁾ for Fe^{++} . The concentration of metal ion, M^{++} , should be the activity of M^{++} at the solid-water interface. Since the activity has not been determined and is difficult to estimate at present, the metal ion concentration in equilibrium with the sulfide when immersed in water was employed for the $[M^{++}]$ in Eqs. (14) and (15), as previously reported.⁴⁾

Then, the following equations can be obtained,

$$[M^{++}] = \sqrt{k_{MS}} \left\{ 1 + \frac{[H^+]}{k_1} + \frac{[H^+]^2}{k_1 \cdot k_2} \right\}^{1/2}, \quad (16)$$

where

$$\begin{aligned} k_{MS} &= [M^{++}] [S^{--}] \\ k_1 &= [S^{--}] [H^+] / [HS^-], \\ k_2 &= [HS^-] [H^+] / [H_2S]. \end{aligned}$$

Figure 1 gives the metal ion concentration, M^{++} , of CuS and FeS as the function of pH values.

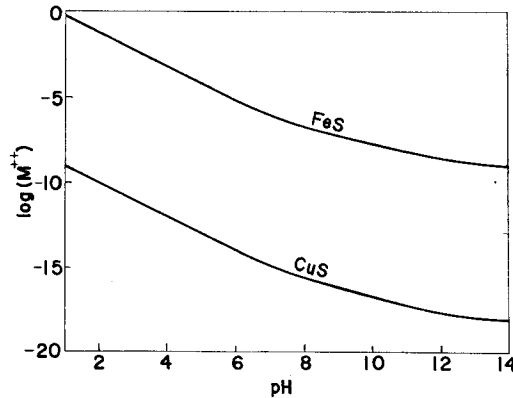


Fig. 1. pH dependence of the metal ion concentration in water saturated with CuS and FeS.

As for xanthate ions, Eq. (17) can be obtained,

$$C_x = [HX] + [X^-] \quad , \quad (17)$$

$$[X^-] = C_x \left\{ 1 + \frac{[H^+]}{k_{HX}} \right\}^{-1} ,$$

where C_x is the addition of xanthate and k_{HX} is represented as

$$k_{HX} = [H^+][X^-]/[HX] .$$

In the case of ethyl xanthate, 10^{-3} is used for k_{HX} .⁸⁾

The free energy changes of the ion-positive site reactions, namely, the reactions of xanthate ion-Cu site, xanthate ion-Fe site, hydroxyl ion-Cu site, and hydroxyl ion-Fe site, were estimated as the function of pH values, using Eqs. (14), (15), (16), and (17), as shown in Figure 2.

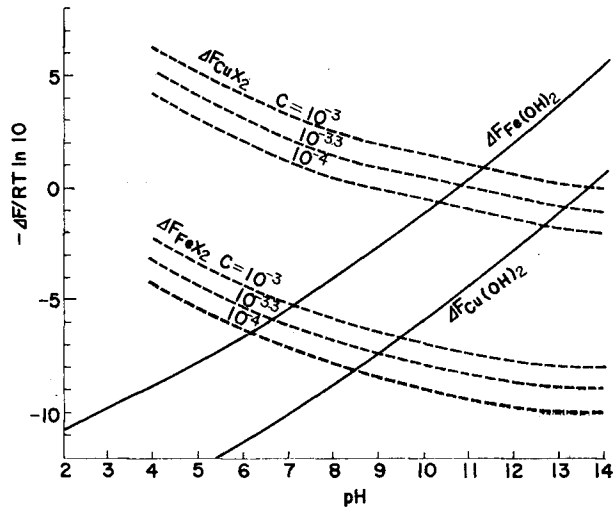


Fig. 2. Chemical affinities of the xanthate ion-CuS site, xanthate ion-FeS site, hydroxyl ion-CuS site, and hydroxyl ion-FeS site reactions with variation of pH value.

In Figure 2, ΔF_{MX_2} is shown where the xanthate addition, C_x , is 10^{-3} , $10^{-3.3}$, and 10^{-4} , respectively. Concerning the reaction of the xanthate ion to the positive sites, it is noted from Figure 2 that the chemical affinity of the xanthate ion to CuS is much greater than that to FeS. On the other hand, the relation is inverse for the hydroxyl ion, namely, the chemical affinity of the hydroxyl ion to FeS is larger than that to CuS. Therefore, it is expected that sulfide minerals having two kinds of reaction sites, like chalcopyrite, are quite different in their flotation behavior from those having only one kind of reaction site, like covellite, because

the kind of positive site to which collector ions and depressant ions mainly react might be either the same or different.

