GEOCHEMICAL PREDICTION AND REMEDIATION OPTIONS FOR THE PROPOSED MARTHA MINE PIT LAKE, NEW ZEALAND

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Abstract. Upon closure in 2007, the Martha gold mine, New Zealand, will be flooded with river water creating a 192-m-deep pit lake. The mine owners intend to rehabilitate the lake into a public recreation area for boating and swimming, which will have additional value as a habitat for waterfowl and fish. This study demonstrates how a geochemical prediction of pit lake water quality can identify modifications to closure plans that will potentially improve post-mining water quality and increase the value of a proposed pit lake resource. The geochemical model PHREEQC was used to construct three, 55-year predictions of epilimnion and mixolimnion water quality in the proposed Martha pit lake, based on recent mineralogic and limnologic investigations. Model 1 considered the current closure strategy, whereas Model 2 covered all wall rocks that produced highly-acidic runoff (HAR) before lake filling (21 ha covered), and Model 3 covered only HAR rocks exposed above the steady-state lake surface (3 ha covered). After 50 years of steady-state conditions, Model 1 predicted that surface water will have a pH < 5.0 and will not comply with New Zealand water quality guidelines for recreational use. The epilimnion will also contain Cu and Zn concentrations that exceed aquatic life protection guidelines. By covering all HAR producing areas, Model 2 showed the epilimnion pH increased to 7.0 and Cu concentrations dropped significantly. Most significantly, Model 3 showed that covering only HAR producing areas exposed above final lake surface produced similar results to Model 2 after 50 years of steady-state conditions, increasing pH to 6.8 and lowering Cu concentrations. Zinc concentrations remained above aquatic life protection guidelines in each modeling scenario, and may limit the number of sensitive waterfowl and fish species utilizing the lake. Because only 11% of the wall rock area exposed above the steady-state lake surface will produce HAR, covering these wall rock areas is a feasible remediation option for the mine owners to consider, which is likely to improve future water quality and allow the pit lake to be used as a recreational resource.

Additional Key Words: modeling, PHREEQC, acid rock drainage
**Introduction**

Geochemical predictions of pit lake water quality are used to assess whether a proposed pit lake will potentially have positive or negative environmental impacts. This information allows mine managers to design a site closure plan that minimizes negative impacts and liabilities, and optimizes the value of the pit lake as a post-closure water resource.

To create a pit lake that becomes a valuable post-closure water resource involves extensive consultation with the surrounding community, because the community will use the resource long after the mining company has been released from its regulatory obligations. Community dialogue identifies one or more end uses which the mining company can progressively work toward producing throughout the mine life. Examples of end uses include public recreation areas and ecological reserves. Once a desired end use has been agreed upon, the results of geochemical predictions of pit lake water chemistry can be compared to water quality guidelines for the desired end use to assess whether a given closure plan will produce the desired outcome.

This paper demonstrates how a detailed geochemical prediction of a pit lake water quality can be used to identify modifications to a pit mine closure plan that will improve post-mining water quality and increase the value of a pit lake as a post-mine resource. The proposed Martha mine pit lake in New Zealand was used as a case study for this demonstration (Fig. 1). Previous research by Castendyk et al. (2005) differentiated the wall rocks of the Martha mine into regions that are likely to produce highly-acidic runoff (HAR) and regions that are likely to produce moderately-acidic runoff (MAR). This study considered two modifications to the existing Martha mine closure plan:

a) Cover all HAR-producing areas with MAR producing wall rocks before lake filling;

b) Cover only HAR-producing areas exposed above the final lake surface with MAR producing wall rocks.

The potential benefits of these closure plan modifications were determined by creating a geochemical prediction of the Martha lake based on the existing closure plans, and performing a sensitivity analysis on the chemistry of runoff inputs.

