

Chapter 2

Electrochemical Aspects of Copper-Activation of Sphalerite

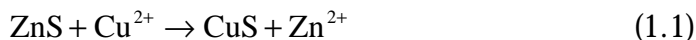
2.1. Abstract

A technique has been developed to study electrochemical reactions on insulating sphalerite. This technique involves embedding sphalerite particles in carbon to form a carbon matrix composite (CMC) electrode. When the mineral is activated by heavy metals ions such as copper, a conducting layer is formed on the mineral surface that allows dynamic electrochemical studies to be conducted. Voltammograms of the activated CMC:ZnS electrode obtained in inert electrolyte solution show similar characteristics of copper sulfides. Further characterization of the electrode show that the anodic sweep of the voltammogram can be used to quantitatively measure the amount of copper uptake on the mineral surface during activation.

Voltammetric studies conducted using CMC:ZnS electrode in cupric solutions and inert electrolytes reveal that the activation process is electrochemical in nature. The activation product and the amount of copper uptake on sphalerite are strongly dependent on time of activation and on the electrochemical potential applied during activation. Activation at potentials increasingly negative of the rest potential causes a progressive increase in the amount of copper on the surface, consistent with the diffusion controlled reduction process between ZnS and Cu^{2+} ions observed in the activating solution. However, activation at reducing potential may affect the selectivity of the activation. On the other hand, activation at potentials positive of the rest potential decreases the amount of copper on the surface. Activation at potentials of 50 to 100 mV positive of the rest potential in the activating solution completely inhibits copper activation. This result is consistent with the anodic stripping voltammetry that shows copper can be removed from the surface of sphalerite at oxidizing potentials. Thus, the results obtained in the present work show that potential control of the activation process provides a means of controlling copper uptake and, hence, flotation.

2.2. Introduction

Sphalerite (ZnS), unlike most other sulfides, floats poorly with short-chain xanthates due to the high solubility of zinc-thiol compounds in water. One solution to this problem is to activate the mineral by heavy metal ions such as copper via Reaction (1.1), i.e.:



the copper sulfide formed can then react with a short-chain thiol collector to form an insoluble collector coating, which renders the mineral surface hydrophobic.

Although Reaction (1.1) is usually written to suggest that the activation product is covellite (CuS), its exact chemical form is not known. In order to improve the recovery and selectivity of sphalerite flotation, enormous amount of research has been conducted in the past eight decades to study the activation product, activation mechanisms and kinetics of the activation (Chapter 1). Majority of the research proposed the activation to be chemical replacement reaction. However, more and more evidence indicates that the activation process may be electrochemical in nature. For example, as early as 1930, Ralston et al. noticed that the copper-to zinc-ratio of the activation system decreased significantly when oxygen is present in the solution. Bushell and his colleagues (1961) found that the abstraction of copper was lower when oxygen was present in solution than when it was absent. Wang et al. (1989) reported that the activation is inhibited in air saturated solutions. Other researchers (Nicol, 1984; Rao and Finch, 1987) also realized that an electrochemical process may be involved in the activation.

Several researchers did propose the electrochemical mechanism of the activation process. One example is Maust and Richardson's doping theory (1976) described in chapter 1. This was proven later by XPS studies (Clifford et al, 1975; Kartio et al, 1996), which showed the presence of Cu(I), instead of Cu(II) on activated sphalerite surface. More recently, Kartio, et al. (1996) used Synchrotron XPS to study the activation product and showed that copper uptake by sphalerite increases substantially in the absence of oxygen. These observations provide further experimental evidence of the potential dependence of the activation process.

Although the insulating nature of sphalerite makes it impossible in the past to be used as an electrode for electrochemical experiments, attempts have been made by researchers to conduct electrochemical studies on sphalerite. For example, Bessiere et al. (1990) used a fluidized bed electrode made of activated sphalerite particles but failed to provide conclusive results due to the limited performance of this technique. More definitive results were obtained by Richardson et al. (1994), who used a carbon paste electrode made of sphalerite particles to investigate the activation and xanthate adsorption on this mineral. Their results show that the activated sphalerite surface behaves similar to the copper sulfide species both in inert electrolyte and in contact with xanthate. This work for the first time confirmed the general belief that the flotation chemistry of sphalerite is essentially electrochemical in nature, and provided a tool which can be used to study the activation process and the reaction between collectors and other reagents and sphalerite. However, the carbon paste electrode is difficult to reproduce, and is not strong enough to withstand any harsh environment. This restricted the use of this electrode in characterizing the surface activation product. More advanced technique needs to be developed to study the electrochemical behavior of the activation process and the activation product(s).

The objectives of the present investigation are:

1. To develop a reliable, reproducible, more durable electrode for a comprehensive electrochemical study of the copper-activation of sphalerite
2. To establish a method for in situ, direct quantitative measurement of the amount of copper uptake on sphalerite surface.
3. To study the activation product, activation mechanism, activation kinetics and the potential dependence of the activation.

2.3. Experimental

2.3.a. Materials

Specimen-grade sphalerite from Santander, Spain, was obtained from Ward's Natural Science Est., Inc. The mineral contained 0.035% Fe, 0.012% Cu and <0.001% Pb by weight, and

its resistivity was greater than 10^{10} ohm-cm. Figure 2-1 shows the illustration of a carbon matrix composite (CMC) electrode. Fabricating CMC electrodes involves three steps. First, chloroform was used to combine sphalerite particles (105-150 μm) and carbon powder with a binder in a water bath at $\sim 75^\circ\text{C}$. The mixture was then vacuum dried for over night. While applying vacuum, appropriate amount of the dry mixture was pressed into a mold to form a cylinder-shaped carbon matrix composite electrode of 6 mm in diameter. The CMC electrode has the following advantages over the carbon paste electrode: i) the surface can be renewed by polishing; ii) the electrodes can be fabricated into various shapes, e.g., ring discs; iii) they are sufficiently strong to withstand the harsh environment in industrial flotation cells; and iv) CMC electrodes containing sulfide minerals other than sphalerite can be made for monitoring pulp potentials.

