September 3, 1999

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University of Nevada Reno
Controller's Office
Reno, NV 89557-0025

RE: BOM # G1155232
Subagreement # 96-15
UNR # 1330-114-0574
End Date: 6/30/98

Dear Mr. Best:

Enclosed you will find a copy of our FINAL REPORT entitled, "Subaqueous Disposal of Mill Tailings."

I am sorry for the delay, which was caused by the departure of Dr. Paul Richardson, who used to serve as Principal Investigator.

Sincerely,

Roe-Hoan Yoon

Enclosure

Cc: Velma Thompson
Kathryn Dew
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FINAL TECHNICAL REPORT

Subaqueous Disposal of Mill Tailings

by

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September 3rd, 1999

Submitted to

Mineral Industry Waste Treatment and Recovery Center
Mackay School of Mines
University of Nevada Reno
Reno, NV 89557-0140

Grant:

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EXECUTIVE SUMMARY

A study of mill tailings and sulfide minerals was carried out in order to understand their behavior under subaqueous conditions. A series of electrochemical experiments, namely, cyclic voltammetry, electrochemical impedance spectroscopy and galvanic coupling tests were carried out in artificial seawater and in pH 6.8 buffer solutions with chloride and ferric salts.

Two mill tailings samples, one from the Kensington Mine, Alaska, and the other from the Holden Mine, Washington, were studied along with pyrite, galena, chalcopyrite and copper-activated sphalerite. SEM analysis of mill tailings revealed absence of sulfide minerals from the Kensington Mine mill tailings, whereas the Holden Mine mill tailings contained approximately 8% pyrite and 1% sphalerite. In order to conduct electrochemical tests, carbon matrix composite (CMC) electrodes of mill tailings, pyrite and galena were prepared and their feasibility was established by conducting a series of cyclic voltammetry tests.

The cyclic voltammetry experiments carried out in artificial seawater and pH 6.8 buffer with chloride salts showed that chloride ions play an important role in the redox processes of sulfide minerals. For pyrite and galena, peaks were observed for the formation of chloride complexes, whereas pitting behavior was observed for the CMC electrodes of the Kensington Mine mill tailings.

The electrochemical impedance spectroscopy conducted in artificial seawater provided with the Nyquist plots of pyrite and galena. The Nyquist plots of pyrite and galena exhibited an inert range of potential indicating a slower rate of leaching of sulfide minerals in marine environments. The galvanic coupling experiments were carried out to study the oxidation of sulfide minerals in the absence of oxygen. It was shown that in the absence of oxygen, ferric (Fe$^{3+}$) ions might oxidize the sulfide minerals, thereby releasing undesirable oxidation products.
in the marine environment. The source of $\text{Fe}^{3+}$ ions may be attributed to iron-bearing sulfide (and oxide) minerals present in the mill tailings. However, the concentration of available $\text{Fe}^{3+}$ ions can be reduced by the precipitation of insoluble ferric hydroxides ($\text{Fe(OH)}_3$) by seawater due to its near neutral pH. In such case, the oxidation of a sulfide mineral is inhibited due to the absence of an oxidizing agent (viz. oxygen and/or $\text{Fe}^{3+}$ ions).

The experiments carried out in this study provided a better understanding of behavior of sulfide minerals and mill tailings in subaqueous conditions and may be useful for further investigation of sulfide minerals and mill tailings in other environments.
# TABLE OF CONTENTS

EXECUTIVE SUMMARY .......................................................................................................... ii

LIST OF TABLES ........................................................................................................................ v

LIST OF FIGURES ..................................................................................................................... vi

1. OBJECTIVES ....................................................................................................................... 1

2. EXPERIMENTAL ................................................................................................................ 1
   2.1 SAMPLES ..................................................................................................................... 1
   2.2 SOLUTIONS ............................................................................................................... 3
   2.3 EXPERIMENTAL PROCEDURES ............................................................................... 3
       Cyclic Voltammetry: ....................................................................................................... 3
       Electrochemical Impedance Spectroscopy: ................................................................. 4
       Galvanic Coupling Experiments: ............................................................................... 4

3. RESULTS .............................................................................................................................. 5
   3.1 SEM ANALYSIS: ............................................................................................................ 5
   3.2 CYCLIC VOLTAMMETRY: .......................................................................................... 5
       Pyrite: .......................................................................................................................... 5
       Galena: ....................................................................................................................... 6
       Kensington Mine Mill Tailings: .................................................................................. 7
       Holden Mine Mill Tailings: ....................................................................................... 8
   3.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY: ............................................. 8
   3.4 GALVANIC COUPLING: ............................................................................................. 9
       Sphalerite: .................................................................................................................... 9
       Chalcopyrite: ............................................................................................................. 11

