

Chapter 3

Electrochemical Studies of Copper Activated Sphalerite at pH 9.2

3.1. Abstract

The mechanism of copper-activation of sphalerite was studied at pH 9.2. The study was conducted using a carbon matrix composite (CMC:ZnS) electrode containing sphalerite particles, and a surface conducting (SC:ZnS) electrode made of a piece of sphalerite mineral. The rest potential measurement and voltammetry experiments conducted on the CMC:ZnS electrodes showed that a CuS-like activation product was formed when the electrode was activated in 10^{-4} M CuSO₄ solutions at open circuit. When the electrode was activated at lower potentials, a Cu₂S-like activation product was formed. Contact angle measurement conducted on a SC:ZnS electrode show that sphalerite activated under slightly oxidizing conditions produced hydrophobic species on the surface, possibly copper polysulfides.

3.2. Introduction

The electrochemical nature of copper-activation of sphalerite and the effect of activating potential on the composition and amount of copper uptake on sphalerite surface at acidic pH were studied using a newly developed CMC:ZnS electrode. It was found in Chapter 2 that when the CMC:ZnS electrode was immersed in a copper sulfate (CuSO₄) solution while holding the electrode at potentials negative of the rest potential, reducing currents were observed. This finding was consistent with the mechanism proposed by Richardson et al. (1976), as suggested by reaction (1.4) in Chapter 1. Furthermore, the copper uptake by sphalerite was found to increase with decreasing activating potential. This is consistent with the observations made by Ralston et al. (1930), who showed that the copper-to-zinc ratio of the activation system decreased significantly when oxygen is present in the solution. Bushell et al (1961) also reported the lower copper uptake when oxygen was present in solution than when it was absent. Wang et al. (1989) found that the activation is inhibited in air saturated solutions.

The results obtained in Chapter 2 also suggest that the selectivity of the activation is poor since copper can also deposit on carbon at low potentials. In practice, flotation is carried out in alkaline pH to achieve better selectivity. In basic solutions, however, most of the copper added as activator are precipitated as $\text{Cu}(\text{OH})_2$, indicating that the activation product and activation mechanism may be different as compared to acidic pHs. For example, Gircys, et al. (1972) suggested that the $\text{Cu}(\text{OH})_2$ coatings are the product layers on the sphalerite when activated by Cu^{2+} ions in alkaline solutions.

Kartio et al. (1996) conducted XPS studies on copper-activated sphalerite in an alkaline solution and showed that a CuS -like activation product is formed in deoxygenated solutions; while in air-saturated solutions, copper polysulfide, which might be hydrophobic in nature, is formed. This finding provides an explanation for the collectorless flotation of copper-activated sphalerite (Yoon, 1981; Craynon, 1985; Bryce et al., 1970; Gauci et al., 1970). Kartio et al's results also showed that, the copper uptake on sphalerite increases in the absence of oxygen, indicating that at alkaline pH, copper activation of sphalerite may also be potential dependent.

It is the objective of the present investigation to study the activation of sphalerite by copper at alkaline pH by means of electrochemical method. Using the newly developed $\text{CMC}:\text{ZnS}$ electrode and $\text{SC}:\text{ZnS}$ electrode, the activation mechanism and the effect of electrochemical potentials on the nature of the activation product, its hydrophobicity, and the amount of copper uptake will be investigated.

3.3. Experimental

3.3.a. Materials

Sphalerite sample and the detailed procedures for fabricating CMC electrodes were the same as being described in Chapter 2. $\text{CMC}:\text{ZnS}$ electrode of 6 mm in diameter was used for electrochemical studies at alkaline pH in this chapter. Specimen grade covellite, chalcocite and

high purity copper metal were used for rest potential measurements. For contact angle measurements, a surface conducting (SC) electrode was used. As shown in Figure 3.1, fabricating SC:ZnS electrode includes following steps: First, a chunk of sphalerite mineral was molded into a glass tube using epoxy resin; then, a small hole was drilled along the edge of the mineral; A platinum wire was inserted into the hole, with one end (flat end) bent, making contact with the mineral surface, and the other end attached to the copper wire. Tests show that the activated SC:ZnS electrode behaves similarly as activated CMC:ZnS electrode and can be used to conduct contact angle measurements while the potential was monitored or controlled.