The critical flotation conditions of the two single positive site sulfides, CuS and FeS, can be given from the thermodynamical viewpoint of the chemical affinity by the following relations,

$$\Delta F_{\text{CuX}_2} = \Delta F_{\text{Cu(OH)}_2} \quad \text{and} \quad \Delta F_{\text{FeX}_2} = \Delta F_{\text{Fe(OH)}_2},$$

as it has already been reported for sulfide minerals of a single positive site. As to the critical flotation condition for chalcopyrite, it should be reasonable to consider that the adsorption of the xanthate ion is due to the chemical affinity of the formation reaction of copper xanthate while the adsorption by the hydroxyl ion is due to that of ferric hydroxide. Accordingly, the critical pH curve for CuFeS₂, shown in Figure 3, was determined by the following relation,

$$\Delta F_{\text{CuX}_2} = \Delta F_{\text{Fe(OH)}_2}.$$

Figure 3 shows the critical flotation curves obtained thermodynamically for FeS, CuS, and CuFeS₂, together with some of the flotation-non-flotation conditions for chalcopyrite and covelline which have been reported so far.

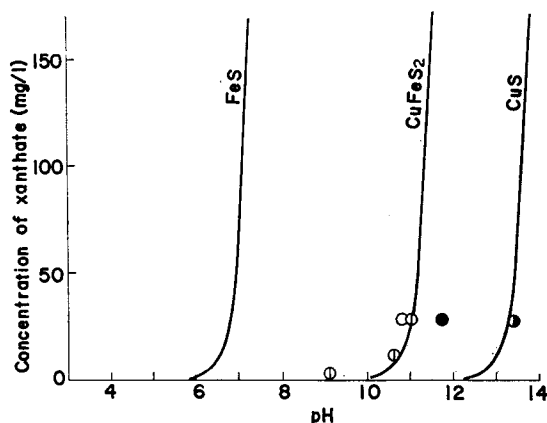


Fig. 3. Critical flotation conditions of CuFeS₂, FeS, and CuS.
 — from the the thermodynamical treatment.
 ○ from the data of I.W. Wark and A.B. Cox for chalcopyrite (35°C).¹⁰⁾
 ● from the data of I.W. Wark and A.B. Cox for chalcopyrite.¹⁰⁾ (Room temperature)
 ⊙ from the data of S. Mukai and Y. Kitae for chalcopyrite.⁹⁾
 ▲ from the data of I.W. Wark and A.B. Cox for covelline.¹⁰⁾

It is clearly observed from Figure 3 that the critical flotation curve for CuFeS₂

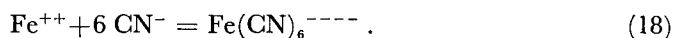
is located midway between those of FeS and CuS, and that it approximately agrees with the actual flotation conditions of chalcopyrite obtained experimentally.

Therefore, concerning the flotation characteristics of chalcopyrite, it can be said from the above fact that the collecting phenomenon for it should be closely related to the chemical affinity between the xanthate ion and the copper site at the mineral surface, while the chemical affinity between the hydroxyl ion and the iron site plays an important role in the depressing phenomenon.

It has been known that the depression of chalcopyrite by such ions as CN^- , SO_3^- , HS^- , and S^{--} , besides OH^- , is much different from that of covellite. Accordingly, the depression of chalcopyrite by a cyanide ion was taken up to discuss on the basis of the chemical affinity viewpoint in which the collecting phenomena by the xanthate ion are due to the chemical affinity of the formation reaction of copper xanthate while the depression by the cyanide ion is due to the chemical affinity of the formation reaction of Fe-CN complex compound.

In water the cyanide ion, CN^- , reacts with the ferrous ion, Fe^{++} , to form a very stable complex formulated as $\text{Fe}(\text{CN})_6^{--}$.

The formation reaction is:



Consider that the chemical affinity of the reaction (18), $\Delta F_{\text{Fe}(\text{CN})_6}$, is important for the depression of chalcopyrite by the cyanide ion. The affinity, $\Delta F_{\text{Fe}(\text{CN})_6}$, is expressed by the following equation:

$$\Delta F_{\text{Fe}(\text{CN})_6} = RT \ln 10 \{ \log K_{\text{Fe}(\text{CN})_6} - \log [\text{Fe}^{++}] - 6 \log [\text{CN}^-] \} \quad (19)$$

where $K_{\text{Fe}(\text{CN})_6}$ is the equilibrium constant for the formation reaction (18) and is given its value as $10^{-35.11}$.