4. CONCLUSIONS .................................................................................................................. 11

5. REFERENCES .................................................................................................................... 13
LIST OF TABLES

Table 1: Kester, Duedall, Connors and Pytkowicz Formula (1967): The Composition of Artificial Seawater. .................................................................15

Table 2: Mineralogical Composition of Mill Tailing From SEM/EDX. .........................16

Table 3: Effect of Fe³⁺ Ions (at pH 2) on the Potentials and the Contact Angles of Copper-Activated Sphalerite in 10⁻⁴ M KEX Solution at pH 6.8. .......................17

Table 4: Comparison of Effect of Fe³⁺ Ions (at pH 2) and Air (pH 6.8) on the Potentials and the Contact Angles of Sulfides Minerals in 10⁻⁴ M KEX Solution at pH 6.8. ..........17
LIST OF FIGURES

Figure 1: Schematic illustration of surface conducting (SC) electrode ........................................18
Figure 2: Schematic illustration of the electrochemical apparatus for galvanic coupling experiments and contact angle measurements. .................................................................19
Figure 3: Cyclic voltammetry of CMC electrode of pyrite in artificial seawater. .....................20
Figure 4: Cyclic voltammetry of CMC electrode of pyrite in pH 6.8 buffer solution in presence and absence of chloride salts ...........................................................................21
Figure 5: Cyclic voltammetry of CMC electrode of carbon in artificial seawater ....................22
Figure 6: Cyclic voltammetry of CMC electrode of galena in artificial seawater ....................23
Figure 7: Cyclic voltammetry of CMC electrode of galena in pH 6.8 buffer solution in presence and absence of chloride salts .................................................................24
Figure 8: Cyclic voltammetry of CMC electrode of Kensington Mine (depyritized) mill tailings in artificial seawater .................................................................25
Figure 9: Cyclic voltammetry of CMC electrode of Kensington Mine (depyritized) mill tailings in pH 6.8 buffer solution in presence and absence of chloride salts ..................26
Figure 10: Cyclic voltammetry of CMC electrode of Holden Mine mill tailings in artificial seawater .........................................................................................................27
Figure 11: Cyclic voltammetry of CMC electrode of Holden Mine mill tailings in pH 6.8 buffer solution in presence and absence of chloride salts .......................................28
Figure 12: Nyquist plots for CMC electrode of pyrite in artificial seawater. The numbers represent the potentials at which impedance spectrum was obtained ......................29
Figure 13: Nyquist plots for CMC electrode of galena in artificial seawater. The numbers represent the potentials at which impedance spectrum was obtained. ..............................................30

Figure 14: Galvanic coupling current between a copper-activated sphalerite electrode in $10^{-4}$ M KEX solution and platinum electrode in $10^{-4}$ M Fe$^{3+}$ solution at different pHs. ...........31

Figure 15: Galvanic coupling current between a chalcopyrite electrode in $10^{-4}$ M KEX solution and platinum electrode in $10^{-4}$ M Fe$^{3+}$ solution at different pHs. ..............................................32
1. OBJECTIVES

The objectives of this study were: (a) to determine the reactivity of tailings by conducting fundamental electrochemical studies, (b) to develop accelerated leaching tests, and (c) to assess the potential of tailings to release heavy metals into the marine environment. This study was designed to compliment the research on mill tailings at the USBM's Spokane Research Center, WA.

2. EXPERIMENTAL

2.1 Samples

Well crystallized cubes of pyrite from Mexico, chunks of galena from Missouri, specimen-grade sphalerite from Spain and chalcopyrite from Colorado were obtained from Wards Earth Sciences, Inc. Two samples of mill tailings, one from the Kensington Mine, Alaska, and the other from the Holden Mine, Washington, were received from the Spokane Research Center. The Kensington Mine mill tailings were depyritized by the Spokane Research Center using flotation.

In order to study the mill tailings, carbon matrix composite (CMC) electrodes of pyrite, galena and mill tailings were prepared. The electrodes were tested for three size classes (-106μ, -150μ+106 μ, +150 μ). The composition of constituents of the CMC electrodes was also varied in order to obtain reliable and sturdy electrodes. It was found that the middle size range (-150μ+106 μ) produced reliable electrodes while covering approximately 70% of the disc face. The diameter of a CMC electrode was 6 mm and it was fitted in a rotating disc assembly for electrochemical studies. For further details on preparation of the CMC electrodes, please refer to
publication by Yoon et al. (1995 & 1996). Similar electrodes were prepared for pyrite and galena. The validity and feasibility of the CMC electrodes of pyrite and galena were verified by cyclic voltammetry as discussed later.

