Prediction of Water Chemistry in Acid Mine Lakes:
The Minewall Technique

by

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Abstract

Water chemistry in acid mine lakes, derived from open-pit and underground mining, has been studied intensively for more than 30 years. The compilation of this work has led to a predictive technique named, “Minewall”, developed for the former Canadian Mine Environment Neutral Drainage (MEND) Program. Minewall includes procedures for collecting relevant data, interpreting the data, and optional computer modelling of complex scenarios.

Key geochemical requirements of Minewall are: unit-surface-area production rates, total reactive rock-surface area in a mine, and time-varying reaction-product retention and flushing. Data from several open-pit and underground mines are presented to illustrate the technique. For example, the measured unit-surface-area rates of sulfide oxidation and zinc production from rock surfaces span approximately three orders of magnitude. At one site, the rate of physical weathering was equivalent to the rate of chemical weathering, indicating new reactive minerals would continue to be exposed through closure. Also, the case studies indicate that up to 90% of weathering products are retained on the rock surfaces each year, and are thus available for relatively fast release upon closure and flooding of a mine, potentially leading to an acid mine lake.

Introduction

One primary concern for post-mining landscapes is the chemistry of water accumulating in, and flowing through, open pits and underground workings, collectively called “mine lakes” in this paper. The water in these mine lakes can be acidic and/or metal laden due to geochemical processes, and these conditions can persist for many decades and longer. Because the recovery of post-mining ecosystems around mine lakes is dependent on water chemistry, the prediction of the duration and severity of mine-lake chemistry is critical.

The detailed prediction of mine-lake chemistry has a relatively long history, reaching back to at least the 1960’s. For example, Morth et al. (1972) summarized studies from the 1960's
delineating the physical and geochemical processes affecting water chemistry in underground mines. A primary process affecting mine-water chemistry is, of course, the release of metals and/or acidity from the walls of the mine. However, Morth et al. (1972) indicated that the release occurs in three distinct modes: diffuse leaching, trickle leaching, and inundation leaching.

Diffuse leaching is generally continuous and represents the release of metal and/or acidity into non-point-source water which slowly and persistently enters the mine, including condensation (Morth et al., 1972). For wider applicability, this leaching is renamed “regular” release here.

Trickle leaching is the release of metals and/or acidity to point-source water, such as from a borehole or fracture, that occurs seasonally or during storm events. It is renamed “occasional” release here.

Finally, inundation leaching represents the release of metals and/or acidity to water which submerges at least part of the mine. Since this occurs by design only after mine closure, this release typically does not occur during operation. As a result, an inventory of readily leachable and soluble metals and acidity can accumulate in the walls of a mine during operation, awaiting post-mining flooding of the walls. The effects of this “recently submerged” release can be significant (e.g., MacGregor, 1966; Wolkersdorfer, 1996), and also has a parallel in submerging oxidized waste rock (Morin and Hutt, 1997; Morin and Hutt, 1999, this conference).

The Minewall Technique

The past work of Morth et al. (1972) and others was condensed and extrapolated to all types of mines under a study for the former Canadian MEND (Mine Environment Neutral Drainage) Project, named “Minewall” (Morin, 1990; MEND, 1995; Morin and Hutt, 1995; Morin and Hutt, 1997). The Minewall technique recognizes that the chemistry associated with water in mines is the result of three basic processes (Figure 1):

\[ \text{Conc}_m = \frac{\left[ \text{Flow}_1 \times \text{Conc}_1 \right] + \left[ \text{Flow}_2 \times \text{Conc}_2 \right] + \ldots + \text{MW}_i}{\text{Flow}_1 + \text{Flow}_2 + \ldots} \]

Each of these processes can be the dominant control on chemistry for a particular mine, depending on its unique combination of physical, chemical, and biological characteristics. As a result, all three must be considered.

During the operation of a mine, the first two processes are represented in Minewall by a basic mass-balance equation. This equation for concentrations in the drained or pumped minewater is relatively simple, using the units of milligram (mg), liters (L), and weeks (wk):

\[ \text{Conc}_m = \frac{\left[ \text{Flow}_1 \times \text{Conc}_1 \right] + \left[ \text{Flow}_2 \times \text{Conc}_2 \right] + \ldots + \text{MW}_i}{\text{Flow}_1 + \text{Flow}_2 + \ldots} \]
where  \( \text{Conc}_m \) = concentration in pumped/drained minewater (mg/L); 
Flow\(_x\) = positive (inflow) or negative (outflow) flowrate such as precipitation or groundwater (L/wk); 
Conc\(_x\) = concentration associated with Flow\(_x\) (mg/L); and 
MW\(_1\) = loading (mg/wk) from occasional and regular flushing of mine walls.

