RATES OF SULFIDE OXIDATION IN SUBMERGED ENVIRONMENTS: IMPLICATIONS FOR SUBAQUEOUS DISPOSAL

Kevin A. Morin
Morwijk Enterprises Ltd., Suite 703, 1155 Harwood Street, Vancouver, British Columbia V6E 1S1

ABSTRACT

The placement of sulfide-bearing tailings and rock in submerged environments has long been recognized as a primary technique for control of acid drainage, and recent field investigations provide further evidence of its success. However, subaqueous disposal does not automatically ensure that acid generation is completely halted. In fact, there are reasons why acid generation might not cease in a submerged environment.

Recent experimental data from a generic experiment and from the proposed Cinola Gold Project are reviewed to (1) obtain rates of pyrite oxidation under submerged conditions and (2) show that ferric iron apparently does not oxidize pyrite in the absence of dissolved oxygen. The rates are then used to estimate consumption of dissolved oxygen along groundwater flowpaths and to determine a first-order-rate relationship between reaction rate and dissolved oxygen for calculations of dissolved-oxygen diffusion. Three relatively simple examples show how to apply the concepts and equations. One example for oxygen diffusion shows that, for constant values of porosity and pyrite content, tailings will generate more acidity than coarse rock because of the steeper oxygen gradients within the tailings. The major conclusions drawn from this work are that site-specific conditions dominate in determining the eventual water chemistry and that environmental (hydrogeological) conditions of the disposal site should be well defined. In this way, the site-specific rates and concentrations can be determined and, if necessary, details of the subaqueous disposal can be refined for optimum performance.
1. INTRODUCTION

A chemically reduced form of sulfur, known as sulfide, is represented by anions which contain at least one sulfur atom with a valence of 2- (S\(^{2-}\)) and polyanions such as S\(_{2}^{2-}\) and S\(_{4}^{2-}\). Solid-phase sulfide typically occurs in rock combined with metals as distinct minerals (Table 1). When exposed to moisture and oxygen, the sulfide can be released to the water and can oxidize to other forms of sulfur such as elemental sulfur (S\(_{8}\)), thiosulfate S\(_{2}O\(_{3}^{2-}\)\), and sulfate (SO\(_{4}^{2-}\)). If the sulfide-bound metal is also redox reactive, it may also undergo oxidation with the sulfide. Examples of common redox-reactive metals are iron (Fe\(^{2+/3+}\)) and manganese (Mn\(^{2+/3+/4+}\)).

Oxidation of sulfide usually receives attention due to the resulting appearance of acidity and leached metals in the water surrounding the mineral. If the rate of oxidation is rapid, all of the water passing over/through a volume of sulfide-bearing mine rock or tailings can take on an acidic pH with elevated levels of acidity and aqueous metals. As a result, water chemistry is determined both by geochemical factors, such as the rate of oxidation, and by physical factors, such as the flowrate of water. For example, a slow rate of oxidation in a nearly stagnant flow system can produce the same pH and acidity that would appear in a fast flushing system with an accelerated rate of oxidation, although the loadings (concentration multiplied by flow) would be much greater in the latter case.

The oxidation pathway of sulfide is complex and can in fact change as environmental conditions change. The metal associated with the sulfide can further affect the oxidation pathway of the sulfide. For example, iron-based sulfides such as pyrite (FeS\(_{2}\)) and pyrrhotite (essentially FeS) can oxidize relatively quickly under certain conditions because (1) the iron acts as a catalyst to pass electrons from sulfide to oxygen and (2) the iron itself can oxidize the sulfide (Luther, 1990). As a result of these complexities and other factors (e.g., Morin et al., 1991, p.81 and 90), sulfide oxidation is not well understood in detail and cannot be accurately simulated under variable conditions.

