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Sensitivity analyses in pit lake prediction, Martha mine, New Zealand 2: Geochemistry, water–rock reactions, and surface adsorption

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Abstract

Mine managers and regulators use geochemical predictions of pit lake chemistry to assess whether open pit mines will have positive or negative environmental effects after closure. Sensitivity analyses are a useful approach to explore uncertainties in these predictions. This study investigates the significance of subaqueous water–rock reactions and surface adsorption reactions on a geochemical model of a proposed pit lake at the Martha Au Mine, New Zealand. Our hypothesis was that subaqueous pyrite oxidation would lower surface water pH over time because pyrite will be present in over 1/3 of the submerged wall rock area, and that surface adsorption reactions would lower trace metal concentrations. An initial geochemistry prediction was created in PHREEQC based on site hydrology, representative input water chemistry, physical limnology, and the precipitation of ferrihydrite, manganite, amorphous gibbsite, and barite. Modeling water–rock reactions required the surface area of the submerged wall rocks, the concentration (volume %) of the dominant minerals found in the wall rock (*i.e.* pyrite, adularia, albite, chlorite, illite, and kaolinite), reaction rates for each mineral, and the volumes of circulating lake layers. These variables determined the mass of each mineral that would react with lake water over a one-year period corresponding to annual turnover. To accommodate for uncertainty in the estimation of surface area, the surface area was increased by × 10, × 100, and × 1000 in three additional models. To model surface adsorption reactions, the mass of ferrihydrite precipitated annually was set equal to the mass of hydrous ferric oxide allowed to adsorb trace metals. Results of the baseline geochemical prediction without water–rock reactions showed the surface water pH dropped from 6.5 to 5.0 over 50 years. The sensitivity analysis on water–rock reactions produced nearly identical results to the initial model for surface areas of × 1, × 10, and × 100. Only the surface area × 1000 model lowered pH more than half a pH unit from the initial prediction. These data suggest that water–rock reactions will not have a significant effect on the pH of the proposed Martha lake owing to the surface area of submerged minerals. Surface adsorption reactions lowered the concentrations of some trace metals (As, Cu, and Pb), whereas other trace metals were unaffected (Cd, Ni, Zn), which emphasized the pH dependence of these reactions. In the absence of model calibration or observed water chemistry, sensitivity analyses are a useful tool to explore uncertainties in pit lake predictions.

Keywords: Pit lakes; Water–rock reactions; Surface adsorption; Acid mine drainage; PHREEQC; Predictive modeling

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1. Introduction

The closure of open pit precious-metal and coal mines frequently leads to the formation of anthropogenic basins called pit lakes. Because pit lakes collect and store mine impacted water, these lakes have the potential to cause deleterious impacts on surface and ground water quality. For this reason, environmental regulators require mining companies to produce post-mining water quality predictions before mining permits are issued. These predictions can also guide mine managers to develop site closure plans that minimize negative impacts and optimize the value of the pit lake as a future water resource.

1.1. Review of pit lake chemistry predictions

Since the first published geochemical study of a pit lake by Davis and Ashenberg (1989), nearly two decades of observations have shown that pit lakes are complex geochemical systems influenced by multiple variables, including wall rock mineralogy, local climate, groundwater hydrology, physical limnology, mineral precipitation, trace metal adsorption, and biological activity (Miller et al., 1996; Davis and Eary, 1997; Shevenell et al., 1999; Castro and Moore, 2000; Bowell, 2002; Moreno and Sinton, 2002). As a product of this complexity, pit lake modelers have developed a variety of prediction techniques. Havis and Worthington (1997) and Lewis (1999) presented simple mass balance approaches to calculate water chemistry based on groundwater hydrology, water balance, and input chemistry. More advanced methods consider temporal variations in wall rock runoff chemistry based on *ex situ* kinetic tests (Pillard et al., 1995; Davis and Fennemore, 1998) or *in situ* kinetic tests (Morin and Hutt, 2001). Eary (1998) discussed the effects of evapoconcentration on the chemistry of pit lakes in arid climates, and Eary (1999) presented an extensive review of metal solubility controls in existing pit lakes.