All the tests were conducted at pH 9.2 using 0.025 M sodium borate as buffer solutions. CuSO_4 was used as activator. Ferric ion solutions were prepared by dissolving FeCl_3 in pH 2.0 buffer solution and was used as an oxidant in this chapter.

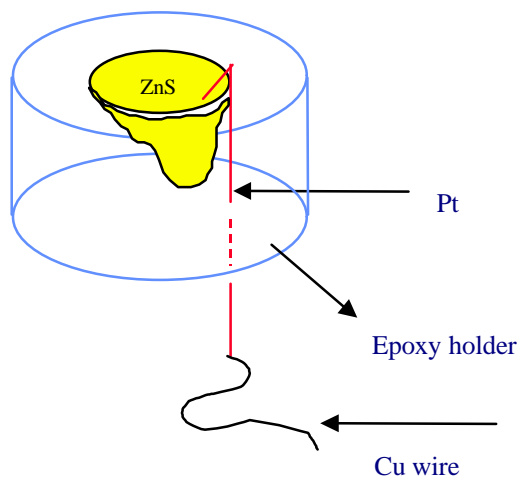


Figure 3-1. Schematic Image of Surface Conductance Electrode

3.3.b. Procedure

The study involved activation and voltammetry using CMC:ZnS electrodes. The instrumentation and experimental procedures are similar as being described in chapter 2.

Contact angle measurements were conducted on activated sphalerite at pH 9.2. The measurements were conducted by generating a small nitrogen bubble on the surface conducting SC:ZnS electrode and the contact angle was measured through the aqueous phase using captive bubble technique.

3.4. Results And Discussion

3.4.a. Open Circuit Activation

Rest Potential Measurement: Figure 3.2 shows the rest potential measurement conducted with a CMC:ZnS electrode as a function of time. Also shown for comparison are the rest potentials of covellite, chalcocite and copper electrodes in a deoxygenated CuSO_4 solution (10^{-4} M) at pH 9.2. All the electrodes were wet-polished with 600-grit silicon carbide paper before being inserted to the solution. Similar to that observed under acidic condition (chapter 2), the rest potential of the CMC:ZnS electrode increases sharply upon the addition of the CuSO_4 stock solution, indicating that a new phase (probably copper sulfide) has been formed on the surface. The blank test using CMC:carbon electrode showed no change in potential upon addition of cupric ions (not shown here), indicating that the other components in the composite did not contribute to the rest potential change. The potential reaches a plateau value of 0.275 V after approximately 1 minute, indicating the fast kinetics of formation of the new phase. Although this potential is close to the rest potential of the covellite electrode, due to the complicated solution condition and the metastable property of the activating product, it is difficult to conclude that the new phase (activation product) is CuS. Therefore, further refinement in the rest potential measurement may be necessary to provide better understanding of the nature of the activation product formed at open circuit.

Voltammetry: To study the electrochemical behavior of activated sphalerite, series of voltammetric experiments were carried out on activated CMC:ZnS electrode. A CMC:ZnS electrode was activated in a deoxygenated 10^{-4} M $\text{Cu}(\text{NO}_3)_2$ solution. After 10 minutes of activation, the electrode was removed from the solution, rinsed with deoxygenated distilled

water, and placed in a deoxygenated pH 9.2 buffer solution (copper free) for voltammetric studies. Figure 3.3(a) shows the first sweep voltammogram obtained by initiating the sweep from the rest potential (0.1 – 0.2 V) to the positive-going direction. An unusual feature needs to be noticed. The rest potentials from which the sweeps were initiated are between 0.1 and 0.2 V.

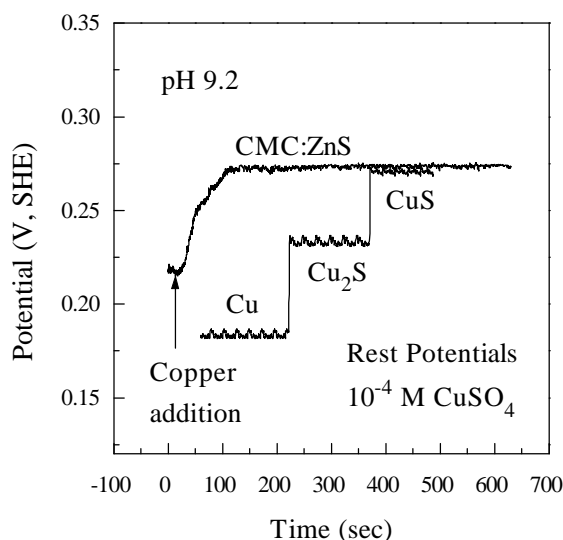


Figure 3-2. Potential-time curve of CMC:ZnS electrode in a deoxygenated pH 9.2 buffer solution. The arrow indicates the time of addition of copper sulfate.