For galvanic coupling studies, solid electrodes were prepared. Chalcopyrite electrodes were prepared from specimens cut into cylinders of 6 mm in diameter. A copper wire was attached to one end by means of a conducting carbon paste or an indium solder and encapsulated with epoxy. The electrode was mounted in a glass tubing filled with epoxy, leaving one end of the cylindrical electrode exposed for contact with the solution. The electrode surface was renewed by wet polishing (600 grit paper) and ultrasonic cleaning before each experiment. The surface was rinsed with double distilled de-ionized water between each step. After rinsing with double-distilled water, the electrode was placed in a deoxygenated pH 6.8 buffer solution in Cell 1 with the mineral surface facing down.

Due to its insulating nature, sphalerite electrode could not be fabricated in the same manner as with chalcopyrite. Therefore, a surface conducting (SC) electrode was fabricated. A sphalerite chunk with dimensions of 15 × 10 mm was molded in a glass tube using epoxy resin. A small hole was drilled along the edge of the mineral and a platinum wire was inserted through it (see Figure 1). The platinum wire was bent at one end to ensure the electrical contact with the mineral surface, whereas the other end was connected with the copper wire. Sphalerite has been studied extensively at Center for Coal and Minerals Processing (CCMP) using carbon paste (Richardson, 1994) and CMC (Yoon et al., 1995 and 1996). Preliminary studies with SC electrode showed that sphalerite behaved in a manner similar to the carbon paste and the CMC electrodes (Chen, 1998; Chen and Yoon, 1999 a and b). The mineral surface was renewed by cleaning in chloroform and cyanide followed by wet polishing (600 grit) and ultrasonic cleaning.
In order to conduct electrochemical studies, sphalerite needs to be activated because of its insulating nature. Therefore, the sphalerite electrode was activated in $10^{-4}$ M CuSO$_4$ solution at pH 4.6 for 30 minutes and placed in a galvanic cell for measurements.

2.2 Solutions

Artificial seawater was prepared using Kester et al. (1967) formula as described by Bidwell and Spotte (1985). The constituents are described in Table 1. The resulting pH of artificial seawater was slightly acidic (pH 6.8–6.9). In order to study the effect of the major seawater constituents, studies were also conducted in pH 6.8 buffer solution, in which the individual components were added incrementally. The pH 6.8 buffer was prepared by mixing 6.8 g KH$_2$PO$_4$ and 1 g of NaOH in one liter of double distilled water. It was observed from preliminary studies that chloride in seawater plays a significant role in the redox process of pyrite and galena. Therefore, electrochemical studies were carried out by addition of NaCl and MgCl$_2$ in pH 6.8 buffer solutions.

For galvanic coupling studies, pH 4.6 buffer (0.05 M acetic acid and 0.05 M sodium acetate) and pH 2 buffer (0.01 M HCl and 0.05 M KCl) solutions were prepared. $10^{-4}$ M ferric (Fe$^{3+}$) ions solution was prepared by dissolving FeCl$_3$ in pH 2 buffer solution. Potassium ethyl xanthate (KEX) was used to study the oxidation of minerals.

2.3 Experimental Procedures

Cyclic Voltammetry:

A Pine RDE-4 bipotentiostat was used to conduct voltammetry. The electrode potentials were measured and controlled with respect to standard calomel reference electrode (SCE).
Cyclic voltammetry was carried out in artificial seawater and pH 6.8 buffer solution with NaCl and MgCl₂ added incrementally.

_Electrochemical Impedance Spectroscopy:_

The impedance system consisted of a 5208 Lock-in Analyzer connected to a computer through a Model 273 Potentiostat, both manufactured by EG&G Princeton Applied Research. In order to obtain the impedance spectra over the entire frequency range of 10⁻² to 10⁵ Hz, single- and multiple-sine waveforms were employed: the former for the range of 5 to 100 KHz; the later for the range of 10⁻² to 6 Hz. The signal amplitude was ~5 mV.