**Scope of Paper**

This paper focuses on the design of the geochemical model, and the sensitivity of the model output to changes in the proportions of HAR and MAR inputs. These changes represent the hypothetical burial of HAR producing rocks using MAR producing rocks obtained from the pit. Geotechnical issues related to the design of the MAR cover, such as the required thickness of the cover and the stability of the cover, are not included in this paper, neither has a cost estimate of the cover been included. Rather, this paper illustrates the potential benefits of covering HAR rocks, which itself provides the incentive for further geotechnical and cost-estimation studies on part of the mining company. Sensitivity studies that explored the effect of trace metal adsorption onto iron hydroxide surfaces, and subaqueous water-rock reactions, including the oxidation of pyrite, were also conducted as part of this modeling effort. The results of this expanded geochemical model will appear in a future publication.
Figure 1. Geologic map of the Coromandel Peninsula, North Island, New Zealand, showing the location of the Martha mine and other epithermal Au-Ag deposits in the Hauraki Goldfield (after Skinner, 1986).
Background on the Martha Mine

The Martha mine is located within the Waihi low-sulfidation epithermal Au-Ag deposit, on the Coromandel Peninsula, North Island, New Zealand (Fig. 1). The Coromandel Peninsula contains andesitic to rhyolitic volcanic rocks produced by regional volcanism that occurred between 7.9 and 3.9 million years ago (Ma) along a continental-margin, volcanic arc system (Brathwaite and Skinner, 1997). Andesitic host rocks at Waihi formed between 7.9 and 6.3 Ma (Brathwaite and Christie, 1996).

In association with volcanic activity, multiple shallow hydrothermal systems became active, and emplaced approximately 50 epithermal Au-Ag deposits and several porphyry copper deposits throughout the peninsula (Brathwaite et al., 1989). Hydrothermal alteration at Waihi occurred within one million years of volcanic deposition, and was controlled by near-vertical tension fractures. These fractures filled with quartz-adularia veins containing the Au and Ag ore minerals, electrum and acanthite (Brathwaite and Faure, 2002). Pyrite is the most abundant sulfide in the deposit, although sphalerite, galena, chalcopyrite, and tetrahedrite have also been reported (Brathwaite and McKay 1989; Panther et al., 1995; Brathwaite and Faure, 2002). Hydrothermal fluids altered the parent andesite to rocks that contain quartz, adularia, chlorite, illite, pyrite, calcite, albite, and kaolinite (Brathwaite, 1980; Brathwaite and McKay, 1989; Jennings et al., 1990; Brathwaite and Faure 2002).

Castendyk et al. (2005) identified the spatial distribution and concentration of these minerals in mine wall rocks, and used this information to evaluate the acid-generating potential and acid-neutralizing potential of the pit walls. Assuming that rocks containing less than 2 moles of calcite for each mole of pyrite would be acid generating, these authors identified 3 mineral associations that were likely to produce HAR (i.e. weathered argillic, fresh argillic, and potassic associations), whereas the remaining wall rocks (i.e. propylitic, oxidized, and weakly-altered associations, plus quartz veins and post-mineralization deposits) were likely to produce MAR. Prior to lake filling, this study indicated 34 % of the wall-rock area (21.2 ha in 2002) would produce HAR, whereas 66 % of the wall rock area (41.0 ha in 2002) would produce MAR. This proportion will change as the lake level rises, so that under steady-state conditions, only 11 % of the wall-rock exposed above the lake surface (3.1 ha in 2002) will produce HAR and 89 % of the wall rock (26.5 ha in 2002) will produce MAR. As the pit is still expanding due to mining, only estimates of mineral association areas in the final pit wall are available, but the proportions of HAR and MAR producing areas are assumed to be consistent with the 2002 values.

The Martha mine has been, and continues to be, a world-class epithermal Au producer. Underground mining from 1878 through 1952 produced approximately 1.2 million kg of Au-Ag bullion. Historic mine shafts extended 600 m below the land surface, and connected over 175 km of horizontal mine tunnels. The mine was closed in 1952, and reopened in 1988 with the excavation of an open pit. Ore rocks contain 3.2 g/metric ton Au and 32 g/metric ton Ag.

