Chapter 5

Studies of Activation of Sphalerite by Copper at Near Neutral pH

5.1. Abstract

The effect of potential on copper activation and the mechanism of xanthate adsorption on sphalerite at near neutral pH were studied using electrochemical and controlled-potential contact angle measurement techniques. Voltammetric studies conducted using carbon matrix composite (CMC) electrode show that ZnS was activated by copper at neutral pH and the activation product was identified as copper sulfide species. Voltammetric experiments conducted in xanthate solution at pH 6.8 using copper-activated CMC:ZnS electrode show that xanthate indeed adsorbs on Cu:ZnS. However, controlled potential contact angle measurements conducted on copper-activated surface conducting SC:ZnS electrode in xanthate solution at pH 6.8 show that although xanthate adsorbs, the mineral surface is hydrophilic. Adsorption mechanisms were proposed. A practical solution was suggested for improving the recovery of sphalerite flotation at near neutral pH.

5.2. Introduction

It is well accepted that the flotation of sphalerite is sensitive to pH. It was observed that although the recovery of zinc concentrate is good at acidic pH, the selectivity is poor. Hence, sphalerite flotation is usually carried out at alkaline pH. On the other hand, flotation of ZnS at near neutral pH is avoided due to the poor recovery at this solution condition. The poor flotation response at neutral pH was usually attributed to the deficiency of activator or xanthate or both. For example, Sutherland and Wark (1939; 1955) showed that there is a narrow region of pH where activated sphalerite exhibits lower water contact angles than in acidic and basic solutions. Steininger et al. (1968) later conducted flotation test and demonstrated that sphalerite flotation was depressed in near neutral pH range (Chapter 1). In both studies, the researchers proposed
that the formation of copper xanthate precipitates at neutral pH depletes the copper as well as xanthate from the solution, and hence, inhibits the flotation.

Laskowski and his co-workers (Girczys et al., 1972; Laskowski et al., 1997) conducted zeta potential measurement in ZnS-Cu system and found that at neutral pH, the zeta potential became positive, which was attributed to the adsorption of Cu(OH)$^+$ ions, whose concentration is the highest at near neutral pH. Based on this observation, they suggested that only when the adsorbed Cu(OH)$^+$ ions transferred with time to a ‘flotation active’ product such as CuS on the sphalerite surface, effective flotation can occur. For this reason, a long conditioning time is required at neutral pH to achieve better recovery (Laskowski et. al, 1997).

Electrochemical study conducted using CMC and SC electrode showed (Chapter 2) that the activation product behaves similar to copper sulfide. The voltammogram of CMC:ZnS electrode conditioned in cupric solution at near neutral pH exhibit electrochemical characteristic similar to that at acidic and alkaline pHs (Figure 2-7), indicating that the activation of sphalerite did occur at near neutral pH.

It is the objectives of this chapter to study the mechanism of activation of sphalerite by copper; the effect of activating potential on copper uptake; the mechanism and hydrophobicity of xanthate adsorption on activated ZnS; and to seek the solution to improve the flotation recovery of zinc concentrate at near neutral pH.

5.3. Experimental

5.3.a. Materials and Experimental Procedures

CMC:ZnS electrode and SC:ZnS electrode were used in the present investigation. The mineral samples and the procedures of fabricating the electrodes are the same as described in Chapters 2 and 3. The instrumentation and experimental procedures for activation and voltammetry are the same as described in Chapter 3.
Near neutral pH solutions were prepared either by addition of NaOH and HCl or by using pH 6.8 buffer solutions (0.05 M KH$_2$PO$_4$ - 0.025 M NaOH). Xanthate was prepared by dissolving purified potassium ethyl xanthate (KEX) or potassium amyl xanthate (KAX) in deionized water. The purification of xanthate includes dissolving commercial grade xanthate in acetone, and reprecipitated by petroleum ether following an established technique (Rao, 1971). These procedures were repeated for three times.

Contact angle measurements were conducted to study the hydrophobicity of activated sphalerite in xanthate solution at pH 6.8. The measurements were conducted by generating a small nitrogen bubble on the surface conducting electrode and the contact angle was measured through the aqueous phase using captive bubble technique. The electrodes were renewed using the procedures described in Chapters 2 and 3.