_Galvanic Coupling Experiments:_

Figure 2 shows the cell designed for galvanic coupling experiments. The cell consisted of two compartments connected by a salt bridge. The working electrode was placed in one compartment (Cell 1), while the counter (platinum) electrode was placed in the other compartment (Cell 2). The two electrodes were galvanically connected with each other. Galvanic currents were measured by means of a zero-resistance ammeter (Keithley 485 autoranging picoammeter). A standard calomel reference electrode (SCE) was placed in Cell 1 to measure the rest potentials. The Cell 1 was equipped with an optical window to enable contact angle measurements. The measured potentials were converted to the standard hydrogen electrode (SHE) scale, taking the potential of the SCE to be 0.245 V against SHE.

As a mean of determining the extent of oxidation, xanthate was used as an adsorbing reagent and the contact angles were measured. The electrodes were used in such a way that the surface to be studied was facing downward. Small nitrogen bubbles were generated on the mineral surface using a syringe whose needle was bent upwards. The contact angles were measured through aqueous phase using Rame Hart goniometer. The values reported are the
average of 3-5 different measurements done on the same mineral surface under the same conditions. The error for contact angle measurements was approximately $\pm 2^\circ$.

3. RESULTS

3.1 SEM Analysis:

Table 2 shows the SEM analysis of mill tailings using Stereoscan 120 (Cambridge Instruments) SEM/EDX analyzer. As it can be seen from Table 2, the Kensington Mine mill tailings contain albite, mica and quartz as the major components, but no reactive sulfide minerals. This is due to the fact that the mill tailings were de-pyritized by the Spokane Research Center using flotation. On the other hand, the Holden Mine mill tailings contain quartz and plagioclase as the major components with pyrite (~8%) and sphalerite (~1%) as the reactive sulfide minerals.

3.2 Cyclic Voltammetry:

**Pyrite:**

Figure 3 shows the cyclic voltammogram of pyrite in artificial seawater (pH 6.8-6.9). The voltammogram exhibits characteristic anodic (A1, A2, A3 and A4) and cathodic (C2 and C3) peaks of pyrite. The redox processes representing these peaks with reversible potentials at pH 6.8 can be described as (Pritzker et al., 1984; Zhu et al., 1991):

\[
\begin{align*}
\text{A1: } & \text{ Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^- + 2\text{e}, & E^0 = -0.063 \text{ V}, E_r = -0.464 \text{ V} & [1] \\
\text{A2: } & \text{FeS}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{S}^0 + 3\text{H}^- + 2\text{e}, & E^0 = 0.628 \text{ V}, E_r = 0.227 \text{ V} & [2]
\end{align*}
\]

The general form of A3 and A4 can be written as:

\[
\begin{align*}
\text{FeS}_2 + (y+3)\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + \text{S}_2\text{O}_3^{2-} + (2y+3)\text{H}^+ + (2y+1)\text{e} & [3] \\
n\text{FeS}_2 + n\text{H}_2\text{O} & \rightarrow n\text{Fe(OH)}_3 + 2\text{S}_n^{2-} + n\text{H}^- + (n-4)\text{e} & [4]
\end{align*}
\]
where sulfoxy ions \((S_2O_7^{2-})\) are further oxidized to sulfate ions \((SO_4^{2-})\).

\[
\begin{align*}
\text{C2: } & \quad \text{Fe(OH)}_3 + 3\text{H}^+ + 3e^- \rightarrow \text{Fe}^0 + 3\text{H}_2\text{O} \quad E^0 = 0.052 \text{ V}, \quad E_r = -0.350 \text{ V} \\
\text{C3: } & \quad \text{FeS}_2 + 2\text{H}^+ + 4e^- \rightarrow \text{Fe}^{2+} + 2\text{HS}^- \quad E^0 = -0.495 \text{ V}, \quad E_r = -0.700 \text{ V}
\end{align*}
\]

The iron produced during reduction processes is oxidized in the forward sweep (peak A1).

Due to the high concentration of chloride ions \([(\text{Cl}^-) = 0.55]\), some of the ferric hydroxide \((\text{Fe(OH)}_3)\) is converted to ferric chloride \((\text{FeCl}_3)\). Since this is a substitution process, which doesn't involve electrons, a peak is not visible on the voltammogram. However, it is evident from the presence of additional cathodic peak, which might be due to the reduction of \(\text{FeCl}_3\) to ferrous chloride \((\text{FeCl}_2)\) as follows:

\[
\begin{align*}
\text{C1: } & \quad \text{FeCl}_3 + e^- \rightarrow \text{FeCl}_2 + \text{Cl}^- \quad E^0 = 0.770 \text{ V}, \quad E_r = 0.780 \text{ V}
\end{align*}
\]

In order to study the role of chloride ions, voltammetry was conducted in pH 6.8 buffer solution. Figure 4 shows the voltammogram in pH 6.8 buffer (solid line), where it can be seen that the cathodic peak C1 is missing in the buffer alone, whereas other peaks are present. After the addition of chloride ions, the cathodic peak C1 re-appears (dotted lines). Therefore, it can be inferred that chloride ions in the seawater play a role in the redox process of sulfide minerals.