The concentration of the cyanide ion, CN^- , is expressed in terms of the cyanide addition, C_{CN} , and hydrogen concentration, H^+ ;

$$\begin{aligned} C_{\text{CN}} &= [\text{HCN}] + [\text{CN}^-], \\ [\text{CN}^-] &= C_{\text{CN}} \left/ \left\{ 1 + \frac{[\text{H}^+]}{K_{\text{HCN}}} \right\} \right., \end{aligned} \quad (20)$$

where

$$K_{\text{HCN}} = [\text{H}^+][\text{CN}^-]/[\text{HCN}] = 10^{-9.3}.$$

For the concentration of the ferrous ion, Fe^{++} , in Eq. (19), values calculated by Eq. (16) were used, and then the chemical affinity of the reaction (18) was estimated as the function of pH values as shown in Figure 4. In Figure 4, $\Delta F_{\text{Fe}(\text{CN})_6}$

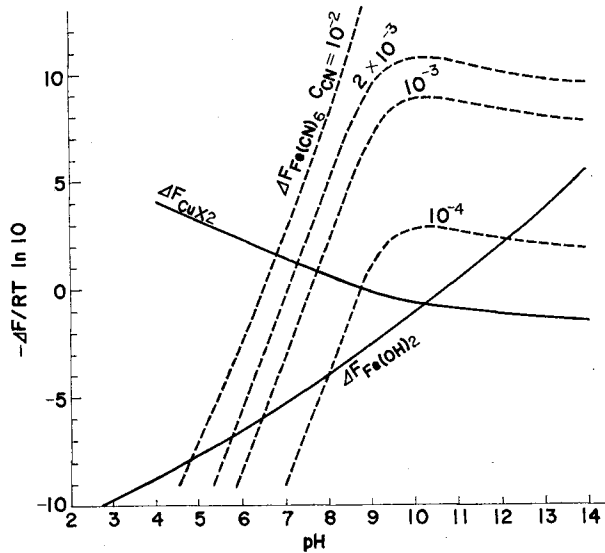
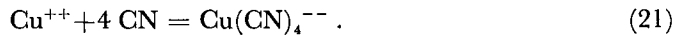


Fig. 4. Chemical affinities of the xanthate ion-CuS site (at 1.5×10^{-4} mol/l xanthate concentration), hydroxyl ion-FeS site, and cyanide ion-FeS site reactions with variation of pH value.

is indicated when $C_{CN} = 10^{-2}$, 2×10^{-3} , 10^{-3} , and 10^{-4} , together with ΔF_{CuX_2} at 1.5×10^{-4} mol/l (25 mg/l) xanthate concentration and $\Delta F_{Cu(OH)_2}$.

On the other hand it was thought that the depression of covellite (CuS) by the cyanide ion is closely concerned with the chemical affinity of the formation reaction of a Cu-CN complex, simultaneously considering the chemical affinity of the copper xanthate formation for the collection of covellite by the xanthate ion. As a cupric-cyanide complex compound, a stable complex of $Cu(CN)_4^{--}$ is considered.

The formation reaction is,



The affinity, $\Delta F_{Cu(CN)_4}$, is expressed by the following equation,

$$\Delta F_{Cu(CN)_4} = RT \ln 10 \{ \log K_{Cu(CN)_4} - \log [Cu^{++}] - 4 \log [CN^-] \}, \quad (22)$$

where $K_{Cu(CN)_4}$ is the equilibrium constant for the complex formation reaction (21) and is also given its value as $10^{-27.3}$.¹²⁾ Figure 5 shows three kinds of chemical affinities calculated by Eqs. (14), (15), and (22), that is, ΔF_{CuX_2} at 1.5×10^{-4} mol/l xanthate concentration (line I), $\Delta F_{Cu(OH)_2}$ (line II), and $\Delta F_{Cu(CN)_4}$ at cyanide additions of 10^{-2} , 6×10^{-3} , 4×10^{-3} , 2×10^{-3} , and 10^{-3} , respectively.

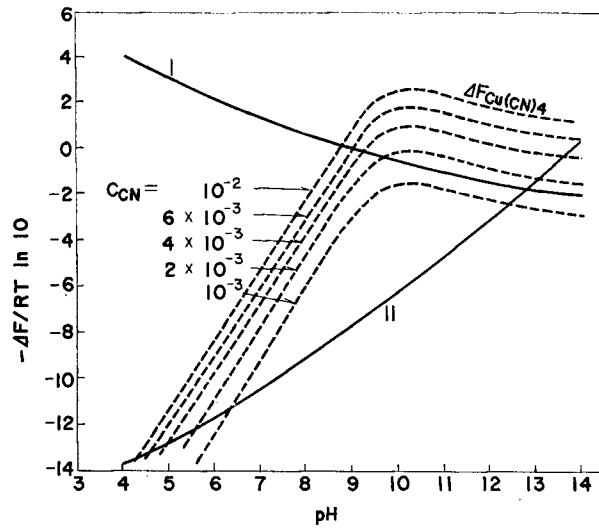


Fig. 5. Chemical affinities of the xanthate ion-CuS site (at 1.5×10^{-4} mol/l xanthate concentration), hydroxyl ion-CuS site, and cyanide ion-CuS site reactions with variation of pH value.

