

Chapter 1

Introduction

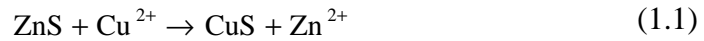
1.1 General

Sphalerite (ZnS) is a major source of zinc metal. It usually coexists with other sulfide minerals such as chalcopyrite, galena and pyrite. Its concentration is accomplished by froth flotation using short-chain thiol collectors such as xanthate. Due to its unique chemical and structural characteristics, the concentration of sphalerite by flotation requires activation, which is a process of making the mineral susceptible to reactions with the thiol collectors. The kinetics of activation, activation mechanism and identification of the activation products have been the subject of intensive research effort since 1920s. However, none of the previous investigations addressed the electrochemical aspects of the activation mechanisms and of the activation products. The reason was that sphalerite is an insulator, which makes it difficult for the mineral to be used as an electrode. A recent electrochemical study conducted using carbon paste electrode, which was made of sphalerite particles (Richardson, et al, 1994) revealed that the activation of sphalerite and the subsequent adsorption of thiol collectors on the surface are controlled by electrochemical mechanisms. However, this electrode is difficult to reproduce, and is not rigid enough to be used as a rotating electrode. More sophisticated technique needs to be developed to study the electrochemistry of sphalerite activation and the activation products, so that new information can be obtained for controlling the activation process and, hence, improving the flotation performance.

1.1.a. Activation and Flotation of sphalerite

Sphalerite (ZnS), unlike most other sulfides, floats poorly with short-chain xanthates and other soluble thiol collectors. The most frequently cited reason is the high solubility of zinc-thiol compounds in water as compared to those of others. For example, the pK value for zinc ethyl xanthate is 8.31, while that of copper ethyl xanthate is 19.3. One solution to this problem is to

activate the mineral by the following reaction:



so that copper sulfide (CuS) is formed on the surface. The xanthate collector can then react with the activation product to form an insoluble copper xanthate coating *via* a corrosion-type, mixed potential reaction such as



coupled by a reduction reaction like:



which renders the mineral surface hydrophobic.

In practice, to separate sphalerite from other sulfide minerals such as galena and chalcocite, typically, copper sulfide and galena are floated first using thiol collectors. Sphalerite is then activated by copper sulfate before floating the mineral using thiol collectors. In this case, efficient activation is important to achieve good recovery and low copper consumption. In some cases, sphalerite is activated and floated together with copper and lead sulfides to obtain a bulk concentrate. While sphalerite is deactivated by cyanide, galena and chalcocite will be floated. In either case, the control of activation, deactivation and depression is essential to the selectivity and recovery of the flotation of sphalerite.

Finkelstein and Allison (1976) defined the process of activation, deactivation and depression as follows:

Activation is a process whereby the surface of a mineral particle is modified so as to make it react more readily or strongly with a collector.

Deactivation is a process whereby an activating agent is removed from the surface of a mineral, thereby rendering it less able to react readily and strongly with a collector.

Depression is a process whereby the surface of a particle is modified in such a way as to render it more wettable by water.

For flotation to occur, it is important to have a stable hydrophobic film of xanthate product on the surface of sphalerite. To achieve this purpose, a stable activation product which can later react with xanthate to form insoluble metal xanthate species needs to be formed first during activation.

1.1.b. Objectives

The purpose of the present work is to develop new electrodes to study *in situ* the electrochemical behavior of sphalerite; to provide a reliable quantitative measure of copper uptake on sphalerite surface; to investigate the E_h and pH dependence of copper activation of sphalerite; to study the mechanisms of the xanthate adsorption on activated sphalerite surface, and to investigate the hydrophobicity of the adsorbed xanthate coating.

To achieve these goals, two new electrodes, namely Carbon Matrix Composite (CMC) electrode and Surface Conducting (SC) electrode, will be developed based on the previously used carbon paste electrode. Using the CMC electrode made of ZnS particles and carbon powder, electrochemical experiments will first be conducted under acidic conditions to test the performance of the electrode and to obtain general characteristics of the activation product(s). Chemical analysis methods will be used to help identify the activation product, and to establish a method for *in situ* quantitative measurement of the amount of copper uptake on the mineral surface. The effect of activating potential on copper uptake and the activation product at acidic pH will then be investigated. Since sphalerite flotation is mostly operated under alkaline conditions, studies will be conducted at alkaline pH using both the CMC and the SC electrode to investigate the activation at open circuit potential and controlled potential conditions. Based on the results collected, the optimum activation condition at alkaline pH will be established. The

activation of sphalerite by copper at neutral pH, the effect of activating potential on the activation process and the amount of copper uptake will also be studied. SC electrode will be used to investigate the subsequent xanthate adsorption process and to develop new methods to increase the surface hydrophobicity at near neutral pH range.