Figure 5 shows the cyclic voltammogram of a carbon CMC electrode in artificial seawater. The voltammogram of the CMC electrode of carbon does not exhibit any major peaks in the region where pyrite was studied in artificial seawater and pH 6.8 buffer. This indicates that the peaks visible in voltammograms of pyrite are solely due to the redox processes involving pyrite and that the CMC electrodes are feasible for this study.

**Galena:**

Figure 6 shows the cyclic voltammogram of galena in artificial seawater. The voltammogram exhibits characteristic anodic peaks (A1 and A3) and cathodic peaks (C1 and C2).
of galena. In addition to these peaks, there exists an additional anodic peak (A2), which is due to the oxidation of galena to lead chloride. The reactions detailing these peaks are as follows (Richardson and Maust, 1976; Gardner and Woods, 1979; Pritzker, et al., 1984):

A1: \[ \text{Pb} + \text{HS}^- \rightarrow \text{PbS} + \text{H}^+ + 2e \quad E^0 = -0.574 \text{ V}, \quad E_r = -0.598 \text{ V} \quad [8] \]
A2: \[ \text{PbS} + 2\text{Cl}^- \rightarrow \text{PbCl}_2 + \text{S}^0 + 2e \quad E^0 = 0.243 \text{ V}, \quad E_r = 0.249 \text{ V} \quad [9] \]
A3: \[ \text{PbS} + \text{H}_2\text{O} \rightarrow \text{PbO} + \text{S}^0 + \text{H}^- + 2e \quad E^0 = 0.764 \text{ V}, \quad E_r = 0.363 \text{ V} \quad [10] \]
\& or \[ \text{PbS} + \text{H}_2\text{O} \rightarrow \text{Pb(OH)}^+ + \text{S}^0 + \text{H}^- + 2e \quad E^0 = 0.596 \text{ V}, \quad E_r = 0.396 \text{ V} \quad [11] \]
C1: \[ \text{S}^0 + 2\text{H}^- + 2e \rightarrow \text{H}_2\text{S} \quad E^0 = 0.144 \text{ V}, \quad E_r = -0.257 \text{ V} \quad [12] \]
C2: Reverse of A1

At higher oxidation potential, elemental sulfur is further oxidized to sulfoxy and sulfate species. The lead chloride formed is highly insoluble and diffuses away from the surface. Therefore a peak corresponding to its reduction is absent from the voltammogram. In order to study the effect of chloride ions, the voltammetry was carried out in pH 6.8 buffer (solid line in Figure 7). It can be seen from Figure 7 that the peak due to the formation of lead chloride is absent in buffer alone and appears when NaCl and MgCl₂ are added.

**Kensington Mine Mill Tailings:**

Figures 8 and 9 show the cyclic voltammogram of the CMC electrodes of the Kensington Mine mill tailings in artificial seawater and pH 6.8 buffer (with incremental addition of chloride salts), respectively. Due to the lack of any reactive sulfide minerals in the Kensington Mine mill tailings, no significant peak is observed. The voltammogram in buffer solution (Figure 9) shows that there exists an anodic peak when NaCl is added to the buffer solution. This may be due to the pitting of the CMC electrode, as observed in corrosion process. This process represents physical alteration of the electrode surface rather than a redox process at that potential. Also, it
can be seen that after addition of MgCl₂ in the solution, the pitting behavior is quantitatively reduced. This indicates that the pitting effect may be due to Na⁺ ions, rather than due to chloride ions.