Despite the mechanistic complexities in sulfide oxidation, we can at least obtain empirical rates of oxidation through laboratory "kinetic" tests (British Columbia AMD Task Force, 1989) and field monitoring. An important lesson learned from this work is that rates of oxidation are often much lower in fully submerged, saturated environments (Robertson, 1991; Rescan, 1990a, b, c; Veillette, 1991). This is a consequence of processes such as oxygen limitation, as discussed below. However, a sometimes overlooked observation is that oxidation will still occur whenever gaseous/dissolved oxygen reach submerged sulfide minerals. Since water exposed to the atmosphere can carry approximately 10 mg L\(^{-1}\) of dissolved oxygen, then at least some oxidation can be expected whenever oxygenated water flows through saturated sulfide-bearing tailings or mine rock.

The purpose of this paper is to present information on rates of oxidation and the factors determining those rates under submerged conditions, as defined by theory and published literature. Examples of resulting water chemistry are then presented for hypothetical sets of environmental conditions.
### TABLE 1

**EXAMPLES OF SULFIDE MINERALS**  
*(selected from Lowson, 1982)*

<table>
<thead>
<tr>
<th>MINERAL NAME</th>
<th>CHEMICAL COMPOSITION</th>
<th>MINERAL NAME</th>
<th>CHEMICAL COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alabandite</td>
<td>MnS</td>
<td>Linnaeite</td>
<td>Co&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>FeAsS</td>
<td>Marcasite</td>
<td>FeS&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu&lt;sub&gt;3&lt;/sub&gt;FeS&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Millerite</td>
<td>NiS</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>CuS</td>
<td>Molybdenite</td>
<td>MoO&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Chalcopirite</td>
<td>CuFeS&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Orpiment</td>
<td>As&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Cinnabar</td>
<td>HgS</td>
<td>Pyrite</td>
<td>FeS&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Cobaltite</td>
<td>CoAsS</td>
<td>Pyrrhotite</td>
<td>Fe&lt;sub&gt;0.8&lt;/sub&gt;S&lt;sub&gt;1.2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>Realgar</td>
<td>AsS</td>
</tr>
<tr>
<td>Cubanite</td>
<td>CuFe&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
<tr>
<td>Enargite</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;AsS&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Stibnite</td>
<td>Sb&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>Tennantite</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;A&lt;sub&gt;13&lt;/sub&gt;S&lt;sub&gt;13&lt;/sub&gt;</td>
</tr>
<tr>
<td>Greenockite</td>
<td>CdS</td>
<td>Troilite</td>
<td>FeS</td>
</tr>
<tr>
<td>Greigite</td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;S&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Violarite</td>
<td>FeNi&lt;sub&gt;1.3&lt;/sub&gt;S&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>Hauerite</td>
<td>MnS&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Wurtzite</td>
<td>ZnS</td>
</tr>
</tbody>
</table>

### 2. THEORY AND PUBLISHED LITERATURE

For simplicity, this paper focusses only on pyrite (FeS<sub>2</sub>). The often-seen "standard" equation for pyrite oxidation is:

\[
FeS_2 + \frac{7}{2} H_2O + \frac{15}{4} O_2 \rightarrow 6 Fe(OH)_3 + 2 SO_4^{2-} + 4 H^+ \tag{1}
\]

In reality, this equation assumes much about the environmental conditions including (1) sulfur occurs only as S<sub>2</sub>²⁻, (2) S<sub>2</sub>²⁻ oxidizes completely to sulfate, (3) pyrite is the only oxidizing sulfide mineral, (4) molecular oxygen and water are the only oxidants, (5) all iron oxidizes to the ferric (Fe<sup>3+</sup>) state, and (6) all iron precipitates as Fe(OH)<sub>3</sub> (Morin, 1990). Obviously these assumptions do not always apply, especially in submerged environments. If there is insufficient oxygen to oxidize the iron, for example, the overall equation would be:
\[
\text{FeS}_2 + \text{H}_2\text{O} + \frac{7}{2} \text{O}_2 \rightarrow 6 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+
\] (2)