A negative value for \( \text{Conc}_m \) in Equation 1 means there is a net loss of water from the mine, which occurs in some circumstances (Morin and Hutt, 1997).

After mining when active pumping or draining ceases, concentrations in the water filling the mine can reflect additional effects like the ongoing accumulation of mine water, additional contributions from chemical retention in the mine walls, and the potential for flow reversals. As a result, all three aforementioned processes can be important (Figure 1). With units of mg, L, and a time step of one week, the general equation for concentrations in minewater during closure is:

\[
\text{Conc}_{m,t} = \left[ \text{Conc}_{m,t-1} \times \text{Volume}_{m,t-1} \right] + \left[ \text{Flow}_1 \times \text{Conc}_1 \right] + \left[ \text{Flow}_2 \times \text{Conc}_2 \right] + \ldots + \text{MW}_1 + \text{MW}_2 + \text{MW}_3 \times \text{Evol}_{m,t} / \text{Volume}_{m,t} \tag{2}
\]

and 
\[
\text{Volume}_{m,t} = \text{Volume}_{m,t-1} + \text{Flow}_1 + \text{Flow}_2 + \ldots \tag{3}
\]

where  \( \text{Conc}_{m,t} \) = Closure concentration (mg/L) in ponded minewater at current week, t 
\( \text{Conc}_{m,t-1} \) = Closure concentration (mg/L) in ponded minewater at previous week, t-1 
\( \text{Volume}_{m,t} \) = volume of ponded mine water at current week (L) 
\( \text{Volume}_{m,t-1} \) = volume of ponded mine water from previous week (L) 
MW\(_1\) = loading (mg/wk) from occasional and regular release from mine walls 
MW\(_2\) = loading (mg/wk) from recently submerged release from mine walls 
MW\(_3\) = any loading (mg/wk) from previously submerged mine walls 
Evol\(_{m,t}\) = factor representing evolution of minewater chemistry between times t-1 and t.

All Flow\(_x\) and Conc\(_x\) in Equations 1 to 3 must be known to predict mine-lake chemistry. Most of this required information on flows and concentrations, such as for precipitation and groundwater, can be obtained from routine monitoring of a minesite in any stage of planning, operation, or closure. Also, concentrations in precipitation and evaporation are often negligible and can thus be ignored. The remaining Conc\(_x\) for groundwater flow can come from monitor wells at the minesite. Therefore, most of the data requirements for Minewall assessments can be relatively easily obtained or estimated from normal monitoring data, except the MW\(_x\) factors and Evol\(_{m,t}\). Furthermore, because operating mines often monitor flow and chemistry (Conc\(_{m}\)) in mine drainage/pumpage, Equation 1 can sometimes be solved in reverse to obtain an unknown Conc\(_x\) or Flow\(_x\).
Minewall Factors ($MW_x$)

Again, the primary unknown factors in Equations 1 to 3 are often the $MW_x$ factors, reflecting loadings from the rock surfaces on and behind the mine walls (Figure 1). These loadings are considered “release rates” into the minewater, such as 300 mg Ca/wk. During operation and closure, these rates are determined by three factors: (1) unit-surface-area production rates, (2) total reactive rock-surface area in a mine, and (3) reaction-product retention and flushing. In other words, for one week of time:

$$\text{Release rate (MW}_x\text{, mg/wk}) = \left\{ \left[ \text{Production rate (mg/m}^2\text{ surface/wk)} \times \text{Total rock surface (m}^2\text{)} \right] + \left[ \text{Previously retained products (mg)} \right] \right\} \times \left\{ \frac{\% \text{Flushed from rock surfaces}}{100\%} \right\} \quad (4)$$

Unit-area production rates can be obtained for Equation 4 from “Minewall Stations” (see procedure in Appendix A). These stations are relatively simple and inexpensive. Nevertheless, they are effective at allowing reactions to proceed unhindered while preventing removal of reaction products until intended sampling.