**Holden Mine Mill Tailings:**

Figure 10 shows the cyclic voltammogram of the Holden Mine mill tailings in artificial seawater. Due to the presence of small amount of reactive sulfides, viz. pyrite (−8%) and sphalerite (−1%), there exists an anodic peak at about 250 mV. This peak may be characterized as:

$$\text{FeS}_2 + 2\text{Cl}^- \rightarrow \text{FeCl}_2 (aq) + 2\text{S}^0 + 2e \quad E^0 = 0.454 \text{ V}, \quad E_r = 0.288 \text{ V} \quad [13]$$

The product, ferrous chloride, is highly soluble and therefore, a reverse cathodic peak is not observed. The oxidation of sulfide by chloride ions was further verified by cyclic voltammetry in pH 6.8 buffer solution (Figure 11). In the absence of chloride ions (solid lines), the area of the peak is comparatively smaller and the anodic process may characterized as:

$$\text{FeS}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{S}^0 + 3\text{H}^+ + 2e, \quad E^0 = 0.628 \text{ V}, \quad E_r = 0.227 \text{ V} \quad [14]$$

After adding chloride ions in the solution, the area under this peak increases quantitatively. Under these solution conditions, the peak may be represented by ferrous chloride formation (superimposed with hydroxide formation).

### 3.3 Electrochemical Impedance Spectroscopy:

Figure 12 shows the complex plane impedance spectra, also know as Nyquist plots, for CMC electrodes of pyrite in artificial seawater. As it can be from Figure 12, pyrite exhibits nearly linear spectra over a range of −600 mV through 650 mV (SHE). A straight line, which is equivalent to a large semicircle with infinite diameter, represents a very high polarization resistance to the redox process. In other words, a straight line represents the slower rate of the
Redox process. Therefore, it indicates that the oxidation and the reduction of pyrite in this range (about 1.2 V) is slow thereby indicating slower leaching of pyrite from the mill tailings.

At strong oxidizing and reducing potentials, the Nyquist plots take a regular semicircle shape with a finite diameter, $R_p$. The polarization resistance decreases with increasing oxidizing (more positive) or reducing (more negative) potentials. This indicates the higher rate of redox processes and therefore, the higher rate of leaching.

Figure 13 shows the Nyquist plots for galena in artificial seawater, where it can be observed that galena exhibits nearly inert behavior in the range of 50 mV through 250 mV. This indicates that the range for slower redox reactions for galena is much narrower compared to that for pyrite. This may be due to the enhanced leaching of galena due to the formation of soluble lead-chlorocomplexes at high (>0.2 M) chloride concentrations (Fuerstenau et al, 1986).

3.4 Galvanic Coupling:

The previous studies done at CCMP have shown that despite low levels of oxygen in the flotation pulps, minerals were sufficiently oxidized and readily floatable. The chemical analysis of the flotation pulps revealed the presence of iron, which may act as an oxidizing agent in the absence of oxygen. The iron can be present due to dissolution of iron-bearing sulfide minerals such as pyrite, marcasite and pyrrhotite. Therefore, galvanic coupling experiments were conducted in order to study the oxidation of sulfide minerals in the absence of oxygen.

**Sphalerite:**

As described in experimental section, sphalerite electrode was activated in $10^{-4}$ M CuSO$_4$ solution (pH 4.6) for 30 minutes. After activation, the electrode was rinsed and placed in Cell 1 of the galvanic cell containing $10^{-4}$ M KEX at pH 6.8. The rest potential and the contact angle were measured to be 165 mV and 15°, respectively. The mineral electrode was connected to the
platinum electrode in Cell 2 containing deoxygenated pH 6.8 buffer solution. Figure 14 shows rest potentials, contact angles and the galvanic current after both the electrodes were connected. Immediately after the electrodes were connected, the ammeter showed no current indicating that no galvanic interactions were taking place between activated sphalerite and the platinum electrode in the absence of oxygen. The rest potential and the contact angle remained unchanged (165 mV and 15°, respectively), further indicating the absence of galvanic interaction.

When 10⁻⁴ M FeCl₃ was added to Cell 2 containing pH 6.8 buffer solution, a small galvanic current was observed, but the mixed potential and contact angle remained unchanged (Figure 14). A small current indicates a galvanic interaction between two electrodes, but to a smaller extent due to smaller Fe³⁺ ion concentration at pH 6.8. Therefore, when pH was incrementally reduced to 3.2 and 2 respectively, larger galvanic currents were observed with substantial change in the rest potential and the contact angle. This indicates galvanic interaction between activated sphalerite and platinum electrodes involving reduction of Fe³⁺ ions as follows:

\[
Fe^3^+ + e^- \rightarrow Fe^{2+}
\]  

[15]

coupled with oxidation of mineral and adsorption of xanthate:

\[
CuS + X^- \rightarrow CuX + S^0 + e^-
\]

[16]

The activation product was assumed to be CuS-like, as shown by Yoon and his co-workers (Kartio et al., 1996; Yoon and Chen, 1996; Chen and Yoon, 1997, 1999 a & b).