In this case, only 1/2 the amount of acidity (H\(^+\)) is generated for each mole of pyrite. If ferric iron is the sole oxidant, the overall reaction would be:

\[
\text{FeS}_2 + 8 \text{H}_2\text{O} + 14 \text{Fe}^{3+} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+
\] (3)

This reaction suggests a great deal acidity is generated from each mole of pyrite, but this is only the case when the ferric iron is derived from a source other than preceding sulfide oxidation within the mass of tailings or mine rock (Morin, 1990). The important observation to be drawn from Equations 1 through 3 is that environmental conditions and mineralogy will determine the overall balance of reactants and products. This holds true for subaqueous disposal, except that Equation 3 is apparently not relevant as discussed below.

In the realm of low-temperature geochemistry, there are two basic approaches to assessing or predicting water chemistry. The first is known as "equilibrium" or steady-state chemistry (Figure 1), which is relatively easily to define and assess. The second is "kinetic" or time-dependent chemistry which approaches equilibrium levels as time passes. Under field conditions, water is rarely stagnant and thus rarely remains in contact with a particular mass of tailings or rock for an extended period of time. In this case, equilibrium levels may not be attained if the kinetic reaction rates are slow or if the water flows quickly over the tailings/rock. As a result, kinetic conditions are more common, but more difficult to assess.

For sulfide oxidation (Equations 1 through 3), equilibrium conditions will rarely be attained for all reactants and products, and thus the more difficult kinetic conditions must often be assessed. However, there are cases where "pseudo-equilibrium" may appear: when one of the reactants (pyrite, water, or oxygen) is (1) completely exhausted and never replenished, or (2) replenished at a constant rate. In the former case, concentrations of the products (aqueous iron, sulfate, and acidity) will climb until the reactant is exhausted and then "steady-state" conditions will apply. In the latter case, a balance is struck between the supply of a reactant and the consumption of that reactant so its concentration remains constant; however, the reaction products continue to be generated and their concentrations change through time. In light of this, there are two basic pseudo-equilibrium conditions relevant to submerged sulfide oxidation. The first is the complete exhaustion of oxygen which is the ultimate desired endpoint that may not be attained. The second is the eventual development of a steady-state diffusion of oxygen. Both of these conditions are examined below.
The discussion of pseudo-equilibrium conditions through oxygen depletion is discussed in the following section as Case Examples 1 and 2. The remainder of this section addresses kinetic conditions and reactions rates as presented in published literature, so that Case Example 3 can address steady-state oxygen diffusion.

There are many studies of how oxygen diffusion and moisture content will limit the rate of oxidation under unsaturated or drained conditions (e.g., Cathles, 1982; Dave, 1992; St-Arnaud, 1992; Sheremata et al., 1991). However, there are few detailed studies that provide numerical rates of oxidation under submerged conditions with descriptions of the environmental (laboratory) conditions. For this paper, two studies were used to obtain rates.

One recent study of pyrite oxidation focussed on neutral-pH conditions (Moses and Herman, 1991), which simulated submerged conditions. Several laboratory experiments were conducted for various combinations of oxygen levels and ferric-iron concentrations. Short-term rates evolved over times less than 1 hour, but eventually stabilized (Table 2). These researchers concluded that pyrite oxidation was negligible in the absence of dissolved oxygen, in spite of whether any ferric iron was present.

<table>
<thead>
<tr>
<th>DISSOLVED OXYGEN?</th>
<th>AQUEOUS FERRIC IRON?</th>
<th>RATE(^*) (nmol FeS(_2) m(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>YES</td>
<td>YES</td>
<td>0.5</td>
</tr>
<tr>
<td>YES</td>
<td>NO</td>
<td>0.5</td>
</tr>
<tr>
<td>NO</td>
<td>YES</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^*\) This rate is expressed as nanomoles of pyrite normalized to one m\(^2\) of exposed pyrite surface in one second. To uses these rates under field conditions, the exposed pyrite surface in 1 tonne of tailings or rock must be determined (see Equation 4).