The pit mine is anticipated to close in 2007. At that time, surface water from the adjacent Ohinemuri River will be diverted into the pit to accelerate the rate of lake filling and to improve post-mining water quality. Hydrologic models and water balances predicted that it will take less than 5 years for the lake elevation to reach its steady-state discharge elevation as a product of river water, groundwater, rain water, and pit wall runoff inputs (Woodward-Clyde, 1997a, Woodward-Clyde, 1997b, Geochimica, 1997a).
Due to the density difference between the warm, low-salinity river water input and the cool, high-salinity groundwater input, a recent limnologic prediction of Martha lake showed that high-density groundwater inputs were unlikely to mix with low-density river water inputs during lake filling, and that a permanently-isolated monimolimnion (Layer 3) was likely to develop at the bottom of the lake (Castendyk and Webster, 2004). This meromictic prediction showed groundwater would accumulate in Layer 3 during lake filling, whereas river water, rain water, and pit wall runoff would accumulate in the epilimnion (Layer 1), and this layer would mix with the mixolimnion (Layer 2) between late autumn and early spring. An earlier limnologic investigation (Spigel, 1997) predicted the lake would undergo complete circulation on a regular basis. This 1997 limnology prediction was used in a 1997 geochemical prediction of lake water quality (Geochemica, 1997a). The new meromictic prediction required a new geochemical prediction of the lake.

The final lake will have a maximum depth of 192 m, a surface area of 28.7 ha, and a volume of 2.16 x 10^7 m^3. Layer 1 of the steady-state pit lake will receive direct precipitation, pit wall runoff, and groundwater, and will discharge water through a surface outlet that will maintain the lake surface at a constant elevation. The mining company has committed to rehabilitate the pit lake into a public recreation area for boating, swimming, and hiking (Waihi Gold Company, 1997; Ingle, 2002). This recreation area is expected to have additional ecological value as a habitat for waterfowl and fish.

**Methods**

**Overview**

The geochemical program PHREEQC, version 2 (Parkhurst and Appello, 1999), was used to construct three 55-year predictions of the water chemistry in Layer 1 and Layer 2:

i) Model 1 was based on the current closure strategy for the Martha mine using a water-balance approach;

ii) Model 2 considered covering all HAR-producing wall rocks inside the pit catchment with MAR-producing material before lake filling;

iii) Model 3 considered covering only HAR-producing wall rocks exposed above the final pit lake surface with MAR-producing material.

Each model considered five years of lake-filling conditions (labeled Year -4, Year -3, Year -2, Year -1 and Year 0), followed by 50 years of steady-state conditions (labeled Year 1 to Year 50). For each model, the resulting water chemistry of Layer 1 was compared to New Zealand water quality guidelines for recreational use and ecological protection (ANZECC, 2000) and other water quality guidelines to evaluate whether future surface water quality would support the desired post-mining uses. The chemistry of Layer 3, the permanently isolated monimolimnion, was not modeled. The thermodynamic database MINTEQ.dat by Allison et al. (1991) was used because it has one of the largest collections of thermodynamic data available and is well suited to model the trace metal chemistry found in pit lakes (Bird et al., 1994).

Representative input water chemistry was determined from 110 water analyses reported in the Martha mine technical reports, with samples collected from groundwater (n = 45), river water (n = 17), MAR (n = 13), and HAR (n = 35) (Table 1). Groundwater samples were collected from over a dozen separate wells located inside the pit, on the periphery of the pit, and from the...
surrounding area within 1 km of the pit. River water data were collected from two points on the Ohinemuri River near the pit water intake point. Only two samples included in the HAR and MAR datasets represent humidity cell leachate data. The remaining water samples were collected directly from puddles, sheet wash from mine walls, and streams inside the pit and surrounding the waste rock stacks following rain events.

All analyses had ionic charge imbalances less than 10%. Rain water was assumed to have H\(^+\) and HCO\(_3\)\(^-\) concentrations in equilibrium with atmospheric CO\(_2\), whereas all other dissolved constituents were assumed to be zero. Redox conditions and dissolved oxygen data were unavailable for most analyses. Instead, Eh values were estimated using the representative pH in Table 1, and Eh-pH graphs for groundwater, rain water, mine water, and river water presented by Baas Becking et al. (1960). All Eh values were converted to pe values using the Nernst equation and a temperature of 15 °C. Groundwater was assumed to be anoxic, while all other inputs were assumed to have a dissolved oxygen concentration of 8.0 mg/L based on observed river water concentrations (Bioresearchers, 1997).