5.4. Results and Discussion

5.4.a. Open Circuit Activation

Rest Potential Measurement: Figure 5.1 shows the rest potential measurements conducted on a CMC:ZnS electrode as a function of activating time. Also shown for comparison are the rest potentials of covellite, chalcocite and copper electrodes in a deoxygenated Cu(NO$_3$)$_2$ solution (10$^{-4}$ M) at pH 6.8. All the electrodes were wet-polished with 600-grit silicon carbide paper before being inserted to the solution. It can be seen that the rest potential of the CMC:ZnS electrode increases sharply upon the addition of the Cu(NO$_3$)$_2$ stock solution, indicating that a new conducting phase (copper sulfide) has been formed on the surface almost instantaneously upon contact with copper solution. The potential reaches a plateau value of ~0.31 V after approximately 2 minute. This potential is close to the rest potential of the covellite electrode, suggesting that the new phase (activation product) is probably CuS, rather than the non-conductive Cu(OH)$^+$, as suggested by Laskawski, et al. The sharp increase in potential upon addition of cupric ions also indicates the fast kinetics of the activation reaction.
Figure 5-1. Rest potential measurement of the CMC:ZnS electrode immersed in a $10^{-4}$ M Cu(NO$_3$)$_2$ solution at pH 6.8.

**Voltammetry:** A CMC:ZnS electrode was activated in a deoxygenated $10^{-4}$ M Cu(NO$_3$)$_2$ solution. After 10 minutes of activation, the electrode was removed from the solution, rinsed with deoxygenated distilled water, and placed in a deoxygenated pH 6.8 buffer solution (copper free) for voltammetry to study the surface product. Figure 5.2(a) shows the first sweep voltammogram obtained by initiating the sweep from the rest potential (~0.1 V) to the positive-going direction. The rest potential was determined using the same procedures described in chapter 2 and 3. A well-defined anodic wave $A_1$ begins at approximately 0.25 V, which may be due to Reaction (2.1), i.e.,

$$
CuS = Cu^{2+} + S^o + 2e
$$

(2.1)

whose thermodynamic potential ($E_h$) is 0.28 V at $[Cu^{2+}] = 10^{-10}$ M; and Reaction (3.1),

$$
CuS + H_2O → CuO + 2H^+ + S^o + 2e
$$

(3.1)

whose thermodynamic potential ($E_h$) is 0.41 V at pH 6.8. The concentration of the cupric ions
was determined to be $10^{10}$ M based on the rest potential of the copper electrode (Figure 5.1). The formation of polysulfide species is also possible through Reaction (3.2), namely:

$$n\text{CuS} + (n - 1)\text{H}_2\text{O} \rightarrow \text{CuS}_n + (n - 1)\text{CuO} + 2(n - 1)\text{H}^+ + 2(n - 1)\text{e}$$  \hspace{1cm} (3.2)

Figure 5.2(a) also shows two cathodic waves $C_1$ and $C_2$ after switching the sweep direction at 0.55 V. These may be the reverse of Reactions (2.1), (3.1) and (3.2), respectively since at pH 6.8, CuO formed is not likely to dissolve and diffuse into the bulk solution. The agreement between experimental observation and thermodynamic calculation suggests that the activation product formed at neutral pH is copper sulfide.

Figure 5.2(b) shows the first sweep voltammogram of a copper-activated CMC:ZnS electrode obtained by beginning the sweep to the negative-going direction from the rest potential. A cathodic peak $C_3$ begins at the potential of approximately -0.1 V. This potential is close to the thermodynamic potential for Reaction (3.3), whose $E_h=-0.16$ V at pH 6.8 and $[\text{HS}^-]=10^{-7}$ M. The onset potential for $C_3$ is substantially higher than the thermodynamic potential ($E_h=-0.5$ V) for the reduction of Cu$_2$S to Cu$^0$. Therefore, the activation product formed on at pH 6.8 is more likely to be CuS rather than Cu$_2$S. After switching the scan direction at -0.4 V, a very small anodic peak $A_3$ appeared, possibly the reverse of Reaction (3.3), i.e.:

$$2\text{CuS} + \text{H}^+ + 2\text{e} \rightarrow \text{Cu}_2\text{S} + \text{HS}^-$$  \hspace{1cm} (3.3)

When further increase the potential, a large anodic peak $A_1$ appeared, most probably the oxidation of CuS formed above via Reaction (3.1).

$$\text{CuS} + \text{H}_2\text{O} \rightarrow \text{CuO} + 2\text{H}^+ + \text{S}^0 + 2\text{e}$$  \hspace{1cm} (3.1)
Figure 5.2(a). Voltammogram of CMC:ZnS electrode after activating in deoxygenated pH 6.8 $10^{-3}$ M Cu(NO$_3$)$_2$ solution for 10 minutes. Sweep rate 25 mV/s. First sweep positive-going.