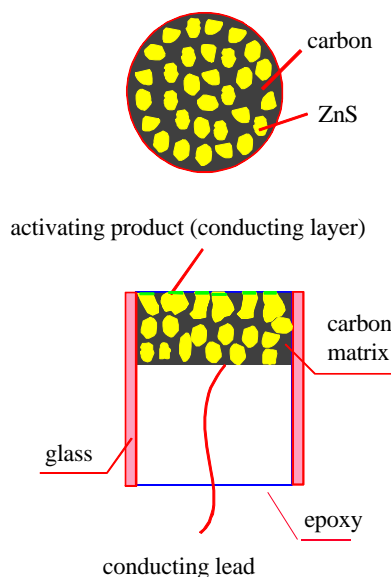


Figure 2-1. Schematic Image of Carbon Matrix Composite Electrode

2.3.b. Procedures

A Pine Instrument Model RDE4 double potentiostat was used for electrochemical studies. A conventional three-electrode system was used for controlled potential activation and voltammetric experiments, with platinum as counter electrode and standard calomel electrode

(SCE) as reference. All potentials quoted are given on the standard hydrogen (SHE) scale, taking the potential of the SCE as 0.245 V vs. the SHE.

The experimental procedures included activation and voltammetry. The activation involved placing a CMC:ZnS electrode in an activation cell containing deoxygenated buffer solution (in this chapter, pH 4.6 buffer made of 0.05 M CH₃COONa - 0.05 M CH₃COOH was used) with its potential either monitored (for open circuit activation) or controlled by a potentiostat (for controlled potential activation). While monitoring the potential or current, an aliquot of deoxygenated CuSO₄ stock solution (10⁻² M) was added to the buffer solution to obtain a 10⁻⁴ M solution. After activation, the electrode was removed from the activating solution, rinsed with deoxygenated distilled water, and immediately placed in an electrochemical cell for voltammetric studies. The voltammetric experiments were conducted in deoxygenated inert pH 4.6 buffer solutions starting from the rest potential. These rest potentials of the activated CMC:ZnS electrodes in the inert solution were determined using a multimeter within 30 seconds after the electrodes were placed in the electrochemical cell. The surfaces of the electrodes were renewed by wet-polishing using 600-grit silicon carbide paper. After rinsing with distilled water, chloroform was used to remove any sulfur species that may be formed during polishing. The electrodes were rinsed with distilled water again before activation. Nitrogen was purged for the entire experimental duration.

2.4. Results and Discussion

2.4.a. Characterization of the CMC:ZnS Electrode

To characterize the electrochemical performance of the newly developed CMC electrodes, rest potential measurements, voltammetric experiments and chemical analysis were conducted using both the CMC:ZnS and CMC:Carbon electrodes.

1. Rest Potential Measurements:

Figure 2-2 shows the changes in the rest potential of a CMC:ZnS and CMC:Carbon electrode before and after copper addition at pH 4.6. The blank test using CMC:Carbon electrode showed no change in potential upon addition of cupric ions, indicating that other components in the composite did not contribute to the rest potential change. The rest potential of the CMC:ZnS electrode, however, increases sharply as soon as CuSO_4 (final concentration is 10^{-4} M) is added, indicating a conducting layer, possibly copper sulfide (to be discussed later), is formed on the sphalerite surface upon contact with cupric ions.

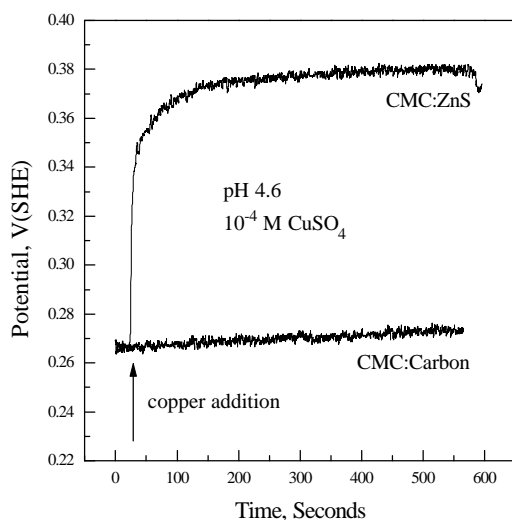


Figure 2-2. Rest potential measurements of a CMC:ZnS electrode and a CMC:Carbon electrode immersed in a 10^{-4} M CuSO_4 solution at pH 4.6.

2. Voltammetry in Acidic Inert Electrolyte Solution:

After activation, the electrodes were rinsed with distilled water and subjected to pH 4.6 solution for voltammetric study to characterize the electrochemical properties of the surface product. Figure 2-3 shows the first sweep voltammetry curves obtained with a CMC:ZnS electrode (solid line) and a CMC:Carbon electrode (dashed line) activated at open circuit in 10^{-4} M CuSO_4 solution for 10 minutes. The potential sweeps were initiated from the rest potential in the

positive-going direction. It needs to be mentioned here that these commencement potential values differ slightly from experiments, possibly because that the surface layer is metastable. 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 potential was determined when the change in potential is relatively small. Repetitive experiments show that although the rest potential of the activated CMC:ZnS electrode in the inert electrolyte solution is slightly different in each experiment, the electrochemical behavior of the activated electrode shows same features under same activation conditions.