Examples of unit-area production rates from Minewall Stations are provided in Table 1. The currently reported range of pH values measured at stations range from 2.2 to 7.3. Also, the rate of physical weathering of the mine walls at Mine 1 averaged 1400 mg of particles/m$^2$/wk, which was generally equivalent to the rate of chemical weathering (Table 1). As a result, fresh minerals at this mine were continuously being exposed for weathering and leaching.

After geochemical reaction rates are obtained for unit surface areas, the next parameter in Equation 4 is the amount of reactive rock surface. This is not synonymous with the visible or exposed surface within a mine due to fractures in the walls. Fractures are always present in mine walls, occurring naturally and induced by blasting and excavation (Evans, 1987; Pusch, 1989; Toran and Bradbury, 1988; Case Studies 3.2.2-1 and 3.2.2-2 in Morin and Hutt, 1997). These fractures can provide significant additional reactive surfaces. For example, Morth et al. (1972) and others have found reactive fracture surfaces that extended as far as 15 meters from the visible mine walls. Consequently, the fracture surfaces behind the mine walls can provide a much greater reactive surface than that indicated simply by the visible walls.

For example, a mine wall that has (1) spacings for vertical and horizontal fractures of 1 meter and (2) oxidation occurring to 10 meters behind the wall will have 41 m$^2$ of reactive surface for each m$^2$ of visible wall (41:1). Based on Minewall studies to date, the average estimated ratio varies from 27:1 to 161:1. Any waste rock, ore rock, tailings, or backfill placed in the mine can add significantly to this reactive surface area (MEND, 1995; see also the example below).

The retained reaction products on the reactive surfaces are released if water flows over and removes them. Because water flow is often intermittent, this leads to the third and last factor in Equation 4 for estimating $MW_x$ (Equations 1 to 4). The Minewall technique recognizes that certain percentages of the total reactive rock surfaces are flushed (1) regularly by precipitation, condensation, etc., (2) occasionally such as during snowmelt or a high-precipitation month, and (3)
not at all during operation, but soon after submergence. These are, in fact, the three types of “leaching” delineated by Morth et al. (1972) and discussed above. Studies of open pits to date show that only a few percent of annual reaction products is removed regularly, roughly 10-30% is removed occasionally, and 70-90% is retained throughout operation until submergence (Morin and Hutt, 1995). In contrast to pits, underground mines typically have lower percentages retained (5-50%) during operation (Morth et al., 1972; Morin and Hutt, 1997). At closure, the recently-submerged category can significantly affect water chemistry as the mine-lake level rises and flushes reaction products accumulated over the years from flooded surfaces (Figure 1). For walls above the flooded level, the first two categories (regular and occasional) continue to play an ongoing role in mine-lake chemistry for as long as the mine exists.

Evolution of Mine-Lake Water (Evol\textsubscript{m,t})

Once the chemical loadings from the inflows and mine walls have been added to the mine waters, water chemistry may reflect the combined loadings (\text{Evol}_{m,t} = 1.0 in Equation 2) or may begin to evolve due to various physical, chemical, and biological mechanisms (\text{Evol}_{m,t} \neq 1.0 in Equation 2). This evolution is one of the three basic processes affecting mine-lake chemistry and, in some cases, can significantly alter chemistry from that determined by mass-balance and MW\textsubscript{x} factors. For example, mineral precipitation/dissolution, controlled by equilibrium or kinetic processes, can greatly increase or decrease concentrations in mine-lake water. Also, redox reactions can change concentrations of some aqueous species through transformation to other ions. For example, sulfate-reducing bacteria can reduce sulfur from sulfate (SO\textsubscript{4}\textsuperscript{2-}) to sulfide (S\textsuperscript{2-}).

There are also physical mechanisms that can affect mine-lake chemistry. For example, “thermoclines” separate water layers with different temperature and “chemoclines” separate those with different chemistries (e.g., Wetzel, 1983). Due to seasonal changes in temperature and climate, unstable thermal stratification and internal waves can arise (Stevens et al., 1994 and 1995) and lead to some or all of the water layers mixing vertically (“turnover”). In turn, concentrations at a particular location in the mine lake can change significantly.