These potential values differ from experiments. This may be due to the fact that the activation product formed is metastable, and it requires longer time to reach the equilibrium. However, the voltammetric experiments were conducted right after the activation process (within 30 seconds) to avoid change in the surface product. To ensure that the scan is initiated from the rest potential, a multimeter was used to monitor the potential of the activated CMC:ZnS electrode in the buffer solution. The commencement scan potential was determined when the change in potential is relatively small. Repetitive experiments show that although the rest potential is slightly different in each experiment, the electrochemical behavior of the activated electrode shows same features under same activation conditions.

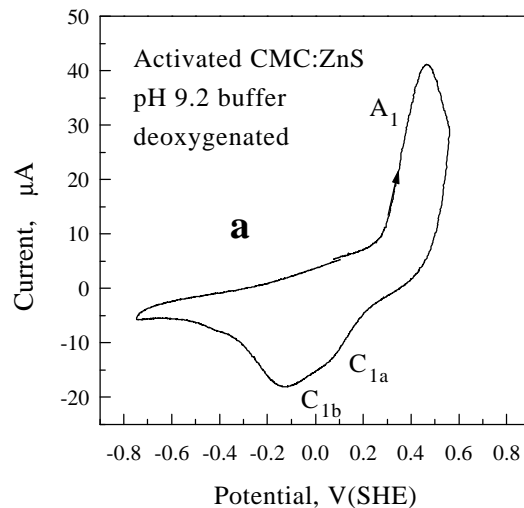


Figure 3-3 (a). Voltammogram of CMC:ZnS electrode after activating in deoxygenated pH 9.2 10^{-4} M CuSO_4 solution for 10 minutes. Sweep rate 25 mV/s. First sweep positive-going.

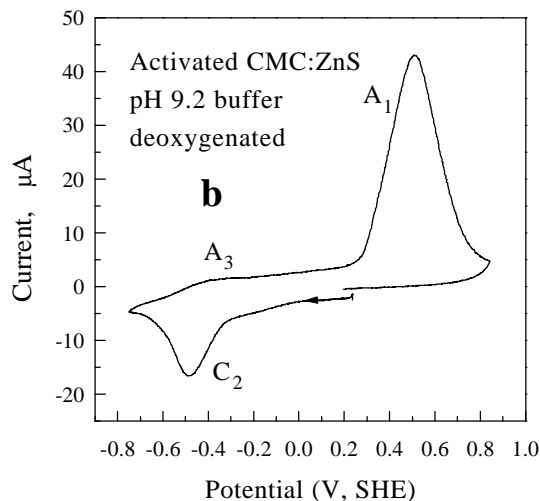
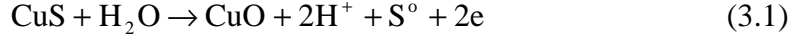


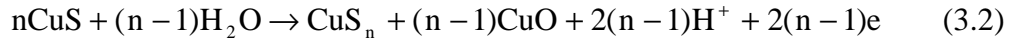
Figure 3-3(b). Voltammogram of CMC:ZnS electrode after activating in deoxygenated pH 9.2 10^{-4} M CuSO_4 solution for 10 minutes. Sweep rate 25 mV/s. First sweep negative-going.