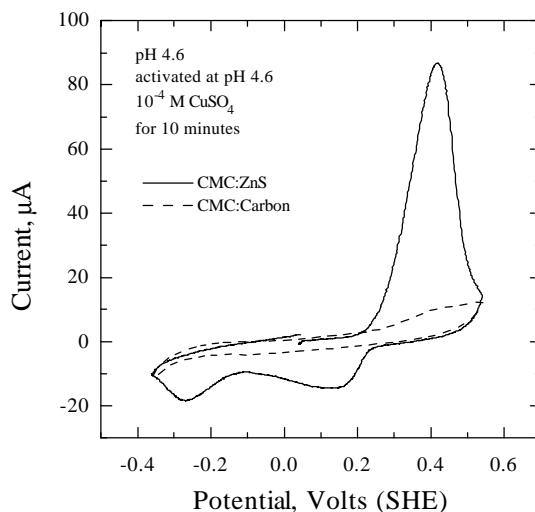


Figure 2-3. Voltammograms of a CMC:ZnS electrode and a CMC:Carbon electrode in pH 4.6 buffer solution after activating at open circuit in pH 4.6 10^{-4} M CuSO_4 solution for 10 minutes.

As can be seen from Figure 2-3, the voltammogram of the activated CMC:Carbon electrode (dashed line) showed no electrochemical waves, which further confirmed that copper did not adsorb on the other components of the composite during open circuit activation. The voltammogram of the activated CMC:ZnS electrode (solid line), on the other hand, showed an anodic peak at ~ 0.4 V, which may represent the oxidation of the activation product. On the return sweep in quiescent solutions, two cathodic waves appeared at 0.15 and -0.27 V, which may be the reverse of the oxidation process (will be discussed in detail later). The voltammetry curves

obtained using the procedure described above exhibited good reproducibility, with only small (<10 %) variations in the size of the anodic peak during repeat experiments.

3. *Measurement of Copper Uptake:*

The reactivity of the surface product was studied by repetitive sweep and rotating ring disk voltammetry. It was found that the height of the anodic peak in Figure 2-3 increases with the increase of activation time (Figure 2-4) and decreases with repetitive sweep (Figure 2-5). Under quiescent conditions, several sweeps are sufficient to reduce the current to the background level. When the electrode is rotated, as shown in Figure 2-6 (a), the current decreases to a negligible value after the first sweep. Figure 2-6 also shows the ring current obtained by holding the ring potential at -0.55 V (curve b). The current is due to the reduction of the metal ions produced during the anodic oxidation of the activation product on ZnS. The collection efficiency of the ring was determined to be ~12%, therefore for a 2 electron oxidation process on the copper activated ZnS, a 2 electron reduction process at - 0.55 V can be accomplished for by the ring current. This strongly suggests that the product of oxidation of copper activated sphalerite is Cu^{2+} which can be reduced to Cu^0 on the Au ring at -0.55 V, and not ions which would require a larger overpotential for reduction (e.g. zinc). ICP analysis (will be discussed later) shows that copper is the only oxidation product during anodic sweep, confirming that the decrease in reactivity is caused by the net loss of copper from the surface during anodic cycle. Therefore, the area or the height of the anodic peak at 0.4 V can be used to represent the amounts of copper uptake during the activation process. Thus, the results given in Figure 2-4 shows that the longer the activation time, the larger the amount of copper uptake.

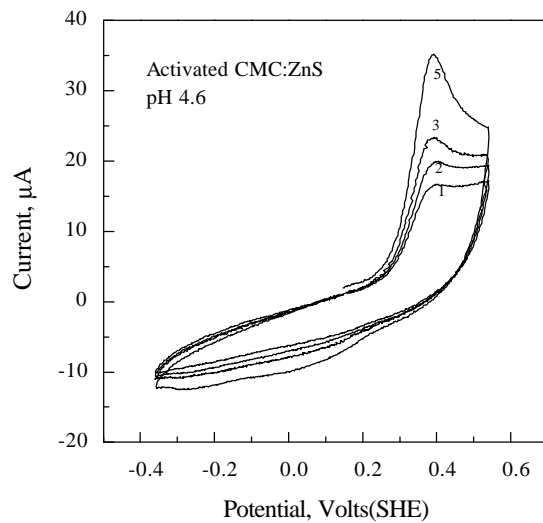


Figure 2-4. Voltammograms of the CMC:ZnS activated in 10^{-4} M CuSO_4 solution for 1, 2, 3, and 5 minutes.

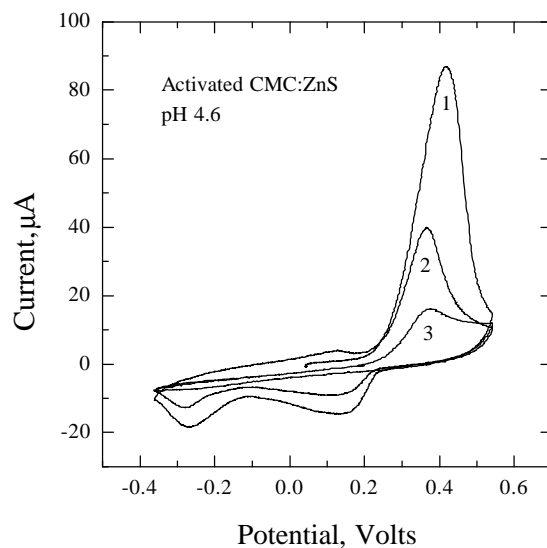


Figure 2-5. Voltammogram of CMC:ZnS electrode after activation in pH 4.6 10^{-4} M CuSO_4 solution at open circuit (~ 0.38 V) for 10 minutes. Sweep rate 25 mV/s; First sweep positive-going.

