

Chapter 6

Improving Flotation of Sphalerite - Effect of pH and Activating Potential on the Kinetics of Copper Uptake and Xanthate Adsorption on Sphalerite

6.1. Abstract

The effect of pH and electrochemical potential on copper uptake, xanthate adsorption and the hydrophobicity of sphalerite were studied from flotation practice point of view using electrochemical and micro-flotation techniques. Voltammetric studies conducted using the combination of carbon matrix composite (CMC) electrode and surface conduction (SC) electrode show that the kinetics of activation increases with decreasing activating pH. Controlling potential contact angle measurements conducted on a copper-activated SC electrode in xanthate solution with different pHs show that, xanthate adsorption occurs at acidic and alkaline pHs and renders the mineral surface hydrophobic. At near neutral pH, although xanthate adsorbs on Cu:ZnS, the mineral surface is hydrophilic. Microflotation tests confirm this finding. Cleaning reagent was used to improve the flotation response of sphalerite at near neutral pH.

6.2. Introduction

It is well known that due to the high solubility of zinc xanthate and the insulating property of sphalerite, flotation of sphalerite requires an activation process prior to the collector addition. In the past eight decades, fundamental studies have been conducted extensively to investigate the activation process, the activation product and the activation kinetics. It is well accepted today that the sphalerite flotation is pH sensitive. For example, Steininger et al. (1968) conducted flotation tests of sphalerite-xanthate system and showed that the flotation of activated sphalerite is suppressed at the pH range of 6 to 9, depending on the amount of CuSO₄ added. They observed, as shown in Figure 6-1, that the larger the addition of copper sulfate, the wider the range of suppression.

The poor sphalerite flotation response at near neutral pH has been observed by a number of researches (Wark and Cox, 1934; Wark and Sutherland, 1939; Sutherland, and Wark 1955; Ralston, et al, 1980 a,b; Steininger, 1968; Girczys et al., 1972; Laskowski, et al, 1997). Most of them attributed the flotation depression at neutral pH to the insufficiency of the activator (Wark and Cox, 1934; Wark and Sutherland, 1939; Sutherland, and Wark 1955), while some blamed it to the lack of collector (Ralston, et al, 1980 a,b). Steininger and his co-workers suggested that a basic copper xanthate precipitate is formed at the near neutral pH (1968) in the presence of excess copper ions, which in turn depletes the solution of xanthate ions via Reaction (1-11). Others (Girczys et al., 1972; Laskowski, et al, 1997) attributed the poor flotation response to the slow kinetics of the activation at near neutral pH. For example, Laskowski suggested that at near neutral pH, “flotation inactive” $\text{Cu}(\text{OH})^+$ ions were adsorbed on the mineral surface, which will slowly convert into a ‘flotation active’ product (CuS) on the sphalerite surface. Based on this theory, they suggested that a longer activation time is needed for better flotation at neutral pH.

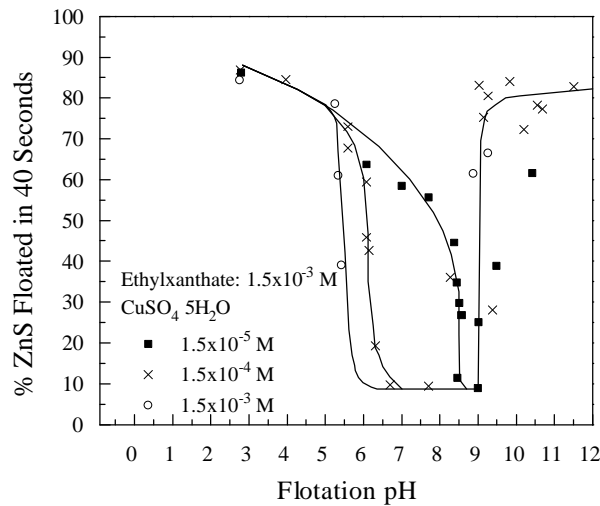


Figure 6-1. Flotation recovery as a function of pH at different CuSO_4 concentration. (from Steininger et al, 1968)

Other than pH, the electrochemical potential was also found to be a key factor in sphalerite flotation. Using the CMC:ZnS electrode and SC:ZnS electrode, it has been established

in the previous chapters that copper activation of sphalerite can be inhibited by increasing the activating potential to a value 50 to 100 mV higher than the rest potential, or enhanced by decreasing the activation potential. By controlling the potential of the activation, optimum activation results can be achieved.