Four mineral phases were allowed to precipitate from solution if they became oversaturated: ferrihydrite [Fe(OH)\(_3\)], manganite [MnO(OH)], amorphous gibbsite [Al(OH)\(_3\)], and barite [BaSO\(_4\)]. The MINTEQ.dat database gives the following equations for the precipitation of these phases:

\[
\begin{align*}
\text{Fe}^{3+} + 3\text{H}_2\text{O} & = \text{Fe(OH)}_3 + 3\text{H}^+ \quad (1) \\
\text{Mn}^{3+} + 2\text{H}_2\text{O} & = \text{MnO(OH)} + 3\text{H}^+ \quad (2) \\
\text{Al}^{3+} + 3\text{H}_2\text{O} & = \text{Al(OH)}_3 + 3\text{H}^+ \quad (3) \\
\text{Ba}^{2+} + \text{SO}_4^{2-} & = \text{BaSO}_4 \quad (4)
\end{align*}
\]

The selection of these phases was based on an extensive review of solubility controls in 24 existing hard-rock pit lakes and 66 existing coal mine pit lakes with pH between 4.5 and 7 undertaken by Eary (1999). A constant temperature of 15 °C was assumed for all input solutions and reactions. Sensitivity analyses were also performed to explore the effects of trace metal adsorption onto ferrihydrite, and interactions between lake water and submerged wall rocks, particularly pyrite oxidation. The results of these analyses will be published separately.

**Modeling Procedure for Lake-Filling Conditions**

Figure 2 summarizes the procedures used to predict the water chemistry of Layer 1 and 2 during five years of lake-filling in Model 1. The mixing quantities were based on a water balance by Woodward Clyde (1997b) that determined the volumes of runoff, groundwater, river water, and rainwater as the lake filled over time. An average runoff volume was specified for each one-year time step during lake filling. This value was multiplied by the percentages of HAR producing wall rock and MAR producing wall rock to determine the volume of each type of runoff added to the lake during each year of lake filling. The combined runoff was mixed with river water and net rainwater to determine the total volume of Layer 1 and 2 after the first year of lake filling, following winter turnover.

To determine the composition of Layer 2 at Year -4, ferrihydrite, manganite, amorphous gibbsite, and barite were allowed to precipitate if they were oversaturated (Eq. 1 to 4). It was assumed that Layer 1 extended to a depth of 20 m during the summer (Castendyk and Webster, 2004), allowing the volume of Layer 1 to be estimated from the lake water balance (Woodward-
Table 1. Representative chemical analyses for lake inputs.