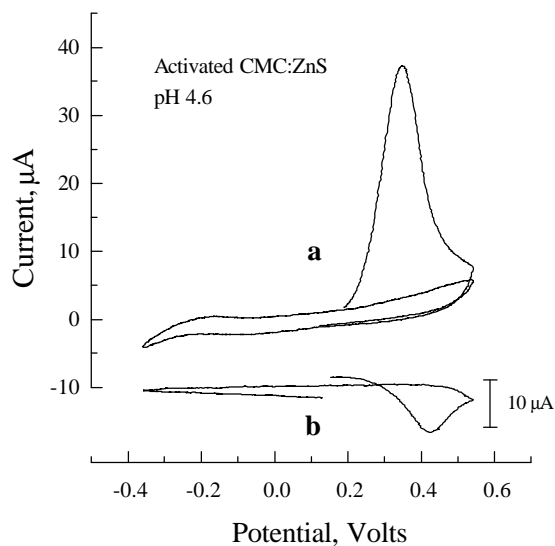


Figure 2-6. Ring (b)-disc (a) voltammograms of the CMC:ZnS electrode after activation in pH 4.6 10^{-4} M CuSO_4 solution at open circuit (~ 0.38 V) for 5 minutes. The ring potential (b) was held at -0.55 V. Rotation rate 2000 rpm.

4. Voltammetry at Different pHs:

The general features of the voltammogram of the copper-activated CMC:ZnS electrode in Figures 2-3 to 2-6 are typical of the behavior that has been observed on a number of metal sulfides in acid solutions. The binary sulfides, e.g., chalcocite (Cu_2S) and djurleite ($\text{Cu}_{1.96}\text{S}$), and the ternary sulfides, e.g., chalcopyrite (CuFeS_2) and bornite (Cu_5FeS_4) are known to oxidize in acid solutions to produce soluble Cu^{2+} and sulfides of lower cation-to-sulfur ratio (Woods, et al, 1987; Young et al., 1988). To further investigate the electrochemical behavior of the activation product, activation experiments were conducted at different pH, followed by voltammetric experiments in inert electrolyte solutions of corresponding pHs.

Figure 2-7 shows the first scan of voltammograms of copper-activated CMC:ZnS electrode obtained at different pHs. It can be seen from the figure that the commencement potential of the anodic peak decreases with increasing pH. If we plot these commencement potentials as a function of pH (Figure 2-8, open circles), one can find that this feature is similar

to that observed for copper sulfide minerals (Figure 2-8, solid lines) (Woods et al, 1989, Young et al, 1988). These results further suggest that the activation product is copper sulfide.

It can be established from the data obtained above that the CMC electrode is a reliable, reproducible and durable tool for studying the electrochemical behavior of the copper activation of sphalerite. It also provides a reliable way for direct in situ measurement of the copper uptake on the mineral surface.

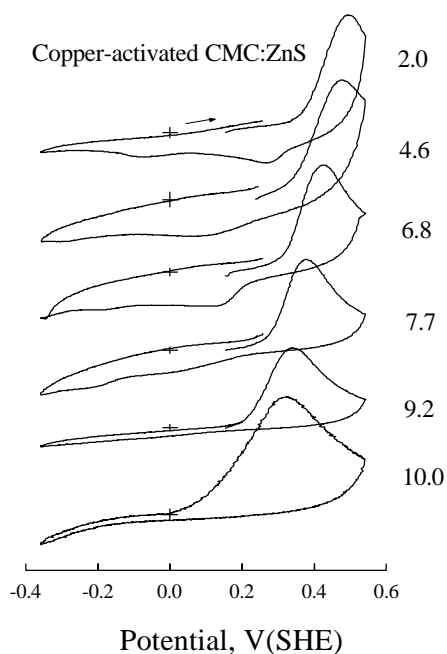


Figure 2-7. Voltammograms of CMC:ZnS at different pH's. Electrode activated in 10^{-4} M CuSO_4 at open circuit potential. sweep rate 50 mV/s. The pH's of activation and voltammetry are indicated on the voltammograms.

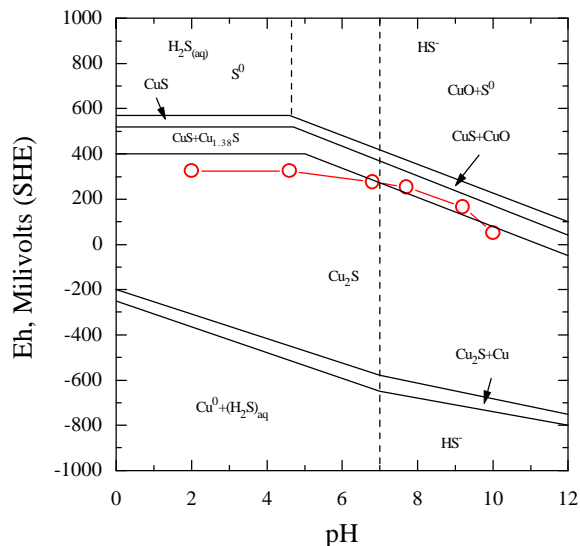


Figure 2-8. Eh-pH diagram of Cu_2S (solid lines; from Young, 1988) and the commencement potentials (open circles) of the voltammograms from Figure 2-7.

5. Voltammetry in CuSO_4 Solutions:

Figures 2-9 shows the voltammograms of a blank CMC electrode (curve a) and a CMC:ZnS electrode (curve b) obtained in a 10^{-4} M CuSO_4 solution at pH 4.6. The electrodes were held at 0.55 V for 3-4 minutes before the initial sweeps in the cathodic direction.

The blank CMC electrode shows a cathodic wave beginning at $\approx 0.12 \text{ V}$, due to the electro-deposition of metallic copper (Cu^0). On the return sweep, Cu^0 oxidizes to Cu^{2+} ions and gives rise to an anodic peak at 0.1 V. Two interesting observations can be made from curve (a) in Figure 2-9: first, the potential at which the reduction started to happen is about 100 mV lower than that calculated from thermodynamic data. This suggests that there is an overpotential required for copper to adsorb on the carbon surface. Second, the adsorption of copper on carbon surface suggests that the selectivity of the activation under low potential in acidic solution is not good.