It was found in chapter 5 that the poor flotation response at near neutral pH is due to the co-adsorption of copper hydroxy species. The surface hydrophobicity can be improved by addition of cleaning reagent to replace the OH group or by increasing the potential to form dixanthogen on the activated mineral surface. The effect of the cleaning reagent on the flotation system is yet to be examined.

It is the objectives of the present investigation to study the effect of pH, and complex reagents on the kinetics of copper-activation of sphalerite and the effect of electrochemical potential on the hydrophobicity of the subsequent xanthate adsorption.

6.3. Experimental

6.3.a. Materials

The mineral sample and the procedures for fabricating CMC electrode and SC electrode were the same as described in chapters 2 and 3.

For flotation test, the sphalerite sample was dry ground in an agate mortar and pestle and sieved to 100-150 μm size range. The particles were dislimed, cleaned with alcohol for three times, rinsed with distilled water, and then dried in a decicator for overnight under inert environment to avoid oxidation. The treated sample was kept in a decicator. For each test, 2 grams of the sphalerite sample was used.

Xanthate solution was prepared by dissolving purified potassium ethyl xanthate or potassium amyl xanthate in deionized water. See chapter 5 for the procedures for xanthate

purification. These procedures were repeated for three times.

Solutions of different pHs were prepared either by addition of NaOH and HCl or by using buffer solutions of the following composition:

pH 4.6 buffer : 0.05 M CH₃COONa - 0.05 M CH₃COOH,

pH 6.8 buffer: 0.05 M KH₂PO₄ - 0.025 M NaOH,

pH 9.2 buffer: 0.025 M Na₂B₂O₄.

6.3.b. Procedure

The instrumentation and experimental procedures for the activation, voltammetry and controlled potential contact angle measurements are the same as described in chapters 2, 3, 4 and 5.

Micro-flotation tests were conducted using a modified Hallimond tube with the following procedures:

1. The sample was first treated with activating solution of certain pH for 5 minutes.
2. The activated sample was then conditioned with 10⁻⁴ M KEX of the same pH for 2 minutes. The pH was monitored as the flotation pH.
3. The water-mineral mixture was then transferred into the microflotation cell, and floated with N₂ at an average flow rate of 25 cm³ for 20 seconds. The final pH was measured to ensure that no appreciable change had occurred during flotation.

6.4. Results and Discussion

6.4.a. Effect of pH on the activation kinetics

Figure 6-2 shows the copper uptake by CMC:ZnS electrode, presented using the height of

the anodic peak in Figure 2-3, after activation at different pH solutions as a function of time. Although the activation was conducted at different pH, all the voltammograms were obtained in pH 4.6 buffer solutions so that the amount of copper uptake at different pH can be compared using the same anodic peak. The effective sphalerite surface area on the electrode was measured by means of SEM. It is calculated (Gaudin et al, 1959) that one monolayer of copper on the electrode gives rise to approximately 20 μA of current in the anodic peak of the voltammogram.

It can be seen from Figure 6-2 that when activation was conducted at acidic pH (solid square), the copper uptake increases with activation time and reaches saturation, which is about 5 monolayers of copper uptake, after about 30 minutes. This observation is close to that reported by Jain and Fuestenau (1985), who followed the adsorption of Cu (II) on sphalerite under acidic conditions over 64 hours, during the first 15 minutes about 3 monolayers were adsorbed.

Under neutral pH condition (Figure 6-2 (open circle)), the copper uptake is very fast in the first 10 minutes and then reaches saturation, which is equivalent to about 2.5 monolayers of copper. It is expected that the activation at neutral pH is slower than in the acidic pH, since the free cupric ions are less at neutral pH. It is not clear what inhibited the further activation of the mineral at this solution condition, although the kinetics of copper uptake in the initial activation stage is as fast as that at acidic pH. One possible reason is based on that proposed in Chapter 5. At near neutral pH, the concentration of $\text{Cu}(\text{OH})^+$ and $\text{Cu}_2(\text{OH})_2^{2+}$ reach maximum. These copper hydroxy species co-adsorb with free cupric ions on some sites of the mineral surface, and may react with ZnS at a much slower rate than the free cupric ions (Laskowski et al, 1997). Hence, after the initial fast activation stage, the activation process slows down. Another possibility is that this monohydroxy species of transition metal copper can form $\text{Cu}_2(\text{OH})_2^{2+}$ or even further form compound with larger structure $\text{Cu}_n(\text{OH})_n^{n+}$ on the mineral surface. This non-conducting layer acts as a block, preventing further contact of cupric ions with the sphalerite surface after the initial activation stage.