<table>
<thead>
<tr>
<th></th>
<th>River Water (^a)</th>
<th>Groundwater (^b)</th>
<th>Moderately-Acidic Runoff (MAR) (^c)</th>
<th>Highly-Acidic Runoff (HAR) (^d)</th>
<th>Rainwater (^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.9</td>
<td>6.7</td>
<td>5.4</td>
<td>3.1</td>
<td>5.7</td>
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<tr>
<td>Eh (mV)</td>
<td>450</td>
<td>200</td>
<td>400</td>
<td>576</td>
<td>600</td>
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<tr>
<td>pe</td>
<td>7.86</td>
<td>3.5</td>
<td>7</td>
<td>10</td>
<td>10.49</td>
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<td>Temp (°C)</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
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<td>n</td>
<td>17</td>
<td>45</td>
<td>13</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td>Na</td>
<td>9.2</td>
<td>49.7</td>
<td>3.6</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>3.6</td>
<td>9.7</td>
<td>0.7</td>
<td>0.4</td>
<td>0</td>
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<td>Ca</td>
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<td>391</td>
<td>0.49</td>
<td>81.5</td>
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<td>Mg</td>
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<td>87</td>
<td>0.366</td>
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<td>Al</td>
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<td>0.05</td>
<td>0.059</td>
<td>7.23</td>
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</tr>
<tr>
<td>Fe (total)</td>
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<td>1.4</td>
<td>0.04</td>
<td>18.3</td>
<td>0</td>
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<tr>
<td>Mn (total)</td>
<td>0.07</td>
<td>10.2</td>
<td>0.022</td>
<td>1.22</td>
<td>0</td>
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<tr>
<td>Cu (total)</td>
<td>0.0018</td>
<td>0.001</td>
<td>0.0027</td>
<td>0.0465</td>
<td>0</td>
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<tr>
<td>Zn</td>
<td>0.0033</td>
<td>0.4</td>
<td>0.053</td>
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<td>NH₄</td>
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<td>0.139</td>
<td>0.026</td>
<td>0.03</td>
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<tr>
<td>As (total)</td>
<td>0.0005</td>
<td>0.017</td>
<td>0.0005</td>
<td>0.003</td>
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<tr>
<td>Ba</td>
<td></td>
<td>0.4</td>
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<td>0.0418</td>
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<td>Cd</td>
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<td>0.000025</td>
<td>0.00032</td>
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</tr>
<tr>
<td>Cr (total)</td>
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<tr>
<td>Pb</td>
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<td>0.0005</td>
<td>0.0016</td>
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<tr>
<td>Ni</td>
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<td>0.022</td>
<td>0.0008</td>
<td>0.17</td>
<td>0</td>
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<tr>
<td>Hg (total)</td>
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<td>0.00012</td>
<td>0.0001</td>
<td>0.0005</td>
<td>0</td>
</tr>
<tr>
<td>HCO₃</td>
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<td>4.0</td>
<td>0.5</td>
<td>0.122</td>
</tr>
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<td>11.8</td>
<td>5.0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>SO₄</td>
<td>35</td>
<td>1109</td>
<td>4.0</td>
<td>424</td>
<td>0</td>
</tr>
<tr>
<td>NO₃</td>
<td>4.91</td>
<td>0.04</td>
<td>0.004</td>
<td>0.007</td>
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<tr>
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<td>0.005</td>
<td>0.001</td>
<td>0.006</td>
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<td>0.109</td>
<td>0</td>
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<tr>
<td>SiO₂</td>
<td>24.3</td>
<td>-</td>
<td>1.7</td>
<td>21.0</td>
<td>0</td>
</tr>
<tr>
<td>% Balance</td>
<td>2.17</td>
<td>8.23</td>
<td>9.23</td>
<td>7.02</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Data sources: Geochimica 1997a; Geochimica 1997b; Bioresearches, 1997.


\(^e\) Bicarbonate concentration calculated by PHREEQC based on equilibrium with atmospheric CO₂ and O₂.

% Balance = % charge balance

*Italicized* values represent half of the detection limit for the corresponding species. These values were used for species with concentrations below detection limits.
Clyde, 1997b). To calculate the composition of Layer 1 at Year -4, the solution for Layer 2 was allowed to equilibrate with atmospheric CO₂ gas (partial pressure = 0.00033 bar), and O₂ gas (partial pressure = 0.21 bar), followed by the precipitation of oversaturated ferrihydrite, manganite, amorphous gibbsite, and barite.

A slightly modified procedure was used to define the composition of Layers 1 and 2 for Years -3, -2, -1, and 0 (Fig. 2). For these years, the combined runoff was mixed with river water, net rainwater, and a solution with the volume and composition of Layer 1 from the previous year (at time \( t - 1 \)) to yield a pre-turnover Layer 1 composition (at time \( t \)). This pre-turnover Layer 1 solution was mixed with Layer 2 from the previous year (at time \( t - 1 \)), followed by the precipitation of oversaturated species, to yield the composition of Layer 2 (at time \( t \)). The
Figure 3. Flow chart of procedures for the steady-state scenario, Years 1 to 50, in Model 1.
composition of Layer 1 was determined by equilibrating the solution for Layer 2 with atmospheric gases and precipitating oversaturated species.

**Modeling Procedure for Steady-State Conditions**

The procedure for the steady-state conditions in Model 1 required careful consideration of layer volumes in order to conserve the total volume of the lake (Fig. 3). First, the composition of Layer 1 at time \( t \) was calculated prior to turnover by mixing combined HAR and MAR inputs (based on steady-state wall rock proportions), groundwater added to Layer 1, and rainwater with Layer 1 at the conclusion of lake filling \( (t - 1) \). Second, the model calculated the volume of Layer 1 after discharge from the surface water outflow by adding the initial Layer 1 volume to runoff, groundwater, and rainfall volumes, and subtracting the volume of the outflow.