Table 3 shows the effect of concentration of Fe³⁺ ions in deoxygenated pH 2 buffer solution in Cell 2, whereas Cell 1 contained copper-activated sphalerite in 10⁻⁴ M KEX solution at pH 6.8. It can be observed from the values in Table 3 that the increasing concentration of Fe³⁺ ions increases both the mixed potential and the contact angle, which indicates the increased oxidation of the mineral.
**Chalcopyrite:**

Similar experiments were conducted on chalcopyrite as it is a source of iron in the solution and may oxidize itself and other sulfides, even in the absence of oxygen. Figure 15 shows the rest potentials and the contact angles of chalcopyrite when galvanically connected to the platinum electrode in Cell 2 with and without Fe$^{3+}$ ions.

As it can be seen from Figure 15, both the potential and the contact angle increased with addition of Fe$^{3+}$ ions and decrease in pH. This indicates the oxidation of mineral due to Fe$^{3+}$ ions in the absence of oxygen.

Table 4 shows the mixed potentials and the contact angles for activated sphalerite and chalcopyrite in the presence of Fe$^{3+}$ ions (at pH 2) and air (at pH 6.8). The sulfide electrodes were mounted in Cell 1 containing 10$^{-4}$ M KEX at pH 6.8. It was observed that it takes about 20-30 minutes of aeration to achieve the potential and the contact angle values close to those obtained almost instantaneously after the addition of Fe$^{3+}$ ions. This indicates faster kinetics of mineral oxidation in the presence of Fe$^{3+}$ ions compared to that due to the air.

4. **CONCLUSIONS**

1. The SEM analysis of mill tailings showed that the Kensington Mine mill tailings does not contain significant amount of reactive sulfide minerals. On the other hand, the Holden Mine mill tailings contain approximately 8% pyrite and 1% sphalerite as reactive components.

2. The cyclic voltammetry of sulfide minerals in the artificial seawater and in pH 6.8 buffer solution in the presence of chloride ions depicts a peak related to chloride complexes.
This indicates that the chloride ions present in the seawater may increase the reactivity of sulfide minerals present in the mill tailings.

3. The impedance spectra of pyrite and galena measured in the seawater exhibit an almost inert behavior in the potential range of slight oxidation. This indicates the slower rate of oxidation of the sulfide minerals and thus the slower rate of leaching under sub-aqueous conditions.

4. In the absence of oxygen, the iron which is present due to iron-bearing sulfide minerals may expedite the oxidation of other sulfide minerals. The seawater, owing to its near neutral pH, may precipitate iron as hydroxides, thereby reducing their galvanic effect and rendering minerals passive.
5. REFERENCES


Chen, Z. and Yoon, R.-H., 1999b, “Electrochemistry of Copper Activation of Sphalerite at pH 9.2”, - accepted for IJMP.


Table 1: Kester, Duedall, Connors and Pytkowicz Formula (1967): The Composition of Artificial Seawater.

<table>
<thead>
<tr>
<th>Inorganic Component</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>5.46 X 10(^{-1})</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>4.68 X 10(^{-1})</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>5.33 X 10(^{-2})</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>2.82 X 10(^{-2})</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1.03 X 10(^{-2})</td>
</tr>
<tr>
<td>K(^+)</td>
<td>9.90 X 10(^{-3})</td>
</tr>
<tr>
<td>HCO(_3^{-})</td>
<td>2.33 X 10(^{-3})</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>8.24 X 10(^{-4})</td>
</tr>
<tr>
<td>B</td>
<td>4.20 X 10(^{-4})</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>9.00 X 10(^{-5})</td>
</tr>
<tr>
<td>F(^-)</td>
<td>7.14 X 10(^{-5})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>5.32 X 10(^{1})</td>
</tr>
</tbody>
</table>
Table 2: Mineralogical Composition of Mill Tailing From SEM/EDX.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Kensington Mine Depyritized Mill Tailings</th>
<th>Holden Mine Mill Tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>23.65</td>
<td>1.24</td>
</tr>
<tr>
<td>Amphibole</td>
<td>-</td>
<td>2.65</td>
</tr>
<tr>
<td>Apatite</td>
<td>0.39</td>
<td>-</td>
</tr>
<tr>
<td>Augite</td>
<td>-</td>
<td>0.38</td>
</tr>
<tr>
<td>Biotite</td>
<td>-</td>
<td>4.25</td>
</tr>
<tr>
<td>Calcite</td>
<td>5.62</td>
<td>0.32</td>
</tr>
<tr>
<td>Chlorite</td>
<td>9.91</td>
<td>5.48</td>
</tr>
<tr>
<td>Epidote</td>
<td>0.81</td>
<td>0.78</td>
</tr>
<tr>
<td>Fe - oxide</td>
<td>1.93</td>
<td>0.62</td>
</tr>
<tr>
<td>K - feldspar</td>
<td>0.63</td>
<td>3.04</td>
</tr>
<tr>
<td>Mica / clay</td>
<td>15.37</td>
<td>2.65</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>8.11</td>
<td>20.42</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-</td>
<td>7.68</td>
</tr>
<tr>
<td>Quartz</td>
<td>32.65</td>
<td>49.14</td>
</tr>
<tr>
<td>Rutile</td>
<td>0.51</td>
<td>-</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>-</td>
<td>0.94</td>
</tr>
<tr>
<td>Sphene</td>
<td>0.43</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Table 3: Effect of Fe³⁺ Ions (at pH 2) on the Potentials and the Contact Angles of Copper-Activated Sphalerite in 10⁻⁴ M KEX Solution at pH 6.8.