Two Examples of Minewall Simulations

A simple example of a Minewall simulation involved the delineation of rock units, static-test parameters (Table 2), and unit-area production rates from stations. The simulation was calibrated to existing monitoring data from the pit to obtain percentages of surfaces flushed at various intervals. The resulting prediction indicated that, although most of the walls were net acid generating and initial flushing of acidity upon floothing, pH would not be acidic through closure (Figure 2). This was a consequence of inflowing background groundwater with sufficient alkalinity to offset the release of retained acidity from the rock (Morin, 1990). This dominance of pit-water pH by inflowing groundwater has been noted at other minesites (MEND, 1995).

Another simple example illustrates the value of Minewall in optimizing chemical controls.
Minewall stations in an existing underground mine showed that the walls could only account for 2-3% of metals and acidity in the water. A review of historical records revealed that approximately 40,000 t of broken massive-sulphide ore was left on some levels. Simple estimates of the particle-surface areas of this ore indicated that it could account for most of the observed acidity and metals. Therefore, control plans focussed on removing or encapsulating the broken ore rather than the walls of the mine.

References


APPENDIX A
Installation and Operation of Monitoring Stations for Minewall Investigations (from Morin and Hutt, 1997)

Equipment (for each station):
- 3 m of 90°-bent, flexible plastic bathtub edging
- 2 tubes of pure silicon bathroom sealant (must be pure silicon)
- 1 sheet of clear plastic 1 m by 1 m
- 8 black metal clasps often used for holding unbound reports
- 1 L of distilled water in a squeeze bottle which allows the direction and pressure of water to be controlled

Installation Procedure (see Figure A1):
- Select a relatively flat surface of rock, preferably with no surface fractures, measuring no more than 1 m by 1 m.
- Mark the intended perimeter of the station on the surface with a pencil, with three, four, or five limbs.
- The lowest, or bottom, limb must slope downwards from horizontal so that all water caught on it will drain in one direction for collection and later analysis.
- Cut the plastic edging to the length required for each limb.
- Install each limb by using pure silicon sealant as glue.
- Ensure silicon sealant fills all open spaces between the edging and the rock surface so that no water can pass through.
- Ensure each limb overlaps so that no gaps exist at any junction.
- Ensure the upper limb(s) will divert water around the sides of the station so that the water will not flow over the isolated area.
- With 1 L of distilled water, wash the entire isolated surface within the edging, rinsing out any loose rock/dust and ensuring all water is caught by the edging and directed to the bottom limb where the water can then be caught in a bottle.
- Cut the clear plastic sheet to extend 2 cm over each limb, then loosely attach the plastic sheet with the metal clasps, ensuring the plastic sheet does not touch the rock surface but prevents all precipitation or runoff from reaching the isolated rock surface.

Regular Sampling:
- Carefully remove the plastic sheet and place it somewhere clean and dry.
- Inspect the station for loose edging and broken seals against the rock; repair any problems AFTER sampling (below), but avoid losing rinse water through any broken seals.
- Record a note if there is any condensation and if any water may have condensed and trickled out of the station between sampling events.
- Place a calibrated collection bottle at the downstream (outflow) end of the lower limb (trough) to catch all subsequent rinse water.
- With a calibrated squeeze bottle, spray at least 200 mL onto the isolated rock surface to rinse the
entire area thoroughly; use as little water as possible; it is important to catch all rinse water in the collection bottle; record the volume of water sprayed on the rock.

Record the amount of water recovered in the collection bottle.

Analyze the water in the collection bottle like any other water sample, including pH, acidity, alkalinity, sulfate, dissolved metals, and total metals as desired.