Figure 5-2(b). Voltammogram of CMC:ZnS electrode after activating in deoxygenated pH 6.8 $10^{-3}$ M Cu(NO$_3$)$_2$ solution for 10 minutes. Sweep rate 25 mV/s. First sweep negative-going.
On the return scan of Figure 5.2(b), cathodic peaks C_1 and C_2, same as shown in Figure 5.2(a), appeared, representing the reverse of Reactions (3.1) (3.2) and (3.3).

Figure 5-3. Voltammogram of CMC:ZnS electrode after activating in pH 6.8 10^{-4} M Cu(NO_3)_2 solution at 0.18 V for 10 minutes. Sweep rate 25 mV/s.

5.4.b. Controlled Potential Activation

Figure 5-3 shows the voltammogram of a CMC:ZnS which was activated in pH 6.8 10^{-4} M Cu(NO_3)_2 solution for 10 minutes while holding the electrode at 0.18 V. Note that the activating potential is lower than the rest potential of the sphalerite activated at open circuit (0.31 V), but is higher than that of Cu^0 (see Figure 5.1). After activation, the electrode was inserted into pH 6.8 buffer solution (copper free) to conduct voltammetric experiment. The initial scan was made toward the cathodic direction from the rest potential. To avoid the formation of Cu^0, the scan was limited to -0.4 V. As can be seen in this figure, the initial scan showed no indication of C_3, suggesting that the activation product formed at 0.18 V is Cu_2S rather than CuS. This result is similar to that observed at pH 9.2 (Chapter 3). After switching the scan direction at -0.4 V, a large anodic wave A_1 is observed. This anodic peak, which represents the copper uptake during activation, is much larger compared to that activated at open circuit potential.
This indicates that the copper uptake increases when activating at lower potential.

It is significant to notice that there are three distinguishable cathodic peaks on the return sweep. The reactions related to the anodic wave A_1 may be:

\[ \text{Cu}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{CuS} + \text{CuO} + 2\text{H}^+ + 2\text{e} \]  

(5.1)

whose thermodynamic potential (E_h) is 0.30 V at pH 6.8; and Reaction (3.6), whose thermodynamic potential (E_h) is between 0.18 and 0.28 V at pH 6.8 (Young et al., 1985). The reverse of reactions (5.1) and (3.6) represent the cathodic peaks C_1 to C_3.

The results obtained above suggest that activating sphalerite at neutral pH forms a CuS-like product at open circuit. However, activation at potentials below the open circuit potential results in the formation of Cu_2S-like species. The composition of the activating product changes with activating potential.

It needs to be mentioned that the above conclusion is not opposed to the experimental observation made by Laskowski, et al. (1997). These researchers conducted electrokinetic studies on copper-activated sphalerite and observed positive zeta potential in the neutral pH range after conditioning in cupric solution for 5 minutes. When the activation time was increased to 15 hours, however, the zeta potential becomes negative at neutral pH range, and the electrokinetic behavior is similar to chalcocite. They attributed the initial positive zeta potential to the adsorption of Cu(OH)_2 on ZnS surface, forming a “flotation inactive” product when the conditioning time is short. However, they suggest that this surface copper hydroxy layer deposited on the ZnS surface is thermodynamically unstable and is converted with time into a layer of copper sulfides, whose zeta potential is negative at neutral pH. Based on this observation, they concluded that at neutral pH, a longer activation time is required to achieve good flotation recovery. Thermodynamic calculations show that, at neutral pH, where Cu(OH)_2 reaches maximum concentration, the following reaction:

\[ \text{ZnS} + \text{Cu(OH)}^+ \rightarrow \text{CuS} + \text{Zn(OH)}^+ \]  

(5.2)
(ΔG° = -68.5 Kcal/mol) is feasible. Hence, CuS should form as a result of activation. In fact, according to the chronopotentiometric experiments (Figure 5.1), the formation of a conducting activation product, possibly CuS, occurs almost instantaneously upon addition of cupric ions. However, at neutral pH, it is impossible to detect copper hydroxy species by electrochemical methods using CMC:ZnS electrode. Hence, it is possible that both CuS and Cu(OH)⁺ coexisted on the mineral surface, some the Cu(OH)⁺ transferred into CuS via reaction (5.2) instantly, while some may still adsorb on the mineral surface, and will convert slowly to CuS with longer activation time. This may explain the fast kinetics of the activation observed by chronopotentiometry, as well as the electrokinetic behavior of ZnS in copper solution observed by Laskowski et al. Moreover, it provided a new possible mechanism on the poor flotation response since the Cu-OH species is hydrophilic in nature. This will be discuss later.