Emphasis will be made throughout the present investigation to study the role of activating potential on copper uptake, activation efficiency and deactivation. The flotation of sphalerite is known to be sensitive to pH, electrochemical methods will be used to study the activation kinetics at different pHs. Efforts will be made to better understand the poor flotation response of sphalerite at near neutral pH conditions from the activation and xanthate adsorption aspects. Based on this study, it may be possible to achieve better flotation response using new chemical and electrochemical treatments. Microflotation tests will be conducted using single mineral to verify these possibilities.

Other than sphalerite, copper can also activate minerals such as pyrite. Since sphalerite always co-exists with other sulfide minerals such as pyrite, chalcopyrite and galena, the effect of copper on these minerals may have direct impact on the selectivity and recovery of zinc flotation. In this dissertation, the activation of pyrite by copper will be studied under flotation related conditions.

1.2. Literature Review

In 1976, Finkelstein and Allison reviewed the work conducted in 50 years related to the activation, deactivation and depression of sphalerite. Twenty years later, Finkelstein (1997) thoroughly surveyed the same topic and updated the literatures again. In the latter review, Finkelstein also included new investigations conducted from 1976 to 1997 on the activation of other sulfide minerals. These two papers have been used as the primary source for the literature survey in the present dissertation.

1.2.a. Activation of sphalerite

Although copper sulfate has been used as an activator many years before xanthate were adopted to flotation, it is believed that copper activation of sphalerite was accidentally introduced to sphalerite flotation in 1914 (Ralston, et al, 1930). Since then, large amount of experiments have been conducted to study the activation process and the subsequent xanthate adsorption in order to achieve better selectivity and recovery in sphalerite flotation.

The past eight decades has seen a lot of improvement on sphalerite flotation thanks to the better understanding of the activation and xanthate adsorption process. It is generally accepted today that sphalerite floats poorly with short chain xanthate collectors. This has been clearly established by Gaudin in 1930, who resolved earlier uncertainty by his demonstration that with pure unactivated sphalerite no recovery was obtained with ethyl xanthate, a moderate recovery with amyl xanthate, and complete recovery with hexyl xanthate. Similarly, Wark and Cox (1934) were able to measure the critical pH values for sphalerite flotation with amyl xanthate but not with ethyl xanthate. There are several explanations for the relatively weak interaction between sphalerite and short chain xanthate. Some (Klassen and Mokrousov, 1963) suggested that zinc xanthate is so soluble that they would dissolve from the mineral surface, while others (Dixon et al., 1975) suggested that the high band gap of sphalerite makes it kinetically inert towards the adsorption of anions such as xanthate. Maust and Richardson (1976) proposed that the electron-to-hole ratio at the surface is too high to permit the lower xanthates to chemisorb. The relatively low free energies of formation of zinc xanthates seem to play a role in the poor interaction between sphalerite and the collector. In fact, this has been shown by Clifford (1975) that at the optimal pH of 3.5, about 7×10^{-2} M of ethyl xanthate is required before an appreciable recovery of sphalerite is obtained.

Due to the reasons described above, an activation process is required prior to the flotation via Reaction (1.1). The activation product (CuS-like species) can then react with xanthate to form insoluble copper xanthate species through an electrochemical reaction such as Reaction (1.2). The insoluble CuX species will render the mineral surface hydrophobic.