As shown in Figure 6-2 (solid triangle), the kinetics of activation is much slower in alkaline solution, and does not reach a plateau even after 50 minutes of activation. After 10 minutes activation, the copper uptake is less than a monolayer. This is expected since at alkaline

pH, most of the cupric ions precipitate as copper hydroxide, so that the free cupric ion available for activation is much less. However, the $\text{Cu}(\text{OH})_2$ can act as a reservoir to slowly provide free cupric ions. Hence the copper uptake still increases slowly with time. This explains why longer activation time is required to achieve better flotation response at alkaline pH. Complex reagent may be used to improve the activation at neutral and alkaline pH.

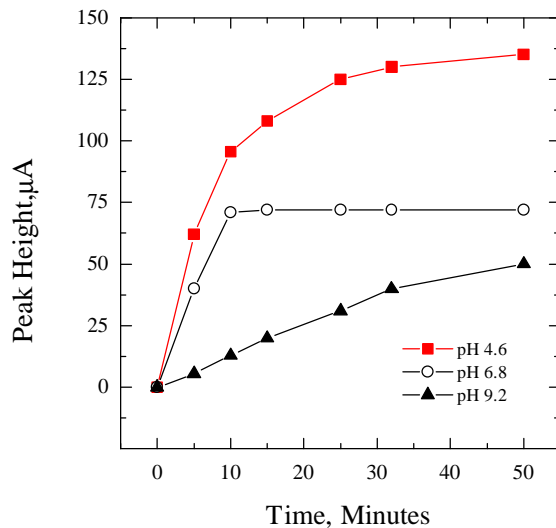
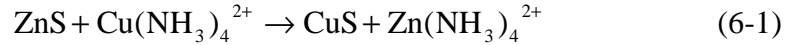


Figure 6-2. Copper uptake measured by means of the height of the anodic peak in voltammograms as function of time at different pH.

6.4.b. Effect of Complex Reagent on the Kinetics of Activation at Different pHs

Figure 6-3 (solid square) shows the effect of the ammonia on the kinetics of activation at different pH. The data shown in Figure 6-2 was plotted in this figure for comparison (open square). Before each voltammetric experiment, the CMC:ZnS electrode was activation in a solution containing 10^{-4} M $\text{Cu}(\text{NO}_3)_2$ and 4×10^{-4} M $\text{NH}_3\text{H}_2\text{O}$ at certain pH for given amount of time. The electrodes were rinsed and subjected to pH 4.6 buffer solutions to conduct voltammetric experiments. It can be seen from Figure 6-3 (b) and (c) that for near neutral and alkaline pH, introducing ammonia into the activation system significantly increases the kinetics of the activation and the copper uptake. This may be because that ammonia forms complex with

copper so that the copper hydroxide precipitate will dissolve and form $\text{Cu}(\text{NH}_3)_4^{2+}$ which can readily react with ZnS to form copper sulfide through a reaction like:



the free energy of the above reaction is -48.76 Kcal/mol.

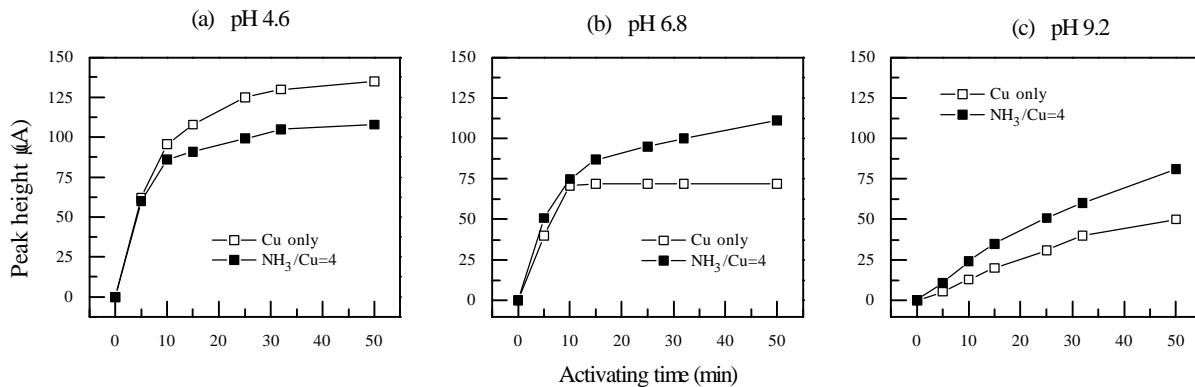


Figure 6-3. Copper uptake measured by means of the height of the anodic peak in voltammograms as function of time at different pH and solution conditions.