For the third step, the model calculated the composition of Layer 2 by mixing the chemistry of Layer 2 from the previous year \( (t - 1) \) with the groundwater input to Layer 2 \( (\text{year } t) \). The fourth step calculated the volume of Layer 2 prior to turnover, by subtracting the volume of Layer 3 \( (\text{at time } t) \) plus the volume of Layer 1 after outflow \( (\text{at time } t) \) from the total volume of the lake \( (2.17 \times 10^7 \text{ m}^3) \). In the final step, the model calculated the chemistry of Layer 2 by mixing a solution that had the chemistry of Layer 1 prior to turnover and the volume of Layer 1 after outflow, with a solution that had the chemistry and volume of Layer 2 before turnover, and allowing oversaturated phases to precipitate. To determine the chemistry of Layer 1, this final solution was equilibrated with atmospheric dissolved oxygen and carbon dioxide and oversaturated phases were allowed to precipitate. This same procedure was repeated for Years 1 to 50.

**Sensitivity Analysis for Remediation Options**

A sensitivity analysis explored remediation options by substituting the chemistry of HAR input with MAR input. Model 2 considered the covering of all HAR-producing wall rock with MAR-producing material before lake filling. Therefore, in Model 2, MAR input chemistry was substituted for HAR input chemistry for the entire model. In contrast, Model 3 considered covering only HAR-producing wall rocks exposed above the final lake surface beginning at Year 1. To be conservative, Model 3 inputs were identical to Model 1 inputs during lake-filling, and MAR input chemistry was substituted for HAR input chemistry during steady-state conditions (Year 1 to Year 50). Apart from changes to the input runoff chemistry, all modeling procedures described for Model 1 were performed for Models 2 and 3 (Fig. 2 and 3).

**Results**

**pH, Total Iron, and Total Manganese**

Under the present closure strategy used in Model 1, the pH of lake water would decrease to 4.8 after 50 years of steady-state conditions (Fig. 4), and would be below New Zealand water quality guideline for recreational use \( (\text{pH } = 6.5, \text{ANZECC, 2000}) \). The pH of Layer 1 increased during lake filling from pH 5.8 to 6.5, due to the addition of river water \( (\text{pH } 6.9, \text{Table 1}) \). Once steady-state conditions were achieved, and river water was no longer added to the lake, the pH of Layer 1 and 2 began to decrease owing to the low pH \( (3.1) \) and high Fe \( (18.3 \text{ mg/L}) \) and Mn \( (1.22 \text{ mg/L}) \) concentrations in the HAR input (Table 1). During lake-filling conditions, Fe and Mn concentrations decreased owing to dilution from river water. Under steady-state conditions, when river water was not added to the lake and runoff constituted a significant portion of the annual input to Layers 1 and 2, Fe and Mn concentrations increased over time. Because Layers
Figure 4. Fe, Mn, and pH from models 1, 2, and 3. Water quality guidelines are from the following sources: 1 ANZECC (2000), 2 WHO (1998), 3 USEPA (2002).
1 and 2 circulated annually, these layers had high dissolved oxygen concentrations and oxidizing redox conditions. The addition of Fe and Mn from HAR to Layers 1 and 2 caused the precipitation of ferrihydrite and manganite which released $\text{H}^+$ according to Equations 1 and 2. These reactions caused the pH of lake water to decrease over time in Model 1.

Model 2 predicted that covering all HAR-producing wall rocks before lake filling would produce lake water with a higher pH and lower concentrations of Fe and Mn that would comply with water quality guidelines for recreational use (Fig. 4). By removing all HAR inputs before lake-filling occurred, Model 2 predicted the pH of Layer 1 would begin at 7.3 and decrease to 6.9 after 50 years of steady-state conditions. Iron and Mn concentrations were significantly lower in the resulting lake water due to the lower concentrations of these components in the MAR input (Table 1). Both Fe and Mn showed a slight increase in lake water between Year 0 and Year 50 due to the input of groundwater under steady-state conditions. This small increase in Fe and Mn coupled with the precipitation of ferrihydrite and manganite caused the slight decrease in pH over time.