The second set of experiments were performed for the proposed Cinola Gold Project in British Columbia (City Resources/Norecol, 1988). As part of the geochemical studies (Volume V), two rock types were placed in replicate sets of columns and subjected to (1) submergence with supernatant constantly recirculated, (2) submergence with both supernatant and porewater constantly recirculated from top to bottom, (3) constant trickling of water through unsaturated rock, (4) weekly cycles of submergence and draining, and (5) partially submerged. The primary difference between the Type (1) and Type (2) columns is that dissolved oxygen would only be transported to the rock through diffusion in Type (1) and by active flow in Type (2). However, the depth of the rock in the columns was approximately 0.4m and the height of the overlying ponded supernatant was 0.5m, and thus recirculation of the supernatant could well have initiated some porewater movement with the Type (1) columns. This would provide oxygen to the rock
The two rock types in the Cinola columns were known as "Skonun Sediments" and "Mixed Breccias" with 2.4% and 1.6% total sulfur (4.5% and 3.0% pyrite), respectively, and little neutralization potential. The Skonun columns often generated near-neutral pH with aqueous iron less than 0.1 mg L\(^{-1}\), reflecting the low solubility of iron in pH-neutral, oxygenated waters. On the other hand, the Breccia columns often generated acidic pH around 3.5 with aqueous iron typically above 0.1-1.0 mg L\(^{-1}\). Nevertheless, the rates among the columns were similar (Table 3) which also suggests that oxidation within the Type (1) columns was not limited by oxygen diffusion.

### TABLE 3

<table>
<thead>
<tr>
<th>DISPERSED OXYGEN?</th>
<th>AQUEOUS FERRIC IRON?</th>
<th>ACID OR NEUTRAL?</th>
<th>RATE(^*) as mg SO(_4) kg(^{-1}) of rock wk(^{-1}) (nmol FeS(_2) m(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OXYGENATED WATER FLOWING THROUGH ROCK (TYPE 2)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YES</td>
<td>YES</td>
<td>ACIDIC (BRECCIA)</td>
<td>11.5 (0.62)</td>
</tr>
<tr>
<td>YES</td>
<td>&lt; 0.1 mg L(^{-1})</td>
<td>NEUTRAL (SKONUN)</td>
<td>13.5 (0.52)</td>
</tr>
<tr>
<td><strong>RECIRCULATING OXYGENATED WATER ABOVE ROCK (TYPE 1)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YES</td>
<td>YES</td>
<td>ACIDIC (BRECCIA)</td>
<td>5.65 (0.30)</td>
</tr>
<tr>
<td>YES</td>
<td>&lt; 0.1 mg L(^{-1})</td>
<td>NEUTRAL (SKONUN)</td>
<td>4.35 (0.16)</td>
</tr>
</tbody>
</table>

\(^*\) Values are means of two replicate columns; the two values were often within 50% of the mean. Values in parentheses are calculated from data (as explained in the text) for comparison with Table 2.

The rates from the two sets of experiments (Tables 2 and 3) can be compared if the Cinola rates are normalized to 1 m\(^2\) of pyrite surface as opposed to 1 kg of rock. This can be accomplished by (1) using the particle-surface areas reported for the Cinola columns and (2) assuming that the percentage of pyrite in the columns is directly proportional to the percentage of the exposed surface area represented by pyrite. These values (Table 3, in parentheses) compare well to the oxygenated rate of 0.5 nmol FeS\(_2\) m\(^2\) s\(^{-1}\) of Table 2, and thus a rate of 0.5 will be used for the following Case Examples in Section 3.