Figures 4 and 5 give a clear picture of which species predominantly reacts with a solid, CuFeS_2 or CuS in the aqueous system including a xanthate ion and a cyanide ion on the thermodynamical viewpoint. Each chemical species has its own predominant pH range in the adsorption process on CuFeS_2 or CuS . As in

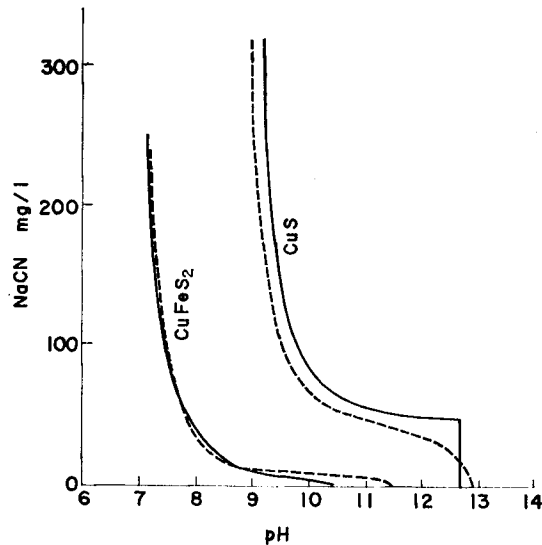


Fig. 6. Critical flotation condition of chalcopyrite and covellite
 --- from the data of I.W. Wark and A.B. Cox.
 — from the thermodynamical treatment.

the case of the depression of minerals by the hydroxyl ion, the critical flotation condition for the depression of CuFeS_2 or CuS by the cyanide ion can be obtained thermodynamically from the relations, $\Delta F_{\text{CuX}_2} = \Delta F_{\text{Fe}(\text{CN})_6}$ for CuFeS_2 and $\Delta F_{\text{CuX}_2} = \Delta F_{\text{Cu}(\text{CN})_4}$ for CuS . The results are shown in Figure 6, together with the critical contact curve for chalcopyrite and covellite obtained by Wark and Cox¹³⁾.

It is recognized from Figure 8 that the critical conditions for the flotation-non-flotation of chalcopyrite and covellite coincide fairly well with those of the above considerations on the chemical affinity. Accordingly, the critical flotation condition of CuS , one of the minerals of single positive site, is explained by the competitive adsorption between a collector ion and a depressant ion onto the same positive site. On the other hand, it must be said that the flotation-non-flotation condition of CuFeS_2 , one of minerals having two kind of positive site, can be determined by considering the collector adsorption on the Cu site and the depressant adsorption on the Fe site. Furthermore, it can be said that the collector or depressant adsorption onto a reaction site is closely concerned with the chemical affinity of the formation reaction of a conceivable compound between the collector or depressant ion and the reaction site.

4. Conclusion

The critical flotation condition for a sulfide mineral having two kinds of positive sites was discussed from the viewpoint of the competitive adsorption of anionic collectors and depressants by means of statistical mechanics and chemical thermodynamics.

On the basis of the statistical mechanics as to the collector-depressant equilibria, the familiar Barsky relation was derived for the double positive site mineral. The Barsky constant can be dependent on all of the collector and depressant adsorptions onto each kind of reaction site on the mineral surface according to their adsorption property.

In the chemical thermodynamics investigation, the chalcopyrite (CuFeS_2)-xanthate-hydroxyl ion system was considered at first. The chemical affinities of the surface reaction of the xanthate ion and the hydroxyl ion onto the positive sites of CuS and FeS , respectively, were calculated. Thermodynamical data for the system was used to determine which species predominantly reacts on the mineral. Consequently, it was ascertained that the depressing action of the hydroxyl ion for chalcopyrite was mainly connected with the adsorption of the hydroxyl ion onto the positive site due to FeS , while the collecting mechanism of the xanthate ion for the same mineral was closely related to the adsorption of the xanthate

ion onto the positive site due to CuS. The critical flotation pH values for chalcopyrite can be theoretically obtained by considering the chemical affinities of both xanthate and hydroxyl ion adsorption processes.

The chalcopyrite (CuFeS_2)-xanthate-cyanide ion and hydroxyl ion system was also considered in the same manner as in the system including the hydroxyl ion alone as depressant. It was recognized that the flotation-non-flotation condition of chalcopyrite can be determined by considering the xanthate adsorption on the positive site due to CuS and the cyanide ion adsorption on the one due to FeS.

Furthermore, the collector or depressant adsorption onto a reaction site was closely connected with the chemical affinity of the formation reaction of a possible stable compound between the collector or depressant ion and the reaction site.

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