Model 3 showed that covering only HAR-producing wall rocks above the final lake surface would also produce lake water that satisfied recreational guidelines for pH (Fig. 4). To create a conservative “worst case” estimate of lake chemistry during lake filling, the proportions of HAR and MAR added during lake-filling in Model 3 were identical to those in Model 1, and these models produced the same results. During steady-state conditions in Model 3, HAR was not added to the lake which made the pH of Layer 1 increase over time from 6.5 to 6.8, whereas the concentrations of Fe and Mn decreased over the same period.

**Trace Metal Concentrations**

Dissolved concentrations of As, Cd, Cu, Pb, Ni, and Zn were equal in Layers 1 and 2 of each model as a result of annual circulation between these layers (Fig. 5 and 6). The models did not allow for the precipitation of mineral phases containing these metals, or the surface adsorption of these metals onto oxide precipitates, which might have produced different concentrations in different layers due to variations in pH and/or redox conditions. River water contained very low concentrations of dissolved metals, therefore metal concentrations decreased during lake-filling conditions owing to river water dilution.

In each model, concentrations of As and Cd (Fig. 5) and Pb and Zn (Fig. 6) increased over time under steady-state conditions, with Zn concentrations exceeding the threshold for 80% aquatic life protection after 30 years in each model (Fig. 6). The substitution of HAR inputs with MAR inputs caused only a slight reduction in dissolved concentrations over time because these species had low concentrations in the HAR. However, groundwater exhibited high concentrations of each metal (Table 1) and groundwater inputs during steady-state conditions were responsible for the observed metal increases over time.

In the absence of rehabilitation, Model 1 predicted that Cu concentrations would show a slight decrease over time and would exceed the threshold for 80% aquatic life protection for the entire 55-year period (Fig. 5), whereas Ni concentrations would show a slight increase over time under steady-state conditions (Fig. 6). Copper concentrations decreased because groundwater contained very low concentrations of Cu (Table 1) and steady-state groundwater inputs diluted Cu concentrations in the lake over time. Nickel concentrations increased because steady-state groundwater inputs contained elevated concentrations of Ni (Table 1) and contributed to Ni concentrations in the lake.
Figure 5. As, Cd, and Cu concentrations from Models 1, 2, and 3. Water quality guidelines are from the following sources: \(^1\) ANZECC (2000); \(^2\) WHO (1998).
Figure 6. Pb, Ni, and Zn concentrations from Models 1, 2, and 3. Water quality guidelines are from the following sources: ¹ ANZECC (2000), ² WHO (1998).
As opposed to Pb, Zn, As, and Cd, HAR contained high concentrations of Ni and Cu. Therefore, the substitution of HAR with MAR caused a significant difference in the concentration of these metals over time, most notably Cu (Fig. 5 and 6). In Model 2, all HAR producing areas were covered, which produced very low concentrations of both metals during lake-filling. Due to groundwater inputs, Cu concentrations showed a slight decrease over time (Fig. 5) whereas Ni concentrations showed a slight increase over time (Fig. 6). For the entire 55 year model, Cu concentrations were below the 80% aquatic life protection guideline and improved to within the 95% aquatic life protection guideline after 30 years (Fig. 5).

Under steady-state conditions in Model 3, both Cu and Ni concentrations decreased over time due to the covering of HAR-producing wall rock above the lake surface. Copper concentrations showed significant improvement in water quality over time. Concentrations were above the 80% aquatic life protection guidelines at the beginning of steady-state conditions, dropped below this threshold after 20 years, and approached the 95% aquatic life protection guideline after 50 years (Fig. 5).

**Discussion and Conclusions**

In the absence of additional rehabilitation, the current closure plan for the Martha pit mine will produce a pit lake with low surface water quality that will prohibit post-mining recreational use and will have limited ecological value. Model 1 showed the lake will have a pH below New Zealand water quality guidelines for recreational use (Fig. 4), and Cu and Zn concentrations in excess of 80% aquatic life protection guidelines (Fig. 5 and 6). As a result, the current mine owners may be unable to achieve the post-mining objectives that they have established (Waihi Gold Company, 1997; Ingle, 2002). In addition to creating an environmental nuisance, this undesirable outcome could have social and economic impacts. The regional regulatory agency could indefinitely delay the release of environmental liabilities by the mine owners, as well as the return of an expensive environmental bond collected at the start of mining. The surrounding community would most likely be disappointed with the mine owners, and could strongly object to future mining operations planned for the region, thereby increasing the expense of permitting future mine sites in the region.