On the other hand, the activation kinetics at acidic pH (Figure 6-3 a) was found to decrease in the presence of ammonia. This is expected since the free energy of reaction (1.1) (without ammonia) is more negative than that of reaction (6.1). In the latter case, it will need more energy to break the Cu-NH₃ and Zn-NH₃ bond before free copper ions can bond with the sulfur in ZnS to form CuS.

6.4.c. Effect of pH and potential on Xanthate Adsorption on Copper-Activated Sphalerite

To understand the collector adsorption process in sphalerite flotation, systematic investigation is conducted to study the xanthate adsorption and its hydrophobicity at different pHs. Same technique described in Chapter 5 was used. Figures 6-4 shows the voltammogram (curve a) and the contact angles (curve b) of copper-activated SC:ZnS electrode in xanthate

solutions at pH 9.2. The SC:ZnS electrode was activated in pH 9.2 10^{-4} M $\text{Cu}(\text{NO}_3)_2$ solution at open circuit for 30 minutes before being inserted into xanthate solution. The angles were measured after holding the potential at each value for 15 minutes. As shown in Figure 6-4 (a), the voltammogram shows three anodic processes in pH 9.2 10^{-3} M xanthate solution. First peak (A_1), appears at ~ 0.05 V, has the characteristic expected of a surface-area-limited adsorption process. It is independent of stirring speed and its height increases with sweep rate and the process is reversible. The increase of contact angle from $\sim 20^\circ$ at potentials lower than -0.2 V to $\sim 35^\circ$ at ~ 0.05 V (curve b) indicates that a xanthate species, possibly chemisorbed xanthate was formed during the oxidation. When increasing the potential, the current started to increase, and another undistinguishable wave (A_2) appears at ~ 0.4 V, followed by a third peak (A_3) at ~ 0.6 V. The second and third oxidation reactions are found to be diffusion-controlled processes. The currents of peaks A_2 and A_3 are much smaller than those obtained on copper-activated CMC:ZnS electrodes in xanthate-free pH 9.2 buffer solution (not shown here), possibly due to the formation of copper xanthate, covering the activation product layer, preventing the oxidation of CuS. The contact angle does not increase when increasing the potential from 0.05 V to 0.4 V ($\sim 35^\circ$), but is much higher ($\sim 55^\circ$) when the potential is further increased to 0.6 V. Peaks A_1 and A_2 are similar to those reported by Richardson et al (1994) using carbon paste electrode, which were characterized to be the formation of chemisorbed xanthate species and copper xanthate, respectively. It is possible that the third peak at ~ 0.6 V represents the formation of dioxanthogen. Further study (surface analysis, e.g. FTIR) is necessary to identify the products.

Figure 6-5 shows the voltammogram of copper-activated SC:ZnS electrode in xanthate solutions at pH 4.6 (curve a), and the contact angles measured on the activated SC:ZnS electrode in the same xanthate solution at different potential values (curve b). The procedures for activation, voltammetry and contact angle measurement are similar to that at pH 9.2. As can be seen in Figure 6-5 (a), an anodic peak A_1 commenced from ~ 80 mV. It is difficult to identify the reaction involved in this process. However, the increase of contact angle from $\sim 20^\circ$ at potentials lower than 50 mV to $\sim 35^\circ$ at ~ 0.25 V indicates that a xanthate species, possibly chemisorbed xanthate was formed during the oxidation. When increasing the potential further, another peak A_2 appears at ~ 0.4 V, possibly due to the formation of copper xanthate. The contact angle, however, remains almost the same ($\sim 35^\circ$). Further increasing the potential results in another

oxidation peak A₃ at ~0.6 V, most probably the formation of dixanthogen. The further increase of contact angle to ~45° supports this assumption.