As shown in Figure 3.3(a), a well-defined anodic wave A_1 begins approximately at 0.25 V. In Chapter 2, it was found that during the anodic sweep, copper is the only cation detected in

the stripping solution using ICP analysis. Hence, the anodic reaction occurring under A_1 may be related to the following reaction:



whose thermodynamic potential (E_h) is 0.30 at pH 9.2. Therefore, the activation product formed on sphalerite at open circuit potential may be CuS-like. The fact that A_1 begins at approximately 0.05 V lower potential than the thermodynamic potential for Reaction (3.1) may be attributed to the possibility that the CuS-like activation product is less stable than CuS. Another possible explanation is that copper polysulfide (CuS_n) is formed as follows:



The possibility of CuS_n formation on activated sphalerite has already been suggested by Yoon (1981) and Craynon (1985), and its spectroscopic evidence given by Kartio et al. (1996). Since CuS_n is a species containing excess sulfur in the form of S^0 -like species, its presence on activated sphalerite provides an explanation of collectorless flotation of copper-activated sphalerite (Yoon, 1981; Craynon, 1985; Bryce et al., 1970; Gauci et al., 1970).

Figure 3.3(a) shows also two cathodic waves C_{1a} and C_{1b} after switching the sweep direction at 0.55 V. These may be the reverse of Reactions (3.1) and (3.2), respectively.

Figure 3.3(b) shows the first sweep voltammogram obtained by beginning the sweep to the negative-going direction. A cathodic peak C_2 begins at the potential of approximately -0.3 V. This potential is close to the thermodynamic potential for the following reaction:



whose $E_h = -0.27$ V at pH 9.2 and $[\text{HS}^-] = 10^{-6}$ M. The onset potential for C_2 is substantially higher than the thermodynamic potential ($E_h = -0.44$ V) for the reduction of Cu_2S to Cu^0 . Therefore, the activation product formed at pH 9.2 is more likely to be CuS rather than Cu_2S .

When the potential becomes more negative, Cu_2S may be reduced to elemental copper (Cu^0) by the following reaction:

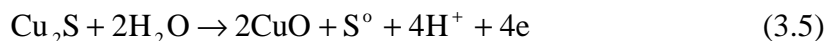


which begins to occur at $E_h = -0.6$ V at $[\text{HS}^-] = 10^{-6}$ M. After switching the scan direction at -0.72 V, a small anodic peak A_3 begins to appear at about -0.6 V, which is most probably due to the reverse of Reaction (3.4) (Woods et al., 1987; Young et al., 1988). Note that the A_3 peak is considerably smaller than C_2 , because much of the HS^- ions formed via Reaction (3.3) diffuse away from the electrode surface.

3.4.b. Activation under Controlled Potential Conditions

Figure 3.4 shows the voltammogram of a CMC:ZnS electrode which was activated for 10 minutes by holding the electrode potential at 0.195 V in a pH 9.2 buffer solution containing 10^{-4} M CuSO_4 . The voltammetry experiment was conducted in a copper-free pH 9.2 buffer solution. Note here that the potential at which the CMC electrode was activated is more cathodic than the rest potential (~ -0.275 V) of the sphalerite activated at open circuit and CuS (see Figure 3.2), but is higher than that of Cu^0 . The initial scan was made toward the cathodic direction. To avoid the formation of Cu^0 , the scan was limited to -0.6 V. The initial scan showed no indication of C_2 and A_3 peaks, suggesting that the activation product formed at 0.195 V is Cu_2S rather than CuS .

On the return scan, a large anodic wave A_1 is observed. Its peak height is approximately twice as large as the case with the CMC:ZnS electrode activated at open circuit (see Figure 3.3(a)). This finding suggests that the oxidation mechanism occurring under A_1 may be given as follows:



which is a four-electron reaction as opposed to the two-electron reaction suggested for the oxidation (Reaction (3.1)) of the activation product formed at open circuit.

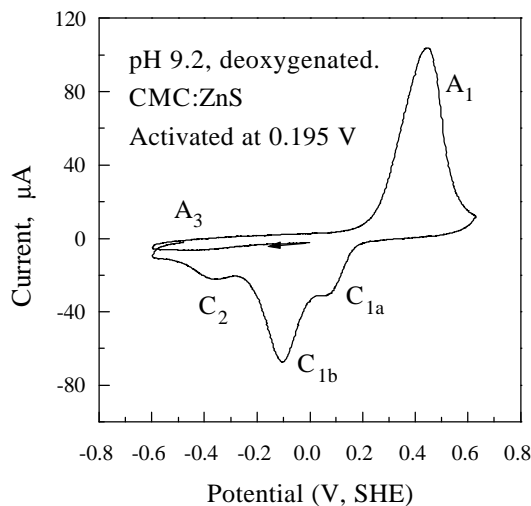
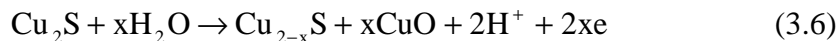


Figure 3-4. Voltammogram of CMC:ZnS electrode after activating in pH 9.2 10^{-4} M CuSO_4 solution at 0.195 V for 10 minutes. Sweep rate 25 mV/s.