Published, site-specific, prediction studies fall into one of four categories based on calibration methodologies (Table 1). Type I studies compile data on local climate, groundwater hydrology, lake water balance, wall rock mineralogy, wall rock runoff chemistry (either through direct observations or kinetic leach tests), and limnology, and build these data into a geochemical computer model which allows for chemical speciation, mineral precipitation, and surface adsorption. Examples include predictions of the Twin Creeks Lake, Nevada (Kempton et al., 1997), and the Martha Lake, New Zealand (Geochimica, 1997a; Castendyk and Webster-Brown, 2006). Though detailed and comprehensive, Type I studies are uncalibrated.

Type II, Type III, and Type IV studies develop geochemical predictions using identical input data as Type I models and calibrate these predictions. In Type II studies, a laboratory-based, chemical model of the pit lake is created using representative input waters. Based on the observed water chemistry, mineral precipitates, and adsorbed species, the thermodynamic database used

Table 1
Approaches used in published, site-specific, predictions of pit lake water quality

Study type	Description	Examples	Duration (years)	Geochemical program used	Reference
Type I	Geochemical prediction based on detailed observations of climate, wall rock mineralogy, and existing water chemistry and/or wall rock leaching tests, plus predictions of ground water hydrology, lake water balance, and physical limnology.	Twin Creeks Lake, Nevada	250	MINTEQA2 (Allison et al., 1991)	Kempton et al. (1997)
		Martha Lake, New Zealand	55	PHREEQC (Parkhurst and Appelo, 1999)	Castendyk and Webster-Brown (2006)
Type II	Geochemical prediction based on a Type I model calibrated with a laboratory/chemical model of pit lake chemistry.	Post-Betze Lake, Nevada	400	PHREEQC (Parkhurst and Appelo, 1999)	Schafer et al. (2006)
Type III	Geochemical prediction based on a Type I model calibrated with water chemistry data from a pre-existing lake within the pit.	North Pit Lake, Getchell mine, Nevada	8.5	EQ3/6 (Wolery and Daveler, 1992)	Tempel et al. (2000)
		Main Pit Lake, Tyrone mine, New Mexico	Unspecified	MINTEQA2 (Allison et al., 1991)	Walder et al. (2006)
		Summer Camp Lake, Nevada (now backfilled)	Unspecified	MINTEQA2 (Allison et al., 1991)	Parshley et al. (2006)
Type IV	Geochemical prediction based on a Type I model calibrated with post-closure pit lake observations.	Lake Bärwalde, Germany	8	PHREEQC (Parkhurst and Appelo, 1999)	Werner et al. (2006)

in the geochemical computer model is adjusted until the predicted geochemical data match the observed data in the laboratory experiment. The calibrated geochemical program is then used to create a long term prediction. Schafer et al. (2006) used this approach to model the Post-Betze Lake, Nevada, which will occupy the largest open pit mine currently in the state. Type II studies are more robust than Type I studies because of the calibration step, yet require more time and resources than Type I studies, and raise questions about the adjustment of thermodynamic data. Type III studies require a sufficient pause in mining activity that results in a temporary pit lake. Mining resumes after the temporary lake is drained, and a future pit lake prediction is created using the observed geochemical data for model calibration. Examples of predictions include the North Pit Lake, Getchell mine, Nevada, (Tempel et al., 2000), the Main Pit Lake, Tyrone mine, New Mexico (Walder et al., 2006), and the Summer Camp Lake, Getchell mine, Nevada (Parshley et al., 2006), now backfilled. Type IV studies compare geochemical predictions to geochemical observations after mine closure, and use these data for model calibration and validation. The study of Lake Bärwalde, Germany, by Werner et al. (2006) is the only publication of this type presently available in the pit lake literature.

The use of *in situ* pit lake data suggests Type III and Type IV studies are likely to produce more accurate predictions than Type I and Type II studies. However, Type III and Type IV studies require an open pit mine that already exists, therefore these approaches cannot be used to make regulatory decisions in advance of mining. In the absence of a calibration step, one way to improve the confidence in Type I prediction studies is through sensitivity analyses on uncertain variables, such as the influence of water rock reactions and the significance of trace metal adsorption onto hydrous ferric oxides (HFO).