1. Identification of the surface activation product

It is important to have a clear identification of the activation product under different conditions, so that effective chemical treatment can be applied for better control of the activation process and, hence, the flotation performance. Early studies were focused on the identification of the surface product formed after activation. Due to limitations in the experimental techniques available at the time, debates on whether a visible film of copper sulfide species is formed on sphalerite surface was the topic of nineteen twenties. Famous investigations include Tucker and Head (1926), who used large cleavage surfaces of pure minerals, covered in half with paraffin and inserted into a copper sulfate containing flotation pulp. They observed that when the paraffin film was removed, the uncovered mineral surface was coated with an unknown film. Other researchers (Taggart and Ince, 1926) have criticized this observation. Ralston et al. (1930) confidently concluded that an invisible but physically detectable film of copper sulfide is formed when using copper sulfate as an activator in the flotation of sphalerite. Their conclusion was evidenced by increased electric conductivity, by chemical metathesis and by the ability to deactivate with solutions of alkali cyanides, which are now known as solvents of copper sulfides. In the fifties, more attempts were made for direct identification of the product of reaction. Cooke (1950) activated sphalerite in a cupric solution under extreme conditions (100°C for 50 days) and obtained a thick blue coating, which X-ray analysis showed to be covellite. Sato (1957) used electron diffraction spectrometry, obtained only the most diffuse diffraction patterns from both thick and thin layers of product and was not able to draw any positive conclusions as to its nature. On the other hand, some researchers (Gircys et al., 1972) suggested that adsorbed cupric hydroxide complexes are the activation species in neutral and alkaline solution. Wentworth pointed out as early as in 1910 that activated sphalerite particles become conductive and were able to be separated from gangue minerals by means of electrostatic separation, like other conducting sulfide minerals. This finding microscopically proved that an invisible conducting film was formed after activation by copper. However, much of the work mentioned above relies on classical solution chemistry methods of determining the rate and extent of the adsorption of copper and the generation of soluble zinc and sulfur compound, and hence gives no direct identification of the product of reaction and their distribution at the surfaces. Moreover, at this stage, debates were focused on whether the activation product is copper sulfide or simply copper

hydroxide adsorbed at alkaline pH. No suggestions were made on what kind of activation product is flotation effective.

In the early eighties, as the new surface analysis techniques were developed, direct identification of the surface product was made possible. A number of studies used XPS (X-ray photoelectron spectroscopy), Auger spectroscopy, and mass spectrometry. These techniques allowed the elements present at the surface to be identified and, in favorable cases, their chemical form to be distinguished. They provided a more definite picture than do deductions from the classical methods. With several exceptions, all XPS studies on the activating system agree that Cu(I) is present at the surface (Perry et al, 1984; Cecile, 1985; Buckley et al, 1989; Kartio et al, 1996; Prestige et al, 1997), and this holds good after the activation penetrated many layers into the lattice (Prestidge et al, 1994). It is also agreed that Cu(II) is not present when the activation is carried out in acidic conditions. However, debate is still focused on whether Cu(II) is present as well as Cu(I) when the reaction is carried out at alkaline conditions. The argument is largely based on the reliability of the experimental results obtained by XPS.

Conventional XPS consists of a Mg or Al anode that produces X-ray, which are bombarded on the surface of the solid surface and the surface release photoelectrons that can be captured and analyzed. Each element, depending on its oxidation state has a characteristic peak associated with a particular binding energy and this is used to identify the elements and compounds. The biggest problem with XPS as with most other spectroscopic methods is that it is an ex-situ method. As a result, the surface chemistry of the mineral may change. The sample may be oxidized during the process of transferring it from solution to the vacuum chamber. Physisorbed species such as metal hydroxy species may be destroyed during sample cleaning and transferring. Some researchers (Smart et al, 1991) claim that they have overcome this problem by placing an aqueous bath outside the XPS in such a way that the sample can be rotated from the bath to the vacuum chamber directly to be analyzed. It yet needs further confirmation.

Another problem associated with the XPS is the risk of photo-reduction. Although, most of the XPS research show that the copper is indeed in the Cu(I) form, supporters of the Cu(II) theory claimed that it is actually the X-ray beam that reduces the existing Cu(II) form to Cu(I).

Perry et al. (1984) reported that in some cases, the spectra indicated Cu(II) to be present in addition to Cu(I). They attributed this to the adsorption of cupric oxide or hydroxides on the sphalerite surface. Prestidge et al. (1994) obtained clear and consistent evidence for the presence of Cu(II) at the surface of ZnS immediately after abstraction of quantities of copper in excess of a monolayer at pH 9. They also showed that only Cu(I) penetrates deeper into the lattice. Skinner et al. (1996) pointed out that the detection of Cu(I) is actually due to the photo-reduction of the copper hydroxide complexes which are held weakly and reversibly at the sphalerite surface at the alkaline conditions. Other factors such as the experimental details (rinsing procedure) may also affect the chemical composition of the surface product.

Another disadvantage of the conventional XPS is that it probes a depth of several nanometers, and therefore provides a picture of the situation in the upper 10 to 30 layers rather than that at the interface itself. The application of synchrotron XPS (SR-XPS) overcomes this problem. It has the advantage that it produces low energy X-rays as compared to conventional XPS. Therefore both the kinetic energy of the photoelectrons and the depth of the surface from which they escape is greatly reduced. Hence, information can be obtained about the top-most layer of the surface. Katio et al. (1996) used SR-XPS to study the copper-activated sphalerite surface and could not detect any Cu(II) species on the surface. They identified, however, a polysulfide species on the mineral surface when the activation product was treated under oxygen saturated environment.