5.4.c. Xanthate Adsorption on Copper-Activated ZnS

Sutherland and Steininger suggested that the formation of copper xanthate in the presence of excess copper is responsible for the low contact angle or recovery since the xanthate is depleted from the solution. To explore the possibility of xanthate adsorption on copper-activated sphalerite surface, voltammetric experiments were conducted in pH 6.8 10⁻⁴ M KEX solution using copper-activated CMC:ZnS electrode. Prior to the experiment, the surface of the electrode was wet-polished on 600-grit silicon carbide paper, rinsed with distilled water, and activated in pH 6.8 10⁻⁴ M Cu(NO₃)₂ solution at open circuit for 30 minutes. While holding the potential of the electrode at -0.4 V (to avoid xanthate adsorption), the activated CMC:ZnS electrode was immediately placed into the xanthate solution to conduct voltammetric experiment.

Figure 5.4 shows the voltammogram of the copper-activated CMC:ZnS electrode in pH 6.8 10⁻⁴ M KEX solution (curve A). Because the thermodynamical data of metastable activation and copper xanthate species are not available, it is impossible to calculate the electrochemical potentials of the xanthate adsorption reactions for identification of the surface product. Hence, it is very important to compare the electrochemical behavior of activated CMC:ZnS electrode in xantheae solution with that of activated CMC:ZnS electrode in inert electrolyte solution to obtain adsorption information.
Also shown in Figure 5-4 are the voltammograms of an unactivated CMC:ZnS electrode in the same xanthate solution (curve B), and a copper-activated CMC:ZnS electrode obtained in copper-free, xanthate-free pH 6.8 solution (curve C). Compare curve (A) with curve (C), there are three different features. First, the anodic peak at ~0.38 V is much smaller in curve (A), possibly due to the formation of copper xanthate, covering the copper sulfide layer, hence inhibits the oxidation of the activation product through Reaction (3.1). Second, a new wave appeared in curve (A) at ~0.0 V, possibly due to the formation of chemisorbed copper xanthate species. These features are similar to the voltammetry of copper sulfide in xanthate solution (Young, 1988). Third, a big anodic peak appeared at ~0.6 V, possibly represents the formation of dixanthagen, both on the activated ZnS surface and the carbon surface. On the other hand, no anodic peak was observed between -0.4 V to 0.3 V when voltammetric experiment was conducted in the same xanthate solution using unactivated CMC:ZnS electrode (curve B). A small anodic wave started to appear at ~0.3 V, most probably due to the formation of dixanthagen on carbon. These distinguishing features in curve (A) strongly suggest that xanthate adsorption did occur on copper-activated sphalerite surface, and the composition of the xanthate species is dependent on the electrochemical potential.

Figure 5-4. Voltammograms of copper-activated CMC:ZnS electrode (curve a) and CMC:ZnS electrode (curve b) in pH 6.8 $10^{-3}$ M KEX solution. Curve c: voltammogram of a copper activated CMC:ZnS electrode in pH 6.8 buffer solution. Sweep rate 25 mV/s.
To study the xanthate adsorption on activated sphalerite and the hydrophobicity of the mineral surface, controlled potential contact angle measurements were conducted in $10^{-4}$ M KEX solutions at pH 6.8 using SC:ZnS electrode. Prior to the contact angle measurement, the SC:ZnS electrode was cleaned in chloroform to remove organic compounds, and then treated with a $10^{-3}$ M sodium cyanide solution to remove copper ions, or any other activating metallic ions, that might be present on the surface. The electrode was wet-polished on 600-grit silicon carbide paper, rinsed with distilled water, and activated in deoxygenated pH 6.8 $10^{-4}$ M Cu(NO$_3$)$_2$ solution for 30 minutes. After rinsing with deoxygenated pH 6.8 buffer solution, the electrode was placed in a deoxygenated xanthate solution while holding the potential at -0.4 V. A small nitrogen bubble was generated on the sphalerite surface, and its contact angle measured through the aqueous phase by means of a goniometer. A voltammetric experiment was also conducted in xanthate solution using activated SC:ZnS electrode for comparison. The results are shown in Figure 5.5.