It has been shown, however, that Cu_2S also oxidizes to non-stoichiometric copper sulfides of the general formula, Cu_{2-x}S , as follows:



According to the E_h -pH diagram constructed by Woods et al. (1987) and Young et al. (1988), this reaction should occur at potentials in the range of approximately 0.18 to 0.28 V. Thus, the anodic reactions occurring under A_1 may include Reactions (3.5) and (3.6). Since the positive-going scan was extended to 0.6 V, which is well beyond the upper potential limit for Reaction (3.6), Reaction (3.5) is probably the predominant of the two. On the return scan, two well-defined cathodic peaks C_{1a} and C_{1b} appeared, which may be attributed to the reverse of Reactions (3.1) and (3.2), respectively. Peak C_2 represents reaction (3.3).

Comparison of the voltammograms obtained at open circuit and controlled potential conditions suggests that the activation product change its composition depending on the potential of activation. The fact that Cu_2S is formed at a lower potential is consistent with the XPS work

of Kartio et al. (1996), which showed that copper uptake by sphalerite increases in the absence of oxygen relative to the case of activating the mineral in air-saturated CuSO_4 solution.

3.4.c. Contact Angle Measurement

Reaction (3.2) suggests that the activation product formed at an open circuit potential can be oxidized to CuS_n , which has been identified as the hydrophobic species responsible for collectorless flotation (Kartio et al., 1996). In an effort to verify the presence of hydrophobic species, contact angles were measured on the surface of the sphalerite sample immersed in solution. In each measurement, a SC:ZnS electrode was cleaned with 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 SC:ZnS electrode was wet-polished on 600-grit silicon carbide paper, wiped with chloroform, rinsed with distilled water, and placed in a deoxygenated pH 9.2 buffer solution. A small nitrogen bubble was generated on the sphalerite surface, and its contact angle measured by means of a goniometer. The angles were measured through the aqueous phase.

Table 3.1. Effect of Oxidation on Contact Angle

Solution Condition	Contact Angle (degree)
deoxygenated pH 9.2 buffer (as reference)	15
addition of deoxygenated CuSO_4	15
addition of air-saturated CuSO_4	25
addition of deoxygenated CuSO_4 , and then inject ferric ions on copper activated ZnS surface	27

As shown in Table 3.1, the contact angle of the sphalerite was 15° in a deoxygenated pH 9.2 buffer solution. It remained the same when 10^{-4} M CuSO_4 was added to the solution. When

the solution containing CuSO_4 was exposed to oxygen, however, the contact angle increased to 25° , indicating that the activation product was oxidized to form hydrophobic species, possibly polysulfides. In another experiment, 10^{-4} M FeCl_3 (pH 2) was added to the deoxygenated pH 9.2 CuSO_4 solution to increase the pulp potential. The contact angle increased further to 27° . The rest potential was monitored to be ~ 0.29 V, about 15 mV higher than the case without ferric ions. It is possible that upon addition of Fe^{3+} solution, although most of the ferric ions precipitate as ferric hydroxide at this pH, the activation product can still be oxidized to form increased amount of polysulfides since ferric ion is a stronger oxidant than oxygen.

3.5. Conclusions

1. The rapid increase in rest potential of the CMC:ZnS electrode upon addition of CuSO_4 solution at pH 9.2 under open circuit conditions suggests the fast kinetics of the activation. It also suggests that a conducting layer of activating product, probably copper sulfide is formed after activation.
2. Superficial oxidation of the sphalerite activated at open circuit may result in the formation of copper polysulfides, which may be responsible for the collectorless flotation of activated sphalerite reported in the literature.
3. The contact angles measurements showed that activated sphalerite becomes more hydrophobic upon superficial oxidation.
4. Activation of sphalerite at potentials cathodic of the rest potential of the sphalerite activated at open circuit forms Cu_2S -like activation product.
5. Activation of sphalerite at lower potentials increases the copper uptake by the mineral.