The most serious problem of XPS is the method of data processing. Since the interpretation of results obtained by XPS relies on the mathematical method of resolution, for the same set of results, different interpretations are possible depending on the choice of the method of resolution. Hence, it is less reliable. Moreover, it is impossible to use XPS to quantitatively measure the amount of the surface product. It is, therefore, necessary to substantiate XPS results with other methods like electrochemistry, etc.

Measurements of electrokinetic properties have also been used to identify the activation product as well as to study the kinetics of the activation process. Girceys, et al. (1972) postulated that the $\text{Cu}(\text{OH})_2$ coatings are likely to be the product layers on the sphalerite activated by Cu^{2+} ions

in alkaline solutions. Hukki, et al. (1952) are among the first to use electrokinetic measurements to study the sphalerite-copper system. They showed clearly a bump on the zeta potential-pH curve for sphalerite in the presence of cupric ions. Laskowski et al. (1997) confirmed this finding after forty-five years. They 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, zeta potential becomes negative at neutral pH range, and the electrokinetic behavior is similar to chalcocite. Healy and his co-worker (1976) also studied the electrokinetic behavior of different sulfide minerals and observed positive zeta potential on oxidized chalcocite (Cu_2S) at neutral pH range. After comparing with the electrokinetic behavior of metal oxide reported by James and Healy (1972), Laskowski et al attributed their observations to the adsorption of $\text{Cu}(\text{OH})^+$ on ZnS surface, forming a “flotation inactive” product when the conditioning time is short. At the mean time, they suggested 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. Hence, a long activation time is required to achieve good flotation recovery in alkaline pH.

Compared with the surface analysis techniques such as XPS, the electrokinetic measurement certainly has the advantage of being made in situ. However, the quantitative measurement of the surface product still relies on chemical analysis to collect the concentration of the ions of interest in the solution before and after activation and, hence, the results are obtained indirectly. More than that, at neutral and alkaline pHs, the presence of copper hydroxide precipitate will largely affect the accuracy of the results.

Like other sulfide mineral systems, attempt has been made by researchers using thermodynamic calculations to predict the surface product on sphalerite in xanthate system. (Wang et al., 1989b). Due to the lack of thermodynamic data, the calculation of sphalerite-activator system is not as promising as obtained in other sulfide mineral systems.

Finkelstein and Allison (1976) thoroughly reviewed the research on activation of sphalerite in 1976, before the experimental evidence of Cu(I) was even provided by XPS. After analyzing the crystal structure of sphalerite and different copper sulfide minerals, they proposed

a different theory. They accepted that the activation would eventually form copper sulfide product. However, they argued that the final stable form of the activation product cannot be $\text{Cu}^{2+}\text{S}^{2-}$ since cupric sulfides are not stable under normal conditions. They also disagreed that the surface product is covellite since the crystal structure of covellite differs markedly from that of sphalerite. In addition, the formation of the covellite structure requires a number of layers of copper to be present. They suggested that the unstable $\text{Cu}^{2+}\text{S}^{2-}$ would be reduced to the form Cu^+S^+ . This was confirmed by XPS later (Perry et al, 1984; Cecile, 1985; Buckley et al, 1989; Kartio et al, 1996; Prestige et al, 1994, 1997).

In the same year, Maust and Richardson (1976) proposed theoretically that for a particular metal ion to be an activator, it must act as an electron acceptor so that it can be reduced as follows:



As a result of which sphalerite becomes a p-type semiconductor at the surface and its band gap is reduced enough to host mixed potential reactions (Ralston et al., 1980a, b). Several research groups (Ralston, 1930; Bushell et al, 1961; Wang et al, 1989d) have in fact observed the electrochemical dependence of copper activation of sphalerite independently. However, no connection between activating potential and the extent of activation was taken into consideration by researches, most probably due to the common sense that sphalerite is an insulator, so that electrochemical study is not possible with sphalerite mineral. Research group in Center for Coal and Minerals Processing at Virginia Tech first conducted electrochemical study using carbon paste electrode and confirmed that the copper-activation of sphalerite and its subsequent xanthate adsorption are electrochemical in nature (Richardson et al, 1994).