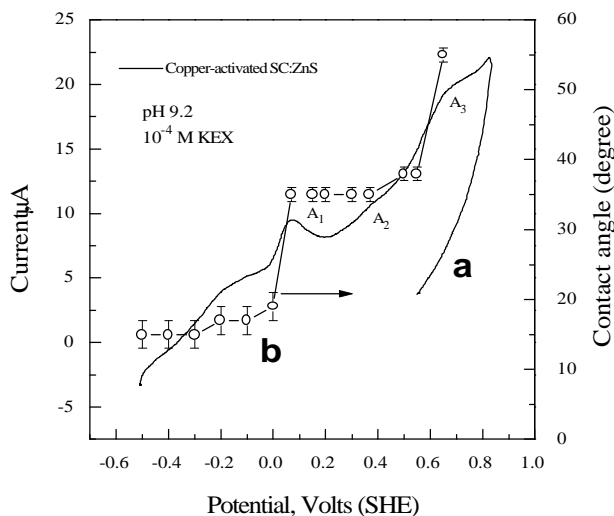


Figure 6-4. Curve a: voltammogram of a copper-activated SC:ZnS electrode in pH 9.2 10⁻³ M KEX solution. Sweep rate 25 mV/s. Curve b: contact angles measured on a copper-activated SC:ZnS electrode in pH 9.2 10⁻⁴ M KEX solution.

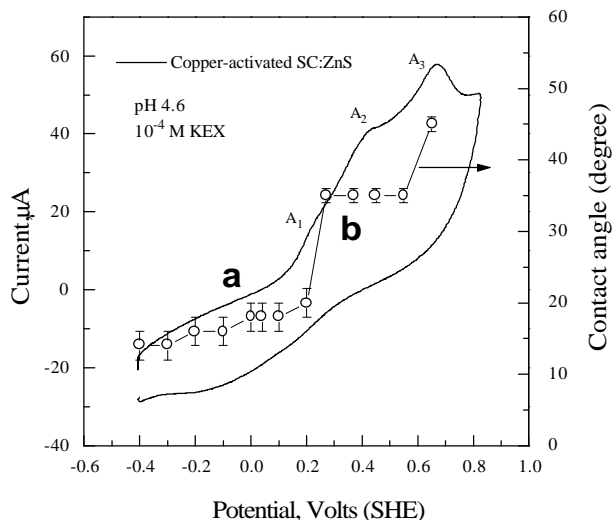


Figure 6-5. Curve a: voltammogram of a copper-activated SC:ZnS electrode in pH 4.6 10⁻³ M KEX solution. Sweep rate 25 mV/s. Curve b: contact angles measured on a copper-activated SC:ZnS electrode in pH 4.6 10⁻⁴ M KEX solution.

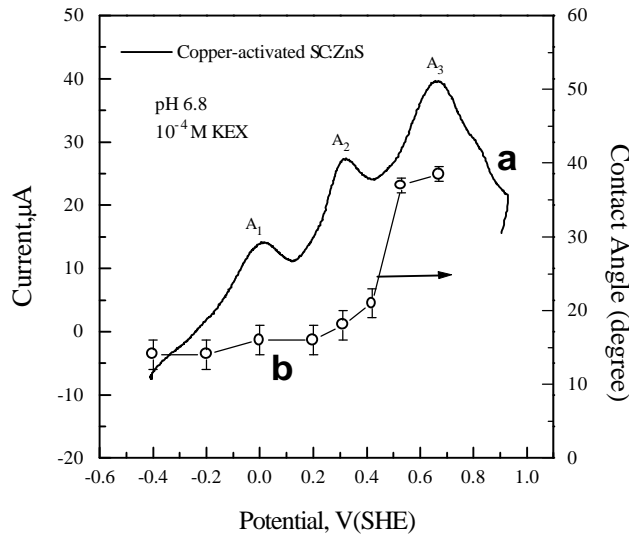


Figure 6-6. Curve a: voltammogram of a copper-activated SC:ZnS electrode in pH 6.8 10^{-3} M KEX solution. Sweep rate 25 mV/s. Curve b: contact angles measured on a copper-activated SC:ZnS electrode in pH 6.8 10^{-4} M KEX solution.

The voltammogram and the contact angles measured on the copper-activated SC:ZnS electrode in xanthate solutions at pH 6.8 has been discussed in detail in Chapter 5 (Figure 5-5). For comparison, they are shown again in Figure 6-6. Two significant features need to be emphasized again. First, the voltammogram of copper-activated SC:ZnS electrode in xanthate solution at pH 6.8 clearly suggests that xanthate adsorption indeed occurs, but the mineral surface remains hydrophilic at potentials lower than 0.4 V. Second, the surface hydrophobicity can be improved by increasing the potential to that for dixanthagen to form, which is > 0.5 V in this case.