The CMC:ZnS electrode (curve b), on the other hand, shows a reduction current beginning

at approximately 0.25 V, which suggests copper uptake on ZnS via an electrochemical reduction mechanism. The copper uptake below this potential may be in addition to that incorporated into the sphalerite lattice *via* metathetical substitution (Reaction (1.1)), for example, formation of CuS with higher Cu-to-S ratio or metallic copper. During the return sweep, the activation product(s) oxidize(s) as indicated by an anodic peak at ≈ 0.3 V. The charge passed during the anodic sweep (11.9 μA) is approximately equal to the charge passed during the cathodic sweep (12.5 μA), suggesting that even when the concentration of the cupric ions is high in the solution (10^{-4} M in this case), most of the copper abstracted by sphalerite is removed during the anodic sweep. It is also interesting to notice that although about 27% of the surface area of the CMC:ZnS electrode is carbon, no oxidation peak was observed at 0.1 V. This indicates that the formation of copper sulfide species on the ZnS surface is more favorable than the reduction of elemental copper.

At very low potentials, however, elemental copper can adsorb on the CMC:ZnS electrode surface. It is easy to distinguish the elemental copper from the copper sulfide species. Figure 2-10 shows the voltammogram and the ring current of a CMC:ZnS electrode after activated in 10^{-4} M CuSO_4 solution at -0.305 V. As can be seen from Figure 2-10 (a), the voltammogram shows two anodic peaks, the larger peak near 0.4 V representing the oxidation of the activation product formed on sphalerite, while the smaller one near 0.15 V representing the oxidation of the metallic copper deposited on the carbon surface of the CMC electrode or on the ZnS. The ring current was obtained by holding the ring potential at -0.55 V (curve b). The larger ring current is due to the reduction of the Cu^{2+} ions produced during the anodic oxidation of the activation product on ZnS, while the smaller current observed at a disc potential of approximately 0.15 V is due to the reduction of the Cu^{2+} ions produced during the anodic oxidation of the metallic copper. These results further established that the anodic peak at 0.4 V can be used as quantitative measure of the copper sulfide species uptake on the electrode surface.

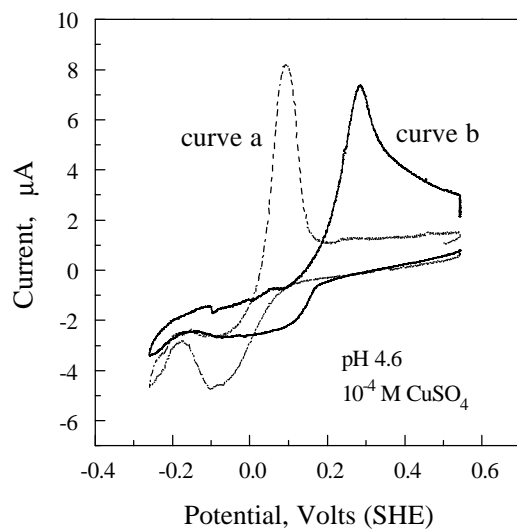


Figure 2-9. Voltammograms of CMC:carbon (curve a) and CMC:ZnS (curve b) electrodes in pH 4.6 10^{-4} M CuSO_4 solution at a sweep rate of 5 mV/s.

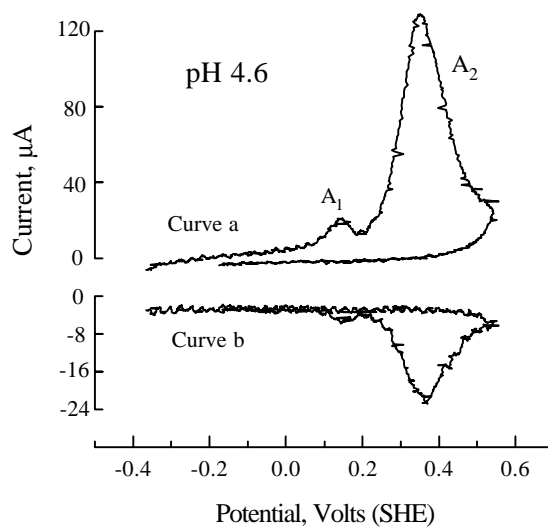


Figure 2-10. Ring disc voltammograms of the CMC:ZnS electrode activated after activation in pH 4.6 10^{-4} M CuSO_4 solution at -0.305 V for 2 minutes. The ring potential was held at -0.55 V. Rotation rate 2000 rpm.

2.4.b. Identification of Open Circuit Activation Surface Product

Figure 2-11 shows the changes in the rest potential of a CMC:ZnS electrode before and after copper activation at pH 4.6. Also shown for comparison are the rest potentials of covellite, chalcocite and copper electrodes measured in the same activating solution. It can be seen from the figure that the increase of the potential upon the addition of cupric ions is rather fast (from 0.2 V to 0.38 V in 30-50 seconds), indicating the fast kinetics of the activation process. The potential of the sphalerite in cupric solution shown in Figure 2-3 (0.38 V) is between the phase boundary of chalcocite (Cu_2S) and covellite (CuS) (but more close to the rest potential of covellite), considering that the copper sulfide formed on sphalerite surface is metastable, it is most likely that the activation product is CuS . However, it is difficult to determine the composition of the activation product based only on the rest potential measurements. Further refinement in the rest potential measurement and more detailed study are necessary to provide a better understanding of the nature of the activation product formed at open circuit.