Although many theories have been put forward regarding the activation product, in flotation, the most important question is what kind of activation product would be effective for the subsequent xanthate adsorption so that hydrophobic surface layer can be formed. Ralston and Healy (1981) stated that flotation requires that the hydrolyzed products be converted to the sulfide form. Wang et al. (1989c) suggested more clearly that it is the sulfide form of the activator at the surface that accounts for the selectivity of the flotation of different sulfide

minerals. Laskowski et al. (1997) proposed that for the xanthate adsorption to occur, a ‘flotation active’ activation product is necessary. These authors pointed out that this ‘flotation active’ product is copper sulfide.

2. *Kinetics of activation:*

From flotation practice point of view, researchers paid a lot of attention on the kinetics of copper-activation of sphalerite. The studies showed that the activation would last as long as the cupric ion is in the solution. Gaudin et al (1959) observed that copper was still being abstracted from solution after 63 hours. Although different research groups used different method to investigate the activation rate, they reached the same conclusion: the activation reaction takes place in two stages. First is a rapid reaction during which the equivalent of 2 to 5 monolayers are taken up in 5 to 15 minutes; and then followed by a much slower reaction. The rate of the copper uptake is defined to be a strong and direct function of the concentration of copper added to the system. Gaudin found that the reaction obeys the first order kinetics and can be fitted to a rate equation:

$$dq/dt = k A [Cu^{2+}] \quad (1.5)$$

Where q is the quantity of the copper adsorbed, A is the surface area of the surface and k is the rate constant.

More systematic research on the adsorption of Cu(II) on sphalerite was conducted by Jain and Fuerstenau (1985) under acidic conditions for more than 64 hours, during which up to 19 monolayers were adsorbed. It was observed that about 3 monolayers were adsorbed during the first 15 minutes (the rapid first stage), during which the rate followed a direct logarithmic law:

$$A = k \log t + \text{constant} \quad (1.6)$$

These authors also found that the rate depended on agitation; hence, it was concluded that diffusion in the solution phase was rate-determining. Bazanova and Mitrofanov’s data (1961,

1962) support this relationship.

The second stage, from 15 minutes to 64 hours, followed parabolic kinetics:

$$A = k t^{1/2} + \text{constant.} \quad (1.7)$$

This is in agreement with the results obtained by Gaudin and other earlier researchers.

Ralston et al. (1980a, b), on the other hand, used ion-selective electrodes and atomic absorption spectroscopy to study the activation kinetics in weakly acidic and neutral to weakly alkaline media and proposed that the activation of sphalerite by copper has three stages. In the first stage, a monolayer was adsorbed in 1.5 minutes, followed by a half monolayer in the second stage of 15 minutes. The adsorption in these two stages was described by a direct logarithmic relationship. After 15 minutes, the third stage, the copper uptake either becomes independent of time of activation or increases very slowly up to 120 minutes. During this period, there is no well-defined rate equation according to their results.

Although the above research provided valuable information on the nature of the activation and the reaction rate of the activation process, none of them can really be related to the flotation practice. First, these studies were conducted at different pH values, which make it difficult to compare with each other. Secondly, the copper uptake reported by the above researchers, were taken from the differences in the concentration of the activating solution before and after the activation process. Therefore, it is not a direct measurement of the copper adsorbed on the sphalerite surface. This makes the reported kinetic relationship less reliable. Moreover, the kinetic study has been over-focused on how to fit the data into rate law. As a result, there is little suggestion on what surface species is effective for the subsequent xanthate adsorption and how to improve or control the flotation process. It is necessary to develop more reliable method to quantitatively study the activation process.

3. *Activation Mechanisms*

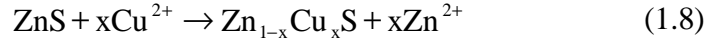
The mechanism of the activation has been studied extensively by a lot of researchers. As suggested by Reaction (1.1), the driving force for the activation reaction is the difference in free energy between ZnS and CuS. However, not everyone agreed that the activation reaction is a simple chemical replacement reaction, as described by Reaction (1.1). In fact, there are three major mechanisms being proposed by different research groups.

a. Chemical replacement: CuS

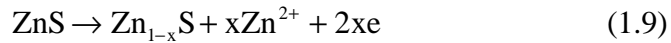
Until 1994, this is the most widely accepted activation mechanism. As early as 1930, Ralston et al. conducted comprehensive studies on the sphalerite-copper system as well as other minerals like pyrite and chalcopyrite. After pure sphalerite samples were treated with copper sulfate solution for 24 hours (acidic pH), the pulps were filtered and the filtrate was analyzed for copper and zinc. They found that in acidic solutions, the ratio between zinc released and the copper consumed is very close to unity. Based on this observation, these authors proposed that a metathetical reaction has taken place between the zinc sulfide and copper sulfate solution. Other researchers (Gaudin et al, 1959; Pomianowski, 1975; Cooke, 1950; Fuerstenau, 1982; Cecile et al., 1985) obtained similar results. Finkelstein et al. (1976) reviewed the work on sphalerite activation in 50 years and agreed that the activation is indeed the replacement of copper with lattice zinc, but the process is complicated. They proposed that the activation first forms a $\text{Cu}^{2+}\text{S}^{2-}$ surface product in the first rapid stage of activation, and then converted to covellite-like Cu^+S^+ . This mechanism is supported by the XPS results that Cu(I), not Cu(II), is detected on the activated sphalerite surface.