Tables 2 and 3 do not provide any detailed information on the relationship of dissolved oxygen to oxidation rate, except that the reaction ceases when dissolved oxygen is not present. However, to examine pseudo-equilibrium under steady-state oxygen diffusion, a relationship is needed. For gaseous oxygen under unsaturated conditions, published literature suggests the...
relationship can be first order in nature, like radioactive decay, but zero-order to second or higher orders may be possible (e.g., Nicholson, 1984; Senes, 1991; Dave, 1992). For consumption of dissolved oxygen under submerged conditions, a first-order relationship is used:

\[
k = 1.1 \times 10^{-7} \frac{RATe \ A}{DO \ V}
\]  

(4)

where 
\begin{align*}
  k & = \text{first-order rate constant (s}^{-1}\text{)} \\
  RATE & = \text{oxidation rate (nmol FeS}_2 \text{ m}^{-2} \text{ s}^{-1}) \\
  A & = \text{exposed pyrite surface area (m}^2\text{)} \\
  DO & = \text{concentration of dissolved oxygen (mg O}_2 \text{ L}^{-1}) \\
  V & = \text{volume of tailings or rock (m}^3\text{)}
\end{align*}

Based on (1) Equation 2 above, (2) values in Table 2, (3) the Cinola data, and (4) the assumption that particles are spherical in shape, Equation 4 can be adjusted for variable values of porosity, percentage of pyrite, and particle diameter:

\[
k = 3.4 \times 10^{-10} \frac{(1-n) \ %PYR}{d}
\]  

(5)

where 
\begin{align*}
  n & = \text{porosity (dimensionless or m}^3 \text{ m}^{-3}\text{)} \\
  %PYR & = \text{percentage of pyrite in tailings/rock} \\
  d & = \text{particle diameter (m)}
\end{align*}

Once \( k \) is calculated for a particular set of conditions, it can then be used to calculate the un consumed concentration of dissolved oxygen with depth (Equation 6) and the total flux of oxygen (Equation 7) into a 1 m\(^2\) vertical column of tailings or rock (Figure 2). This approach is based on Equation 5 above, Equations 27 and 28 in Dave (1992), and equations in Cathles (1982):

\[
DO(z) = DO(pond) \ exp\left[-\frac{k}{De} \ z\right]
\]  

(6a)

\[
= DO(pond) \ exp\left[-\sqrt{\frac{0.17 \times %PYR \times (1-n) \times T}{d \times n}} \ z\right]
\]  

(6b)

(variables are explained on next page)
\[ J = DO(\text{pond}) \sqrt{k \times De} \quad (7a) \]

Post-publication errata: Equation 7a has been corrected from the original publication

\[ = 8.2 \times 10^{-7} \ DO(\text{pond}) \sqrt{\frac{(n-n^2) \times \%PYR}{d \times T}} \quad (7b) \]

and

\[ De = \frac{D \times n}{T} \quad (8) \]

where

- \( DO(z) = \) concentration of dissolved oxygen at depth \( z \) below the water/material interface (mg O\(_2\) L\(^{-1}\))
- \( z = \) depth below water/material interface (m)
- \( DO(\text{pond}) = \) concentration of dissolved oxygen in the overlying pond (mg O\(_2\) L\(^{-1}\))
- \( k = \) calculated from Equation 5 (s\(^{-1}\))
- \( De = \) effective diffusion coefficient of oxygen in water (m\(^2\) s\(^{-1}\))
- \( J = \) flux of dissolved oxygen into a 1 m\(^2\) vertical column of tailings/rock at the water/material interface (mg O\(_2\) m\(^2\) s\(^{-1}\))
- \( D = \) diffusion coefficient of oxygen in water (2x10\(^{-9}\) m\(^2\) s\(^{-1}\) from Cathles, 1982)
- \( n = \) porosity (dimensionless)
- \( T = \) tortuosity (dimensionless; assume a value of 3 for rock and 5 for tailings)

Also, rates of pyrite consumption and acid generation can be determined within the 1 m\(^2\) vertical column (Figure 2) for a specific value of \( J \):

\[ CP = FACT1 \times J \quad (9) \]

where \( CP = \) rate of pyrite consumption in a 1 m\(^2\) vertical column of tailings/rock (mg FeS\(_2\) m\(^{-2}\) s\(^{-1}\))