As a quality-assurance procedure for one round of sampling, also filter a similar volume of the distilled water through a 0.45 µm filter, then analyze like all other water samples.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mine 1</th>
<th>Mine 2</th>
<th>Mine 3</th>
<th>Mine 4</th>
<th>Mine 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Stations</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>pH (pH units)</td>
<td>6.43-7.28</td>
<td>4.9-6.1</td>
<td>6.23-7.31</td>
<td>2.15-2.60</td>
<td>4.49-6.39</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>21-280</td>
<td>7.0-73</td>
<td>4.8-25</td>
<td>0</td>
<td>0-200</td>
</tr>
<tr>
<td>Acidity</td>
<td>1.4-22</td>
<td>3.6-54</td>
<td>-</td>
<td>-</td>
<td>1.6-28</td>
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<tr>
<td>Sulfate</td>
<td>120-2700</td>
<td>48-540</td>
<td>8.9-190</td>
<td>-</td>
<td>3.6-35</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.0082-1.5</td>
<td>0.080-3.2</td>
<td>-</td>
<td>-</td>
<td>0.032-0.11</td>
</tr>
<tr>
<td>Aluminum</td>
<td>&lt;0.3</td>
<td>0.013-0.13</td>
<td>0.13-1.1</td>
<td>-</td>
<td>0.0078-2.0</td>
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<tr>
<td>Cadmium</td>
<td>&lt;0.014</td>
<td>0.00095-0.033</td>
<td>&lt;0.01</td>
<td>-</td>
<td>0.0049-0.037</td>
</tr>
<tr>
<td>Calcium</td>
<td>41-250</td>
<td>-</td>
<td>9.2-75</td>
<td>-</td>
<td>3.6-120</td>
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<tr>
<td>Copper</td>
<td>0.0086-0.88</td>
<td>0.0087-2.4</td>
<td>0.0089-0.062</td>
<td></td>
<td>0.015-1.4</td>
</tr>
<tr>
<td>Magnesium</td>
<td>17-530</td>
<td>0.15-3.3</td>
<td>-</td>
<td>-</td>
<td>0.24-9.9</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.015-2.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.025-1.0</td>
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<tr>
<td>Molybdenum</td>
<td>0.0082-0.36</td>
<td>0.00021</td>
<td>0.0000204</td>
<td>-</td>
<td>1.7x10⁻⁵-0.0053</td>
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<tr>
<td>Sodium</td>
<td>1.2-4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.39-2.0</td>
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<tr>
<td>Zinc</td>
<td>0.0022-0.092</td>
<td>0.20-3.9</td>
<td>&lt;0.10-0.17</td>
<td>-</td>
<td>0.073-3.2</td>
</tr>
</tbody>
</table>

¹ all parameters in units of mg/m²/wk, except Number of Stations (integer) and pH (pH units).
TABLE 2
Partial Input Data for the Simulation of the Main Zone Pit at Equity Silver Mines
(adapted from Morin, 1990)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rock Unit #1</th>
<th>Rock Unit #2</th>
<th>Rock Unit #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock Type</td>
<td>Gabbro</td>
<td>Volcanics</td>
<td>Volcanics</td>
</tr>
<tr>
<td>Net Neutralization Potential from Acid-Base Accounting (t CaCO$_3$/1000 t)</td>
<td>&gt; 0.0</td>
<td>-40 to 0.0</td>
<td>&lt; -40</td>
</tr>
<tr>
<td>Orientation on Pit Wall</td>
<td>Vertical</td>
<td>Vertical</td>
<td>Vertical</td>
</tr>
<tr>
<td>Exposed Surface Area (m$^2$)</td>
<td>315000</td>
<td>234000</td>
<td>214000</td>
</tr>
<tr>
<td>Sloping Walls - Percentage of Total Area</td>
<td>35%</td>
<td>35%</td>
<td>35%</td>
</tr>
<tr>
<td>Sloping Walls - Angle from Horizontal (degrees)</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Exposed Acid-Generating Sulfur (g S/m$^2$)</td>
<td>48</td>
<td>64</td>
<td>144</td>
</tr>
<tr>
<td>Exposed Neutralization Potential (g CaCO$_3$/m$^2$)</td>
<td>225</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>Reactive Surface (m$^2$) for each m$^2$ of Pit Wall</td>
<td>21</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td>Fracture Flushed: - percentage flushed monthly</td>
<td>28%</td>
<td>28%</td>
<td>28%</td>
</tr>
<tr>
<td>- percentage flushed once a year</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>- percentage not flushed during operation</td>
<td>70%</td>
<td>70%</td>
<td>70%</td>
</tr>
</tbody>
</table>
FIGURE 1. Schematic Diagram of Interactions between a Mine Wall and Adjacent Mine Lake after Mine Closure.
FIGURE 2. Predicted pH from a Minewall Simulation in Drainage (during Operation) and in the Mine Lake (after Closure).
FIGURE A1. Example of a Minewall Station, Plan View and Cross-Section (from Morin and Hutt, 1997).