b. Formation of bi-metallic sulfide compounds: $\text{Zn}_x\text{Cu}_y\text{S}$

Maust and Richardson (1976) suggested that during the early stages of activation, a distinct copper sulfide compound is not formed. Rather, copper substitutes zinc in the lattice, forming an acceptor-like surface state. More recently, Buckley et al. (1989) concluded from XPS studies that during the early stages of activation, copper ions from solution substitute zinc ions in the lattice



forming a mixed sulfide, which may be considered as a solid-solution. The authors considered the initial oxidation product metastable because copper ions substitute zinc ions without significantly distorting the lattice structure in the vicinity. The S(2p) spectrum of the sphalerite sample activated in an air-saturated copper sulfate solution showed an additional component at higher binding energy. The shift was attributed to the oxidation of sphalerite by the following reaction:



and not to the incorporation of copper in the sphalerite lattice *via* Reaction (1.8). The S(2p) component at higher binding energy accounted for 20% of the total sulfur on the surface. Thus, Reaction (1.9) suggests an oxidation mechanism of activated sphalerite. Buckley and Woods (1989) named the activation product under oxidation condition a ‘metal deficiency’ sulfide.

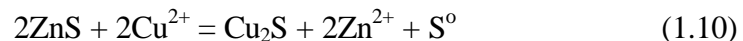
c. Electrochemical reaction: potential dependent activation product

The electrochemical nature of the activation process was first taken into consideration by Maust and Richardson, who proposed that for a particular metal ion to be an activator, it must act as an electron acceptor by reduction reaction through Reaction (1.4), so that sphalerite become a p-type semiconductor at the surface and its band gap is reduced enough to host mixed potential reactions (Ralston et al., 1980a). XPS studies conducted by many investigators (Clifford et al., 1975; Kartio et al., 1996) showed indeed the presence of Cu(I) rather than Cu(II) on activated sphalerite surfaces, supporting the activation suggested by Reaction (1.4). The potential dependence of the activation process has actually been observed by other researchers long before the electrochemical studies have been conducted. Ralston et al. (1930) 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. (1989d) 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. The XPS results

obtained by Kartio et al. (1996) showed that copper uptake by sphalerite was higher in deoxygenated CuSO_4 solution as compared to the case of activation in air-saturated solutions.

Although attempt has been made by Bessiere et al. in 1990 to study the electrochemical behavior using a fluidized bed electrode of activated sphalerite particles. However, inconclusive results were obtained due to the limited performance of this technique. Richardson et al. (1994) used a carbon paste electrode made of sphalerite particles to investigate the activation process and found that the activated surface product 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 as well as the reaction of collectors and other reagents with activated sphalerite. More work needs to be conducted to characterize the electrochemical behavior of the activation process and the activation product(s).

Other mechanisms have also been proposed. For example, some (Prestidge et al., 1994; Nefedov et al., 1980; Perry et al., 1984) suggested that the activation forms chalcocite (Cu_2S) and elemental sulfur through reaction like:

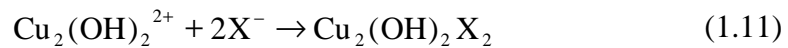


Others suggest that the activation in fact does not replace the lattice zinc with copper. Rather, a copper complex was attached to the mineral surface. These theories were not well accepted due to lack of convincing evidence.