1.2. Uncertainty in subaqueous water–rock reactions

One area of uncertainty in existing pit lake predictions is the effect of subaqueous water–rock interactions on lake chemistry, such as the oxidation of pyrite and the dissolution of silicates. Several modelers have assumed that the oxidation of sulfide minerals in wall rocks will not have a significant influence on lake water quality after the wall rocks have been submerged due to the reduced supply of oxygen in lake water compared to the supply of oxygen in air (Geochimica, 1997a; Kempton et al., 1997; Meyer et al., 1997; Neukirchner and Hinrichs, 1997). Kempton et al. (1997) further assumed that dissolution reactions between wall rocks and lake water, specifically carbonate dissolution, would have a negligible effect on water chemistry.

In contrast, Temple et al. (2000) factored concentrations and reaction rates of sulfides, carbonates, and silicates directly into their model, and allowed subaqueous water–rock reactions to occur. Williamson and Rimstidt (1994) provided oxidation rates for pyrite by dissolved oxygen in water, which enabled the approach used by Tempel et al. (2000). It follows that if pit wall rocks contain sulfide minerals, and if oxygen-saturated surface waters circulate annually with deep lake waters during lake turnover, then dissolved oxygen will be available to oxidize submerged sulfide minerals in pit wall rocks. Bowell and Parshley (2005) discussed how dissolved oxygen in the Summer Camp Pit Lake, Nevada, USA, may have caused subaqueous pyrite oxidation leading to a reduction in lake water pH. In the absence of dissolved oxygen, Madison et al. (2003) showed that in acidic pit lakes ($pH < 4$), Fe(III) behaves as an oxidant for the subaqueous oxidation of wall rock pyrite. The dissolution of carbonate and silicate minerals may also affect pit lake chemistry over time, as discussed by Castendyk et al. (2005). Geochemical models allow the effects of subaqueous water–rock reactions on pit lake predictions to be explored.

1.3. Uncertainty in trace metal adsorption

A second area of uncertainty is the adsorption of trace metals onto HFO precipitates, such as ferrihydrite. Previous studies have shown that sorption reactions are an important control on the fate and transport of trace metals in mine waters (Webster et al., 1998; Smith, 1999; Swedlund and Webster, 2001). Temple et al. (2000) did not use a surface adsorption model, and concluded that As adsorption to hydrous oxide surfaces may explain discrepancies between observed and modeled data. In contrast, Kempton et al. (1997) modeled the adsorption of SO_4, As(V), Se(IV), Cu(II), Pb, Cd, Zn, Mg, Ca, and Ni onto hydrous ferric oxide (HFO), but did not discuss which species were strongly influenced by these reactions and which were not. A comparison of model results with and without trace metal adsorption reactions can illustrate the value of these reactions in a geochemical prediction.

1.4. Research objectives

The hypothesis of this research is that subaqueous water–rock reactions significantly affect the pH of pit lake waters, and that the adsorption of trace metals onto HFO surfaces significantly reduces trace metal concentrations. We use a series of sensitivity analyses to test this hypothesis as follows:

i) Develop a baseline geochemical model for a pit lake which does not include water–rock reactions or surface adsorption reactions (Model 1);
ii) Develop a second geochemical model for the same pit lake which includes water–rock reactions and excludes surface adsorption reactions (Model 2);
iii) Develop a third geochemical model for the same pit lake which includes surface adsorption reactions and excludes water–rock reactions (Model 3).
iv) Compare the results of Models 1 and 2, and Models 1 and 3, to observe the significance of each reaction.

1.5. Background on the Martha Mine, New Zealand

This study uses the Martha Au–Ag Mine in Waihi, New Zealand, as a case study for a pit lake prediction model (Fig. 1). The mine is situated in a low-sulfidation, epithermal, quartz-adularia deposit hosted by hydrothermally-altered andesite (Brathwaite and Faure, 2002). Castendyk et al. (2005) quantified the wall rock mineralogy of pit, and showed that one-third of the exposed wall rocks contain pyrite, one mineral association contained calcite, and the remaining wall rock minerals included quartz, adularia, albite, chlorite, illite, and kaolinite. Acid-base accounting showed that over one-third of the wall rocks have the potential to generate acid to some degree.