By covering those wall rocks that produce the greatest acidity, Models 2 and 3 showed that surface water quality could be significantly improved to allow for recreational use (Fig. 4, 5, and 6). Though surface waters may contain elevated levels of Zn regardless of these remediation efforts, reductions in acidity and Cu concentrations will allow the lake to be utilized as a recreational area, fulfilling the mining company’s commitments, and increasing the potential ecological value of the lake.

Most importantly, Model 3 showed that rehabilitating only those areas exposed above the final lake surface will produce a similar benefit as rehabilitating all highly-acidic runoff producing areas before mine closure. Of the estimated 21 ha of HAR producing rock exposed in the pit upon mine closes, only 3 ha will be exposed above the steady-state lake surface (Castendyk et al., 2005). Hence, focusing rehabilitation efforts on covering wall rocks exposed above the steady-state lake surface will save the mining company significant cost and resources. These data were recently presented to the mine management in June 2005 and they are considering the proposed modifications to the closure strategy.
For the closure plan modifications recommended by this study to be implemented, a geotechnical study of wall rock covers is now required. The geotechnical study should determine the quantity of MAR producing material available to be used as a wall rock cover, as a portion of this material is currently used in the waste rock stacks to isolate HAR producing material. The required thickness of the cover needs to be explored, along with maximum slope angle required for the cover to maintain its integrity without eroding or slumping over time. A geotechnical membrane at the base of the cover may add to its efficiency, and should also be considered in this study. A field trial of this cover over HAR producing wall rocks will indicate its ability to improve runoff water quality, as well as indicate the stability of the cover over time. A field trial at the Martha Mine which began in 2000 has shown positive results and will provide useful information for the cover design. As part of the geotechnical study, the cost of covering HAR producing rocks should be estimated.

Multiple factors influence pit lake chemistry, and though this study has endeavored to be comprehensive, the model presented herein has made several simplifying assumptions which affected the results. One assumption was that trace metals did not adsorb onto Fe and Mn hydroxide precipitates, which would have reduced the dissolved concentration of some trace metals. A second assumption was that submerged wall rocks did not react with pit lake water over time apart from providing groundwater input. Both of these assumptions have been examined in two additional sensitivity studies based on Model 1, and the results of these analyses will be published in a future paper. Other factors that might influence the model results are the presence of organic matter in river water inputs, and the development of aquatic flora on the lake surface, both of which affect redox conditions at depth as a product of decomposition. It may be valid to exclude these effects because the Ohinemuri River has a low concentration of dissolved organic carbon near the lake intake point (Bioresearches, 1997), and the barren pit catchment is unlikely to supply the phosphorous and nitrate concentrations necessary for significant floral productivity (Table 1). In addition, organic material will accumulate in the monimolimnion of the Martha Lake, which will be geochemically isolated from the shallower lake layers considered in this study, according to limnologic models (Castendyk and Webster, 2004).

This study has demonstrated that geochemical models of pit lake water quality are not only useful prediction tools, but models can also be an integral part of developing an effective remediation strategy toward the achievement of post-mining objectives. If a pit lake is predicted to have a water chemistry that would prohibit a desired end use, additional modeling may identify minor modifications to the closure plan that produce a more favorable outcome. In an effort to increase the sustainability of mining operations, the global mining industry has committed to rehabilitating mine sites into reusable post-mining resources (MMSD, 2002). To this end, we anticipate that sensitivity analyses which test multiple remediation options will become standard practice for pit lake geochemical predictions in the future.

Despite rigorous efforts, extensive investigations, and considerable capital investments, the most detailed pit lake predictions are merely scientific hypotheses that require decades of reproducible field observations to confirm their accuracy. In order for the science of pit lake prediction to advance, the procedures used to develop models must be peer-reviewed and publicly-distributed well in advance of mine closure, and validated with field data long after pit lakes are flooded. This study presented the methods used to predict the Martha pit lake, New Zealand. Future work will involve the collection of water samples from the Martha lake as it develops, and the comparison of observed water quality analyses to our predicted values.
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