4. *pH dependence of sphalerite flotation:*

It was well accepted that the flotation of sphalerite is highly pH-dependent. 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. The poor bubble-particle contacts at the near neutral pH region was attributed to the precipitation of copper xanthate in the presence of excess copper ions, which in turn depletes the solution of xanthate ions. Sutherland

and Wark (1939) considered that copper xanthate formed at the near neutral pH was more insoluble than those formed in acidic or alkaline solutions. 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 that the larger the addition, the wider the pH range of suppression. Based on the solution chemistry of the copper-water system, these authors suggested that a basic copper xanthate precipitate is formed at the near neutral pH in the presence of excess copper ions, which in turn depletes the solution of xanthate ions via reaction:



where X⁻ represents a xanthate ion. The basis of Steininger's explanation was that the concentration of Cu₂(OH)₂²⁺ ions reaches a maximum at the near neutral pH. Laskowski and his co-workers (Girczys et al., 1972; Laskowski et al., 1997) showed similar results as Steiningers. However, they attributed the poor flotation response at near neutral pH to the presence of Cu(OH)⁺, whose concentration is highest at neutral pH. In fact, flotation tests conducted by Iskra and Laskowski in 1969 using methylated silica supported this assumption. In this paper, it was reported that the flotation of methylated silica is depressed by Cu(OH)⁺ in near neutral solutions. These authors proposed that because there are some sites of the silica surface that are not covered by surfactant, Cu(OH)⁺ will adsorb on those naked silica sites, causing the mineral hydrophilic.

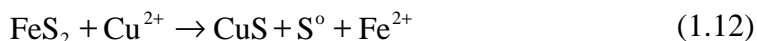
1.2.b. Activation of Pyrite

Compared to the many studies on the Cu(II) activation of sphalerite, there has been much less work on the activation of pyrite by Cu(II).

Allison (1982), Wang et al. (1989b) and Leppinen et al. (1995) studied the activation of pyrite by heavy metal ions and showed that the adsorption of Cu²⁺ and Pb²⁺ on pyrite did not involve exchange with the lattice cation. Based on this observation, they concluded that it was the hydroxides that adsorbed on pyrite during the initial stage of activation. Wang et al. (1989b)

and Voigt et al. (1994) agreed that the activation products were CuS_2 or $(\text{Cu, Fe})\text{S}$, together with surface cupric hydroxide which interacted with the ferric hydroxides resulting from the oxidation of the pyrite surface. The adsorbed cupric hydroxide was found to dissolve readily in water. Voigt and his co-workers studied the relationship between the adsorbed cupric hydroxides and cuprous sulfides. They found that the adsorption in the cuprous form is independent of the pH, whereas the adsorption of the cupric form rises sharply with the pH and reached a peak at about 9. They also observed that the adsorption of the cupric hydroxide has an induced stage: Cu(II) is detected at the surface only after it has been exposed to the activating solution for about 15 minutes. It takes about 2 minutes for Cu(II) to reach its maximum density at the surface at pH 5; at pH 10 it takes far longer. At pH 10, Cu(I) seems to form in two distinct stages, the second stage starts only after the adsorption of the hydroxide has commenced. This study shows that the activation of sulfide minerals under alkaline conditions involves complex interactions between the sulfide products, which are thought to be responsible for activation of the reaction with the collectors, and the hydroxides which are formed through oxidation of the mineral surface and hydrolysis of the activating ion. Voigt et al. (1994) also found the amount of copper adsorbed on pyrite, measured by the atomic surface ratio Cu/S , to be limited. The Cu(I) does not exceed a monolayer on pyrite and may not penetrate below the surface.

Bushell and Krauss (1961), on the other hand, proposed that pyrite is activated with Cu(II) by the reaction



which essentially involves oxidation of the pyrite with the formation of elemental sulfur. They also reported that pyrite did not activate at pHs less than 7. This is in agreement with Nicol (1984), who concluded that pyrite is unlikely to become activated with Cu(II) in the pH range (4 to 6) generally employed in pyrite flotation. There remains considerable uncertainty regarding both the mechanism by which pyrite is activated by Cu(II) and the chemical nature of the activation product. There was no study regarding the electrochemical nature of the activation of pyrite by copper.

1.3 Structure of the present dissertation

Most of the study was focused on the activation of sphalerite by copper, the effect of activating potential and pH on the activating process, activation product and the subsequent xanthate adsorption process. The activation of pyrite by copper was studied for comparison. The results of the study will be arranged in seven chapters in the present dissertation.

Chapter 2

In this chapter, primary study was conducted at acidic pH to investigate the activation of sphalerite by copper using the newly developed carbon matrix composite (CMC). This technique was developed based on the former invention of carbon paste electrode (Richardson et al., 1994) but has the advantage of better reproducibility, renewable surface and more durable feature. Chronopotentiometry, chronoamperometry, cyclic voltammetry, rotating ring-disc voltammetry together with ICP analysis were used to identify the activation product and the potential dependence of the activation process at acidic condition.

The results indicate that the kinetics of copper uptake, the chemical composition (stoichiometry) of the activation product, and the selectivity of the activation are controlled by the electrochemical potential during activation. Moreover, it is established that CMC:ZnS electrode can be used to study the activation process *in-situ* and accurately to collect the information about the amount of copper uptake on the mineral surface during activation.