As can be seen in Figure 5.5(a), the activated SC:ZnS electrode shows similar characteristics as activated CMC:ZnS electrode on the anodic sweep. Three anodic waves appeared at 0.0 V, 0.3 V and 0.6 V representing the formation of chemisorbed copper xanthate, copper xanthate and dixanthagen, respectively. Notice here that the current of peak 3 is mostly caused by the adsorption of dixanthagen on activated ZnS surface, rather than on the Pt wire since the surface area of the platinum wire is very small compared to the surface area of carbon of the CMC:ZnS electrode. Contact angle of the sphalerite at different potentials was shown in curve (b). At -0.4 V, the contact angle is ~15°, indicating that the mineral surface is hydrophilic. This is expected since xanthate adsorption will not occur at this low potential. When the potential is increased to ~0 V, chemisorption of xanthate occurs (peak A$_1$ of curve a). The contact angle measured remains small, ~17°. When the potential is further increased to that of the formation of copper xanthate (peak A$_2$ of curve a), the contact angle is still less than 20°. This unusual phenomenon suggests that although xanthate adsorption does occur on copper-activated sphalerite surface, it did not render the mineral surface hydrophobic. Further increasing the potential to 0.4 V, the contact angle started to increase to ~40°. This may be attributed to the formation of dixanthagen at this potential (peak A$_3$ of curve a).
5.4.d. Proposed Mechanisms of Xanthate Adsorption on Copper-Activated ZnS at pH 6.8

The results of voltammetry and contact angle measurements obtained above show that copper activation at neutral pH forms copper sulfide product (CuS-like at open circuit) on ZnS. The subsequent xanthate adsorption does occur on copper-activated ZnS surface at pH 6.8, but the mineral surface is not hydrophobic. This observation indicates that the mineral surface is covered by both hydrophobic entities (xanthate) and hydrophilic entities (most possibly Cu-OH species). A possible mechanism is that at neutral pH, the concentration of the Cu(OH)$^+$ and Cu$_2$(OH)$_2$$^{2+}$ ions reach maximum. These positively charged Cu(OH)$^+$ and/or Cu$_2$(OH)$_2$$^{2+}$ species adsorb on the mineral surface, some instantly react with the ZnS and form CuS, which was demonstrated by the sharp increase in rest potential, as indicated in Figure 5-1; while some still adsorb on the mineral surface, as proposed by Laskowski et al, to be converted to CuS slowly. These adsorbed Cu(OH)$^+$ and/or Cu$_2$(OH)$_2$$^{2+}$ species act as hydrophilic entities on the ZnS surface. When the activated mineral was immersed into short chain xanthate solution (e.g. KEX), xanthate adsorption occurs on the CuS site and behave like hydrophobic entities. The hydrophobicity of the mineral is hence depending on the ratio of the hydrophobic and
hydrophilic entities on the surface. When using short chain xanthate as collector, e.g. KEX, the hydrophobic effect of the Cu-EX entities is may be easily masked by the hydrophilic effect of the copper hydroxy entities, and hence causing the mineral surface hydrophilic.

In fact, similar observation was made by Iskra and Laskowski in 1969, who conducted flotation tests using methylated silica. In their investigation, it was observed that the flotation of methylated silica is depressed by Cu$^{2+}$ in near neutral solutions. These authors contributed the depression to the presence of hydrophilic copper-containing species such as Cu(OH)$_2$ or Cu$_2$(OH)$_2$$^{2+}$ ions, which adsorb on the naked sites (mica sites which are not coated by surfactant), causing the mineral hydrophilic.