Comparing Figures 6-4 through 6-6, one can conclude that xanthate adsorption occurs on copper-activated sphalerite surface at all three pHs. At potentials higher than the decomposition of copper sulfide, dixanthagen will form to render the mineral surface hydrophobic. This finding suggests that aggressive increase of the electrochemical potential after copper activation can improve the flotation of sphalerite at neutral pH.

6.4.d. Effect of pH and Complex Reagent on ZnS recovery

Recall from Chapter 5 that in pH 6.8 KEX solution, the contact angle of copper-activated sphalerite increases with the addition of ammonia. Flotation tests were conducted to study the effect of ammonia on sphalerite recovery. Figure 6-7 shows the flotation recovery as a function of pH at different copper and ammonia concentrations in the presence of 10^{-4} M KEX. It can be seen from the plot that in the absence of ammonia, the flotation response is similar to that reported by Steininger et al (see Figure 6-1). As shown by the open squares and solid squares, the flotation recoveries were good in acidic and alkaline pH ranges, while was inhibited at near neutral pH. The recovery is 10% at pH range 6 to 8, and the pH range of suppression increases with increasing copper concentration. In the presence of ammonia (open triangles), however, the flotation recoveries of acidic and alkaline pH are still high, and the recovery at near neutral pH increased significantly from 10% to more than 80%. These results confirmed the mechanism proposed for the xanthate adsorption at near neutral pH condition in Chapter 5.

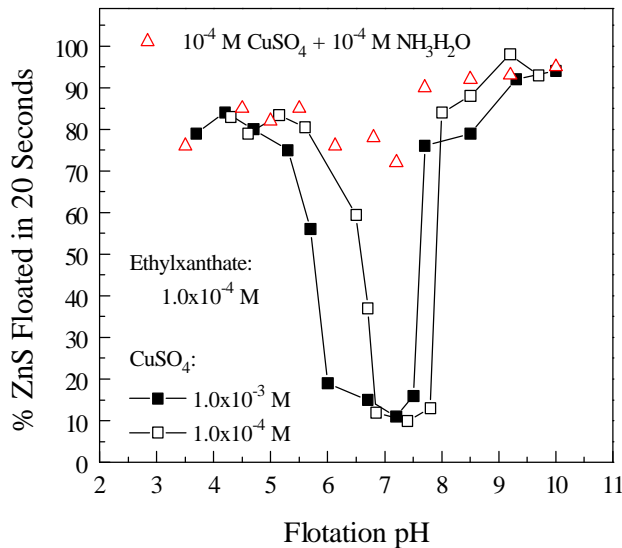


Figure 6-7. Flotation recovery of sphalerite as function of pH at different solution conditions.

The results obtained in the present investigation suggest that the poor flotation recovery of sphalerite at neutral pH is not caused by the deficiency of the copper ions or xanthate in the system, nor by the slow kinetics of activation. In fact, the copper uptake at neutral pH is more compared to that at alkaline pH. The activation kinetics is also faster at neutral pH than at alkaline pH. Xanthate adsorption occurs readily on activated sphalerite surface. Two valuable conclusions can be drawn from this investigation. First, copper-activation of sphalerite can be improved by addition of complex reagent. Second, the flotation recovery can be improved by electrochemical control and by addition of complex reagent.

6.5. Conclusions

1. The activation kinetics was found to decrease with increasing pH. The activation kinetics in acidic and near neutral pH has two stages: a rapid first stage up to 10 minutes, followed by a slow second stage and then reaches saturation. The activation kinetics is much slower in alkaline solutions.
2. The activation kinetics at near neutral and alkaline pHs can be significantly improved by addition of small amount of ammonia to the activating solution. Small decrease in copper uptake was observed when ammonia was introduced to the activating solution at acidic pH.
3. Control potential contact angle measurements conducted in xanthate solution of different pH using copper-activated SC:ZnS electrode show that xanthate adsorption indeed occurs on activated sphalerite surface at all pH conditions. The xanthate species formed is dependent of the potential. In acidic and alkaline solution, the xanthate formed at open circuit potential render the mineral surface hydrophobic; while at near neutral pH, the mineral surface is hydrophilic due to the co-exist of copper-hydroxy species with the xanthate surface product.
4. Microflotation tests show that addition of small amount of $\text{NH}_3\text{H}_2\text{O}$ to the flotation system can significantly improve the flotation response of sphalerite at near neutral pH range.