- \( FACT1 = \) factor based in part on ratio of oxygen and pyrite in Equations 1 or 2
  - \( FACT1 = 1.00 \) for Equation 1 and \( FACT1 = 1.07 \) for Equation 2

Post-publication errata: FACT1 values have been corrected from the original publication

and

\[ ACP = FACT2 \times J \quad (10) \]

where \( ACP = \) rate of acidity production in a 1 m\(^2\) vertical column of tailings/rock (mg CaCO\(_3\) equivalent m\(^{-2}\) s\(^{-1}\))

- \( FACT2 = \) factor based in part on ratio of oxygen and to acidity in Equations 1 or 2
  - \( FACT2 = 3.33 \) for Equation 1 and \( FACT2 = 1.79 \) for Equation 2 if 1 \( \text{H}^+ : 1 \text{CaCO}_3 \); or 1.67 and 0.90, respectively, if 2 \( \text{H}^+ : 1 \text{CaCO}_3 \)

Post-publication errata: FACT2 values have been expanded from the original publication
3. CASE EXAMPLES OF SUBAQUEOUS OXIDATION

3.1 Example #1: Oxygenated Ponded Water Moving Downward as Groundwater Flow

This example is one of the pseudo-equilibrium conditions discussed in Section 2. In this case, the ponded water over the sulfide-bearing tailings or rock is fully saturated with dissolved oxygen and, due to hydrogeologic conditions, this water moves vertically downward through the tailings/rock as groundwater flow (Figure 2). For the calculations, the water is assumed to be calm, but another option will be examined in the following example.

The concentration of dissolved oxygen in equilibrium with the atmosphere varies with temperature, but is generally around 10 mg L\(^{-1}\) (0.3 mmol O\(_2\) L\(^{-1}\)). By Equation 1, one mole of O\(_2\) generates 1.07 moles of acidity and thus 10 mg L\(^{-1}\) would generate 33 mg CaCO\(_3\) equivalent L\(^{-1}\) of acidity. However, if the water then remains oxygen-free and the submerged material contains no entrapped air, then iron may remain in the ferrous state and Equation 2 would be more appropriate. By Equation 2, one mole of O\(_2\) generates 0.571 moles of acidity and thus 10 mg L\(^{-1}\) would generate only 18 mg CaCO\(_3\) equivalent L\(^{-1}\) of acidity. The rates from Tables 2 and 3 can be used to determine how far the water must flow before the oxygen is fully consumed.

After the initial acidity is generated in each liter of water from the dissolved oxygen, no additional acidity would appear unless acidity or entrapped air had accumulated in the material prior to submergence. Additionally, if the material contains some carbonate minerals and neutralization potential (NP), then the acidity would be neutralized in the manner described by Ferguson and Morin (1991) which takes into account site-specific, non-ideal reactions. Nevertheless, as more liters of water follow, more oxidation occurs and the NP is slowly, but consistently, consumed.
From the perspective of daily acid generation within a 1 m$^2$ vertical column of tailings or rock (Figure 2), the ACP (the active-flow version of Equation 10; not shown) is simply the rate of groundwater flow (e.g., from Darcy’s Law) multiplied by DO(pond) and FACT2 from Equation 10. Based on a simple relationship between particle diameter and hydraulic conductivity (Freeze and Cherry, 1979), the ACP rate of acid generation due to groundwater flow varies significantly with particle size (Figure 3).

3.2 Example #2: Turbulent Ponded Water
(or Submergence of Partially Saturated Material)

Conditions for this example are identical to those of Example #1, except for waves on the ponded water. If the wave action is minor, the results of Example #1 still apply. However, if air is entrained in the water (air bubbles) and this air reaches the submerged material, then additional acidity will be generated until the oxygen is consumed or the contact is broken. This situation is essentially the same for the scenario in which the tailings or rock are submerged in a partially saturated condition. Additional acidity is generated until the porespace oxygen is consumed.