**5.4.e. Improving the Hydrophobicity of ZnS Surface at pH 6.8**

Based on the above discussion, the poor flotation response in near neutral pH may be attributed to the existence of surface hydroxy species, which masks the hydrophobic effect of short chain xanthate. To improve the hydrophobicity of the mineral at neutral pH, two methods may be applied, independently or in combination: i) substituting OH group with less hydrophilic function group such as S$_2^-$ and NH$_3$; ii) using collector of longer carbon chain to enhance the hydrophobic effect of the xanthate-coated mineral surface. To explore these possibilities, contact angles of copper-activated SC:ZnS electrode were monitored at pH 6.8 while adding NH$_3$, NaHS, KEX or KAX alone or in combination to the solution. Before each measurement, the SC:ZnS electrode was wet-polished on 600-grid silicon carbide paper, rinsed with distilled water, and activated in pH 6.8 10$^{-4}$ M Cu(NO$_3$)$_2$ solution for 30 minutes. The activated SC:ZnS electrode was then rinsed and placed in a pH 6.8 buffer solution containing different chemicals. A tiny air bubble was generated on the SC:ZnS electrode surface and the contact angle was measured using captive bubble technique. The results are shown in Table 5.1.

As can be seen from the table, when the activated SC:ZnS electrode was placed in a pH 6.8 solution containing 10$^{-3}$ M KEX, the rest potential is measured to be ~0.2 V, contact angle is 15°. This is consistent with the result obtained in Figure 5.5 (b). When 10$^{-4}$ M of ammonia or 10$^{-5}$ M of NaHS was introduced to the xanthate solution, although the rest potential remained...
almost the same (~0.187 V with the addition of NaHS), the contact angle increased to 28 and 44 degrees respectively. This indicates that the hydrophilic OH group has been replaced by NH$_3$ or NaHS and hence the surface hydrophobicity was increased. Besides of the benefit of increase in contact angle, it was found that the addition of ammonia to the sphalerite-copper system can increase the copper uptake and the activation kinetics. This will be discussed in chapter 7. On the other hand, when using 2×10$^{-4}$ M KAX instead of KEX in the system, the contact angle increased to 35 degrees, supporting the assumption that increasing carbon chain length of xanthate can enhance the hydrophobicity of the mineral at neutral pH condition. When using NH$_3$ and KAX in combination, the contact angle increased to 51°. Better result (58°) was observed by using NaHS together with KAX. Although more surface analysis study needs to be conducted to further identify the structure of the surface products, the results obtained in the present investigation suggest that both cleaning reagent and long carbon chain xanthate can be used to improve the flotation response at near neutral pH.

Table 5.1. Effect of Cleaning Reagent and Carbon Chain Length on Contact Angle

<table>
<thead>
<tr>
<th>Solution Condition (pH 6.8)</th>
<th>Contact Angle (air/water/solid) Copper-activated CMC:ZnS</th>
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<tbody>
<tr>
<td>$10^{-3}$ M KEX</td>
<td>15°</td>
</tr>
<tr>
<td>$10^{-3}$ M KEX + $10^{-4}$ M NH$_3$H$_2$O</td>
<td>28°</td>
</tr>
<tr>
<td>2×$10^{-4}$ M KAX</td>
<td>35°</td>
</tr>
<tr>
<td>2×$10^{-4}$ M KAX + $10^{-4}$ M NH$_3$H$_2$O</td>
<td>51°</td>
</tr>
<tr>
<td>$10^{-3}$ M KEX + $10^{-5}$ M NaHS</td>
<td>44°</td>
</tr>
<tr>
<td>2×$10^{-4}$ M KAX + $10^{-5}$ M NaHS</td>
<td>58°</td>
</tr>
</tbody>
</table>
5.5. Conclusions

1. Electrochemical studies conducted using CMC:ZnS electrode suggest that the activation product is copper sulfide. The composition of the surface product varies with activating potential.

2. Activation of sphalerite at open circuit potential forms CuS-like product; while activation at potentials cathodic of the rest potential forms Cu₂S-like activation product.

3. Activation of sphalerite at lower potentials increases the copper uptake by the mineral.

4. Control potential contact angle measurements conducted in pH 6.8 xanthate solution using copper-activated SC:ZnS electrode show that xanthate adsorption indeed occur on activated sphalerite surface; yet the mineral surface is hydrophilic due to the formation of a copper-hydroxy-xanthate surface product at neutral pH.

5. Addition of small amount of NH₃H₂O to the activation solution and xanthate solution increases both copper uptake and the hydrophobicity of the mineral surface. Addition of small amount of NaHS to the xanthate solution after adsorption can also improve the hydrophobicity of the mineral surface.

6. Using xanthate with longer carbon chain length such as KAX can increase the surface hydrophobicity of the mineral surface. The combination of KAX with cleaning reagent such as ammonia and NaHS leads to pronounce improvement in surface hydrophobicity, hence flotation response.