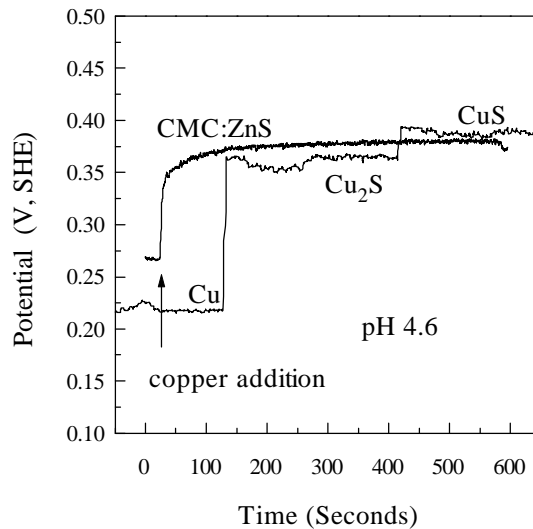


Figure 2-11. Rest potential measurement of the CMC:ZnS electrode immersed in a 10^{-4} M CuSO_4 solution at pH 4.6. The measurement was conducted while stirring the solution.

Figures 2-12 and 2-13 show voltammograms obtained on the CMC:ZnS electrode in the inert buffer electrolyte after activation at open circuit for 5 minutes in 10^{-4} M CuSO_4 . For Figure 2-12, the voltammogram was initiated in the positive-going direction from the rest potential (~ 0.2 V); for Figure 2-13, the voltammogram was initiated in the negative-going direction from the rest potential. These two figures established that the product(s) of copper activation is both oxidizable (Figure 2-12) and reducible (Figure 2-13). The anodic peak occurring at ~ 0.35 V (Figure 2-12) is probably due to the reaction:

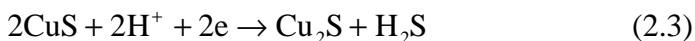


On the return cathodic scan following oxidation, there are two reduction peaks at 0.15 V and -0.3 V, respectively. The first peak at 0.15 V maybe the reverse of Reaction (2.1); while the second peak at -0.3 V may be the reduction of elemental sulfur to HS^- at this pH through reaction:

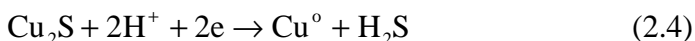


whose $E_h = 0.076$ V at pH 4.6, when $[\text{H}_2\text{S}] = 10^{-7}$ M.

On the other hand, when the first sweep was initiated in the negative-going direction, a well-defined reduction process occurs with a peak at ~ -0.25 V. (Figure 2-13). Ring disc studies (not shown) show that a soluble product is produced by this reduction reaction on the gold ring. The peak at -0.25 V is thus consistent with the reduction of the product of activation to form H_2S and copper sulfide of higher copper-to-sulfur ratio, e.g. Cu_2S through reaction like:



whose $E_h = 0.04$ V at pH 4.6, when $[\text{H}_2\text{S}] = 10^{-7}$ M, and reaction:



whose $E_h = -0.37$ V at pH 4.6 and 10^{-7} M $[H_2S]$.

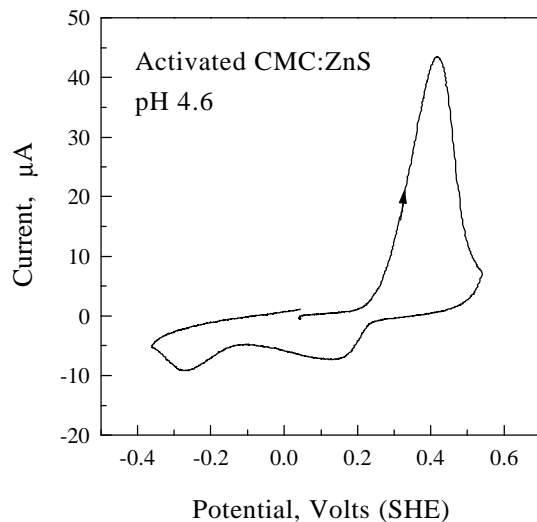


Figure 2-12. Voltammogram of CMC:Zn electrode after activation in pH 4.6 10^{-4} M $CuSO_4$ solution for 10 minutes. Sweep rate 25 mV/s. First sweep positive-going.

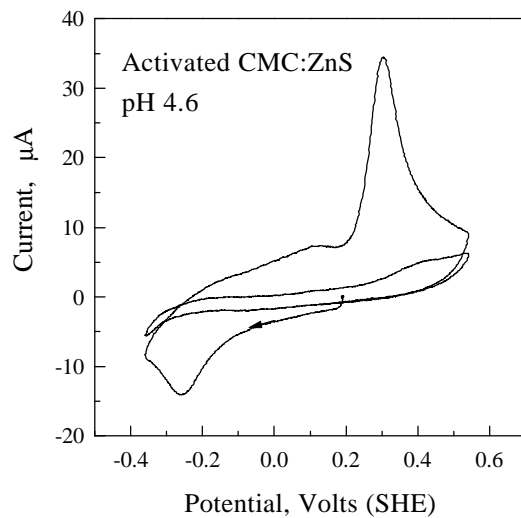


Figure 2-13. Voltammogram of CM:ZnS electrode after activation in pH 4.6 10^{-4} M $CuSO_4$ solution for 5 minutes. Sweep rate 25 mV/s. First sweep negative-going.

On the return anodic sweep, a new oxidation process is observed at 0.15 V, which can be attributed to the oxidation of elemental copper.

The results shown in Figures 2-11 to 2-13 suggest that the product formed during the open circuit activation is most likely CuS-like.