Chapter 3

Chronopotentiometry and voltammetry were conducted using CMC:ZnS electrodes to study the activation product at alkaline pH. It was established that a CuS-like activating product is formed after activation at open circuit potential. This product can be further oxidized to form a hydrophobic polysulfide species, which may be responsible for the collectorless flotation. The increase in the surface hydrophobicity upon superficial oxidation of the activation product was verified using a surface conducting (SC:ZnS) electrode. It was also found that a Cu₂S-like

product was formed when activating at reducing potentials. The amount of copper uptake increases when activating at reducing potential.

Chapter 4

The effect of activating potential on copper uptake at alkaline pH was systematically studied and the results were presented in this chapter. It was found from the controlled potential activation experiments that although the selectivity of the activation is not dependent on the activating potential at alkaline pH, there exists an optimal activation potential within which the activation efficiency E_a reaches maximum. Here activation efficiency E_a was defined as the ratio between the net copper uptake by mineral after activation and the copper consumed by reduction during activation, i.e.,

$$E_a = \frac{\text{copper uptake on ZnS}}{\text{copper consumed during activation}} \quad (1.13)$$

Activating at potentials lower than the formation of elemental copper lowers the activation efficiency E_a and leads to high copper consumption. Activation at potentials higher than these potential range inhibits the copper uptake. These findings offers a means of controlling activation during sphalerite flotation at alkaline conditions, and hence the flotation performance.

Chapter 5

Aiming to understand the poor flotation response of sphalerite at near neutral pH, Chapter 5 studies the copper activation of sphalerite and the subsequent xanthate adsorption and the hydrophobicity of the mineral surface at pH 6.8. Electrochemical research conducted using the combination of CMC:ZnS electrode and the surface conducting (SC:ZnS) electrode show that copper-activation does occur on sphalerite surface at neutral pH, and the activation product is CuS-like. The activation can be inhibited by increasing the activating potential above the open circuit potential. The activation can be improved by decreasing the activating potential moderately.

Controlled potential contact angle measurements conducted using copper-activated SC:ZnS electrode show that xanthate adsorption occurs on copper-activated sphalerite, yet the mineral surface is hydrophilic. Improvement in contact angle can be achieved by addition of some surface-cleaning reagent such as ammonia and sodium sulfide. These results suggest that at near neutral pH, copper hydroxy species as well as copper sulfide may co-adsorb on the mineral surface, either in the form of CuOHX , or CuOH-CuX . The copper sulfide sites will react with the xanthate to form hydrophobic affinities, while the copper hydroxy sites act as hydrophilic affinities.

Chapter 6

The kinetics of the activation process was studied using CMC:ZnS electrode. The results show that the kinetics of copper activation decreases with increasing activating pH. It was also found that the kinetics of activation under neutral and alkaline pHs can be improved by introducing a small amount of ammonia into the activating solution. The addition of ammonia at acidic solution slightly decreases the activation kinetics.

The effect of potential on the xanthate adsorption on copper-activated sphalerite and its hydrophobicity was studied using surface conducting (SC:ZnS) electrodes. Simultaneous contact angle measurements show that at acidic pH, different xanthate species, namely chemisorbed xanthate, copper xanthate and dixanthagen, were formed at different potential regions, all of which are responsible for the surface hydrophobicity. Same observation was made at alkaline pH. At near neutral pH, however, voltammetric study showed that xanthate adsorption does occur on the activated sphalerite surface, yet the contact angle measurements show that the surface is still hydrophilic. These findings were further confirmed by microflotation results, which show a region of depression at near neutral pH. The introduction of cleaning reagent such as ammonia (at the activation stage) and sodium sulfide (after the xanthate adsorption) significantly improves the flotation recovery of sphalerite at both near neutral pH and alkaline pH.

Chapter 7

The activation of pyrite by copper under flotation-related conditions was studied. It was established that approximately a monolayer of copper is produced on pyrite when it is treated in oxygen-purged, near neutral and acid (pH 4.6) solutions of 10^{-4} M CuSO₄ for 10 minutes under open-circuit conditions. Activation by copper was found to be sensitive to the source of pyrite and to be dependent most strongly on the redox potential in the activating solution. Activation at potentials slightly negative of its open-circuit potential, which can be achieved by galvanically coupling the pyrite electrode with mild steel, copper uptake is greatly enhanced; and at slightly positive potentials it is inhibited.

Summary and future work are given in Chapter 8.