<table>
<thead>
<tr>
<th>Cell 2 - pH 2 buffer solution</th>
<th>Potential (mV)</th>
<th>Contact Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>165</td>
<td>15</td>
</tr>
<tr>
<td>10⁻⁵ Fe³⁺</td>
<td>170</td>
<td>25</td>
</tr>
<tr>
<td>4 X 10⁻⁵ Fe³⁺</td>
<td>220</td>
<td>30</td>
</tr>
<tr>
<td>9 X 10⁻⁵ Fe³⁺</td>
<td>255</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 4: Comparison of Effect of Fe³⁺ Ions (at pH 2) and Air (pH 6.8) on the Potentials and the Contact Angles of Sulfides Minerals in 10⁻⁴ M KEX Solution at pH 6.8.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Cell 2</th>
<th>pH - Cell 2</th>
<th>Potential (mV)</th>
<th>Contact Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>Air (30 minutes)</td>
<td>6.8</td>
<td>405</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>10⁻⁴ Fe³⁺</td>
<td>2</td>
<td>390</td>
<td>31</td>
</tr>
<tr>
<td>Copper-Activated Sphalerite</td>
<td>Air (20 minutes)</td>
<td>6.8</td>
<td>253</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>10⁻⁴ Fe³⁺</td>
<td>2</td>
<td>260</td>
<td>36</td>
</tr>
</tbody>
</table>
Figure 1: Schematic illustration of surface conducting (SC) electrode.
Figure 2: Schematic illustration of the electrochemical apparatus for galvanic coupling experiments and contact angle measurements.
Figure 3: Cyclic voltammetry of CMC electrode of pyrite in artificial seawater.
Figure 4: Cyclic voltammetry of CMC electrode of pyrite in pH 6.8 buffer solution in presence and absence of chloride salts.
Figure 5: Cyclic voltammetry of CMC electrode of carbon in artificial seawater.
Figure 6: Cyclic voltammetry of CMC electrode of galena in artificial seawater.
Figure 7: Cyclic voltammetry of CMC electrode of galena in pH 6.8 buffer solution in presence and absence of chloride salts.
Figure 8: Cyclic voltammetry of CMC electrode of Kensington Mine (depyritized) mill tailings in artificial seawater.
Figure 9: Cyclic voltammetry of CMC electrode of Kensington Mine (depyritized) mill tailings in pH 6.8 buffer solution in presence and absence of chloride salts.
Figure 10: Cyclic voltammetry of CMC electrode of Holden Mine mill tailings in artificial seawater.
Figure 11: Cyclic voltammetry of CMC electrode of Holden Mine mill tailings in pH 6.8 buffer solution in presence and absence of chloride salts.
Figure 12: Nyquist plots for CMC electrode of pyrite in artificial seawater. The numbers represent the potentials at which impedance spectrum was obtained.
Figure 13: Nyquist plots for CMC electrode of galena in artificial seawater. The numbers represent the potentials at which impedance spectrum was obtained.
Figure 14: Galvanic coupling current between a copper-activated sphalerite electrode in $10^{-4}$ M KEX solution and platinum electrode in $10^{-4}$ M Fe$^{3+}$ solution at different pHs.
Figure 15: Galvanic coupling current between a chalcopyrite electrode in $10^{-4}$ M KEX solution and platinum electrode in $10^{-4}$ M $\text{Fe}^{3+}$ solution at different pHs.