2.4.c. Activation under Controlled Potential Conditions

XPS studies of sphalerite by Katio et al. (1996) showed that copper uptake increases when the activating solution is purged of oxygen. This suggests that by controlling the activating potential, one can control the copper uptake on the sphalerite during activation. To study the effect of potential on copper uptake, a CMC:ZnS electrode was immersed in a 10^{-4} CuSO₄ solution at pH 4.6 while holding the potential at a given value and measuring the current as a function of time. After 10 minutes of activation, the electrode was replaced in a copper-free pH 4.6 buffer solution to conduct voltammetry experiments. Figure 2-14 shows the results obtained after activation at -0.05 V. The insert shows the current-time curve obtained during the controlled potential activation. As discussed in the earlier section, the anodic peak starting at ~0.2 V represents the oxidation of elemental copper deposited on CMC:ZnS electrode, while the larger anodic wave is due to the oxidation of the activation product (copper sulfide species). The negative current in the insert indicates that copper-activation of sphalerite at such a low potential involves a reduction reaction between copper activated ZnS and Cu²⁺ ions in solution. At open circuit, however, the activation process may be represented by the metathetical substitution given by Reaction (1.1). Compare Figure 2-14 with the voltammogram obtained after open circuit activation (Figure 2-5), it is clear that activation at reducing potential significantly increases the copper uptake, as indicated by the height of the peak at 0.4 V.

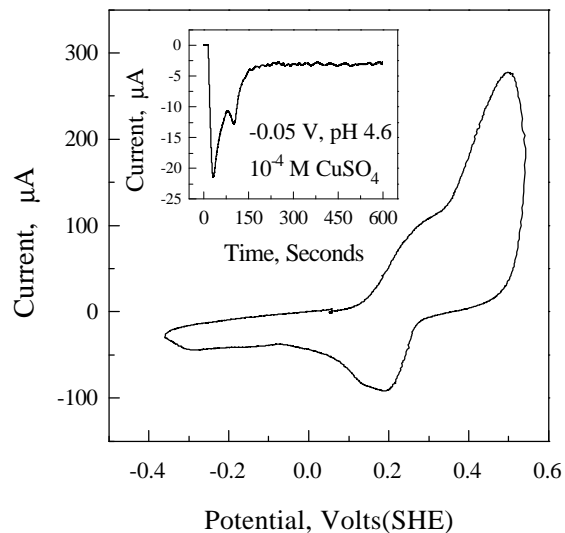


Figure 2-14. Voltammograms of CMC:ZnS electrodes after activation in pH 4.6 10^{-4} M CuSO_4 solution at -0.05 V for 10 minutes. The insert is the current-time curve obtained during activation. Sweep rate 25 mV/s.

2.4.d. Chemical Analysis of Stripping Solutions

A CMC:ZnS electrode was activated in a CuSO_4 solution, electrochemically stripped off the activation products in a small volume of pH 4.6 buffer solution, and the stripping solution was analyzed for copper and zinc by means of an inductively-coupled plasma (ICP) analyzer. The activation was carried out in a pH 4.6 10^{-4} M CuSO_4 solution for 10 minutes. The chronoamperometry curves were recorded during activation. The stripping was done by sweeping the electrode from the rest potential to 0.55 V at a sweep rate of 5 mV/sec. Table 2-1 shows the results obtained with the CMC:ZnS electrodes activated at open circuit (0.375 V) and at 0.145 V (to avoid Cu^0 formation). The amounts of copper determined by ICP are compared with those determined from the charges passed during activation (from the chronoamperometry curve) and during stripping (from the area under the anodic stripping peak of the voltammogram).

The results given in Table 2-1 show that only copper is dissolved during the anodic polarization. One might expect that zinc should also be detected in the stripping solution, because ZnS is less noble than CuS. However, the ICP analysis shows no detectable zinc. It is important to note also that the copper uptake increased substantially when sphalerite was activated at a potential

(0.145 V) lower than the open circuit potential (0.375 V).

Table 2-1. Amount of Copper Present in Stripping Solutions as Determined by ICP

<u>Potential for Activation</u>	<u>Amount of Copper in 10 ml Solution, μg</u>		<u>ICP</u>
	<u>Charge Analysis Activation</u>	<u>Stripping</u>	
Open Circuit (0.375V)	-	0.88	0.29
0.145 V	2.33	2.15	0.54

Zn was below detection limit.

When the CMC:ZnS electrode was activated at 0.145 V, the amount of copper abstracted during activation (2.33 μg) was close to that stripped during anodic polarization (2.15 μg). Apparently, the activation product forms a thin film on sphalerite, which is readily removed by anodic polarization. Note, however, that the amount of copper detected by ICP is 3 to 4 times lower than the amounts determined by the charge analysis for activation at open circuit and at 0.145 V. It is possible that some of the copper was deposited on the counter electrode during stripping, or that the oxidation process during stripping involves more than 2 electrons.

2.4.e. Potential Dependence of the Activation Process

The results obtained in Figure 2-14 indicate that there might exist an optimum activation potential at which the efficiency and selectivity of the activation is the best. A series of activation and voltammetric experiments were carried out in search of the optimum activation potential condition. Figure 2.15 shows chronoamperometry curves obtained while holding the potentials at different potentials during activation. Typically, a current begins to flow approximately 3 seconds after the addition of CuSO_4 . The current reaches a maximum 20-50 seconds after the addition of the activating agent, depending on the activation potential, and then decays rapidly and

reaches a steady-state value several minutes after the Cu^{2+} ion addition. As shown, cathodic currents were observed below 0.2 V partly due to the reduction of Cu^{2+} to Cu^+ ions and partly due to enhanced copper uptake on ZnS. The reducing current increases with decreasing potential, indicating a faster kinetics. On the other hand, an anodic current was observed at 0.375 V, most probably due to the oxidation of the oxidation product formed via Reaction (1.1). As shown earlier by the ring disc voltammetry and the ICP analysis of the stripping solutions, oxidation of activation product results in a loss of copper from activated sphalerite, i.e., deactivation occurs.