3.3 Example #3: Stagnant Porewater

For this example, the overlying ponded water is assumed to be fully oxygenated at 10 mg L$^{-1}$ and the porewater in the underlying tailings/rock is assumed to be stagnant. According to Table 2, no oxidation will occur unless dissolved oxygen reaches the tailings, in spite of the presence of any ferric iron. In this case, dissolved oxygen can only reach the pyrite through diffusion. The general equations for oxygen diffusion are well discussed in published literature (e.g., Dave, 1992; Nicholson et al., 1989; Yanful, 1991) and the equations make use of the factors discussed in Equations 4 through 8.

With an average pyrite content of 10% and average porosity of 0.30, one mass of tailings (particle diameter = 0.0005m) and one mass of mine rock (diameter = 0.10m) would have ACP rates of acid generation (Equation 10 with FACT2 = 1.79) of $4.3 \times 10^{-4}$ and $3.9 \times 10^{-5}$ mg of CaCO$_3$ equivalent m$^{-2}$ s$^{-1}$, respectively. The faster rate in the tailings may seem initially surprising because the finer-grained tailings should restrict entry of oxygen. However, the finer grain size exposes more pyrite surface for each m$^3$ of tailings, which in turn leads to faster consumption of oxygen in each m$^3$, steeper oxygen gradients, and thus a greater flux of oxygen into the tailings. The rock cannot create such steep oxygen gradients because of the lesser amount of pyrite exposed, and lesser oxygen consumed, in each m$^3$ of rock. This relationship is depicted in Figure 3.

Figure 3 shows that, for particle diameter greater than roughly $10^{-6}$ to $10^{-5}$ meters (clay to medium silt), the rate of acid generation (ACP, Equation 10) could be dominated by groundwater flow rather than diffusion. This highlights the importance of characterizing the physical hydrogeology of a potential disposal site and the sulfide-bearing materials.
As a further complication, the concentrations (as mg L$^{-1}$) of products in the stagnant porewater are only partially dependent on the preceding fluxes and rates. Truly stagnant conditions will lead to (1) the eventual attainment of equilibrium conditions (Section 2 and Figure 1) and (2) the upward diffusion of products into the overlying pond water. The attainment of equilibrium could lead to secondary mineral precipitation, which in turn could begin to encapsulate reactive minerals within the tailings/rock. The upward diffusion could create a restriction of finely precipitated minerals at the water/material interface and could affect concentrations in the pond water, which are issues currently being examined as part of a MEND project (St-Arnaud, 1992). With time, however, interactions of the ponded water with the tailings/rock can be expected to decrease (Pedersen et al., 1991).

### 3.4 Actual Field Conditions

The preceding three examples are relatively simple scenarios which may be applicable to many disposal sites. Nevertheless, there are combinations of the examples and even other scenarios which may be more representative of a site. For example, downward groundwater flow may carry dissolved oxygen into tailings at a specific site, but the groundwater velocity may be sufficiently slow to allow upward diffusion of reaction products into the ponded water. Also, wave action could be strong enough to physically erode and suspend tailings in the water column, which in turn exposes more tailings to oxygen and minimizes the diffusion limitation of oxygen. The environmental conditions of a disposal site must therefore be well characterized before water chemistry can be evaluated or predicted.

### 4. SUMMARY

This paper has reviewed and further developed the theory of pyrite oxidation in submerged environments. This theory was then applied to three relatively simple scenarios. The most important conclusions are that site-specific conditions dominate in determining the eventual water chemistry and that environmental conditions of the disposal site should be well defined. In particular, the physical and chemical hydrogeology of the disposal area and the submerged materials should be characterized in sufficient detail to identify the applicable scenario and to reasonably estimate concentrations in the porewater and overlying ponded water.
ACKNOWLEDGEMENTS

Many thanks go to Mike Filion and Teck Corporation for the invitation to re-examine and summarize the issue of oxidation in subaqueous environments. This empirical assessment is based on the detailed research and field work of many others, who are helping the mining industry, the regulatory agencies, and the people of Canada to come to terms with acid drainage.

REFERENCES