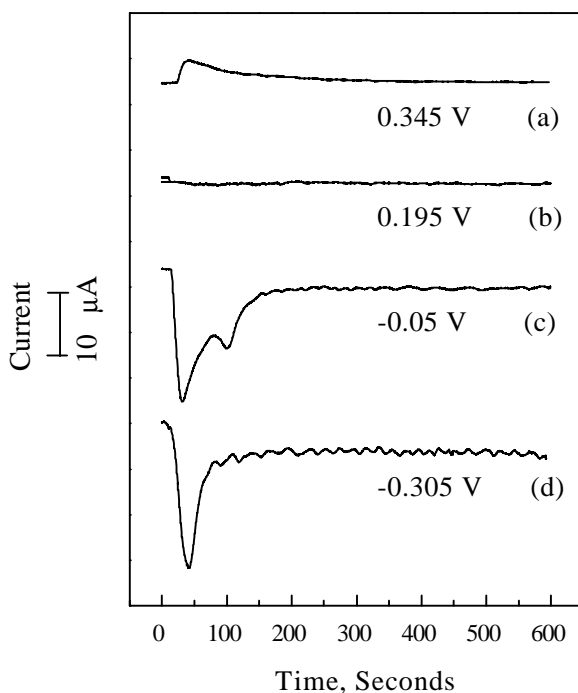


Figure 2-15. Current-time curves obtained when activating CMC:ZnS electrodes in pH 4.6 10^{-4} M CuSO_4 solution at different potentials for 10 minutes.

Figures 2-16 shows a series of voltammograms of the CMC:ZnS electrodes activated at different potentials. Each curve shows the first-sweep voltammogram obtained by sweeping in the positive-going direction from the rest potential in the copper-free solution. The area under each anodic wave effectively represents the total copper uptake during the 10-minute oxidation time.

As shown, the copper uptake increases with decreasing potential of activation, which may be of considerable practical importance as a method of increasing the efficiency of copper activation and reducing consumption of CuSO_4 .

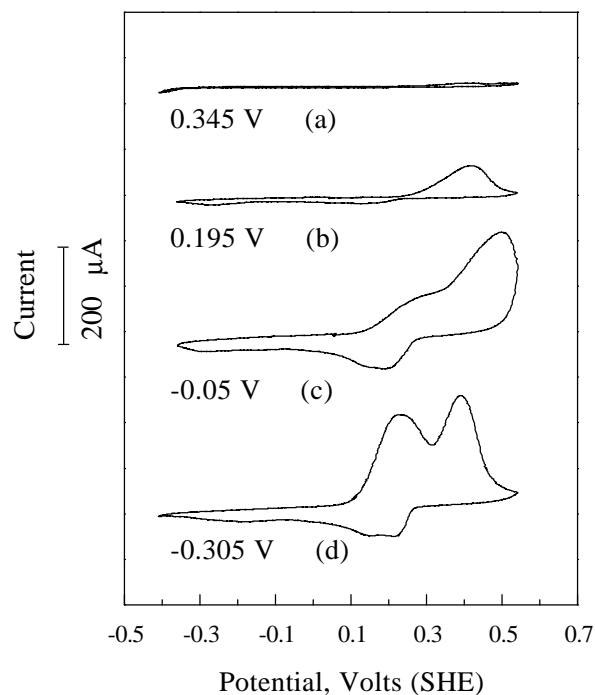
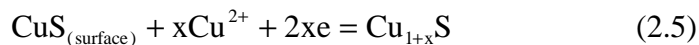


Figure 2-16. Voltammograms of CMC:ZnS electrodes after activation in pH 4.6 10^{-4} M CuSO_4 solution for 10 minutes at different potentials. Sweep rate 25 mV/s.

When the CMC:ZnS electrode is activated at potentials -0.05 V and below, the charge passed during the activation process is equal to that calculated by integrating the anodic oxidation peaks during voltammetric experiments. For activation at potentials above the open circuit potential, oxidation currents were observed during activation; therefore, charges passed during anodic scan is much smaller than those observed during open circuit activation. These results suggest that activation under reducing conditions can greatly increase the copper uptake. The increased copper uptake may involve a reduction of the form:



However, if the activation was conducted at potential below the formation of elemental copper, the selectivity of the activation will be worsened since copper can also deposit on carbon and other minerals.

The most important result of the present investigation is the possibility that controlled potential activation of sphalerite may offer a means of controlling the activation process. If the activation is carried out under mildly reducing conditions, copper uptake increases substantially, which may be conducive to increased flotability of the mineral. On the other hand, activation under oxidizing condition provides a means of deactivating the mineral or a means to prevent inadvertent activation.

2.5. Summary and Conclusions

1. Rest potential measurement, rotating ring disk voltammetry and chemical analysis conducted using the CMC electrode established that the CMC:ZnS electrode is a reproducible, durable tool for electrochemical study of the activation of sphalerite. It provides a reliable means of quantitative direct measurement of copper uptake on the sphalerite surface.
2. Voltammetric experiments conducted in cupric solution using CMC:ZnS electrode show that a conducting layer started to form on ZnS when the potential is lower than 0.2 V. Elemental copper may form on the mineral and carbon surface when the potential is lower than that for elemental copper to form, affecting the selectivity of the activation.
3. The rest potentials of activated CMC:ZnS is close to CuS phases in the E_h -pH diagram of the Cu-S-H₂O system; suggesting that the activating product at open circuit is CuS-like. The voltammetric experiment of activated CMC:ZnS electrode also showed that the activation product is both oxidizable and reducible and may be CuS-like. Depending on the potential of the activation, the activating product may vary from CuS to Cu₂S and even Cu⁰.

4. Activation at reducing potentials increases the copper uptake substantially. The additional copper uptake may involve an electrochemical activation mechanism, in which Cu^{2+} ions are reduced to Cu^+ ions, as is evidenced by the reducing currents during activation. Activating at oxidizing conditions leads to loss of copper from the surface.

5. Activation of sphalerite under controlled potential conditions provides a means of controlling the amount of copper on the mineral surface and, hence, the flotation process.