The mine is scheduled to close in 2007. At that time, surface water will be diverted into the pit from the nearby Ohinemuri River during moderate and high flow periods. The lake will fill to a maximum depth of 194 m by 2012, after which time river water input will be discontinued. An overflow outlet will maintain the lake level at this depth. Groundwater modeling by Woodward Clyde (1997a) has indicated the lake will be a discharge point for local groundwater. The steady-state lake will have a surface area of 28.7 ha, and a volume of 2.16×10^7 m^3. A prediction of the physical limnology by Castendyk and Webster-Brown (this issue) showed that the proposed lake will be meromictic, with the upper two-thirds of the water column circulating annually and the lower third remaining permanently isolated. The mining company plans to rehabilitate the mine site into a public recreation area for boating and hiking and a desirable habitat for fish and waterfowl (Waihi Gold Company, 1997; Ingle, 2002). Previous geochemical modeling by Geochimica (1997a) showed the lake would have a circumneutral pH 50 years after lake filling. This prediction did not account for water lost from the surface water outlet, meromictic limnology, water–rock reactions, or surface adsorption reactions.

2. Methods

2.1. Representative input water chemistry

The Martha lake will receive water from 5 different inputs: groundwater, river water, highly-acidic runoff (HAR), moderately-acidic runoff (MAR), and rainwater. Moderately-acidic runoff is defined as runoff from the weakly-altered, propylitic, and oxidized mineral associations plus post-mineralization deposits described by

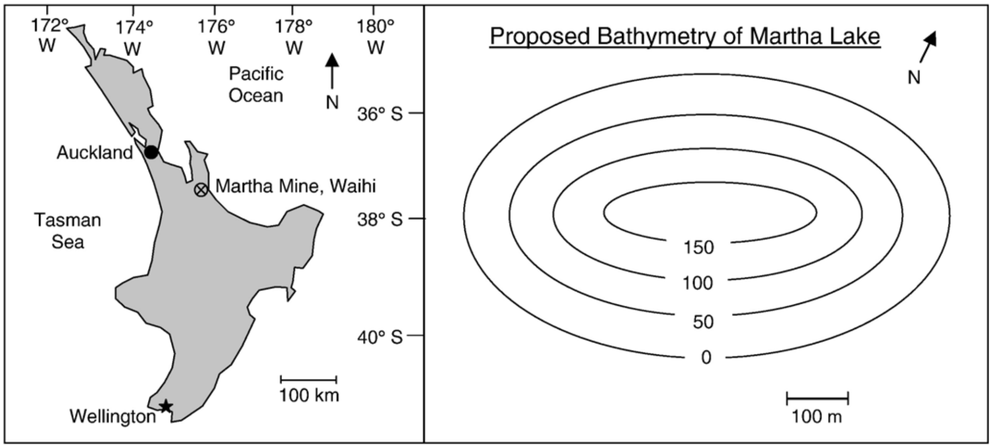

Fig. 1. Location map of the active Martha Au–Ag Mine, Waihi, North Island, New Zealand, and a schematic diagram of the bathymetry (in meters) of the proposed Martha Lake drawn from current mine closure plans.

Castendyk et al. (2005), whereas HAR is defined as runoff from the fresh-argillic, weathered-argillic, and potassic mineral associations.

Representative input water chemistry was determined from 110 water analyses reported in the Martha mine technical literature, with samples collected from groundwater ($n=45$), river water ($n=17$), MAR ($n=13$), and HAR ($n=35$). All sample analyses had ionic charge imbalances of <10%. For each dissolved species included in the PHREEQC model, a graph was generated which plotted pH versus species concentration for each water type, and the median concentration of each species was identified. The representative input water chemistry for each water type was a composite of the median concentrations of each dissolved species for a given water type. Table 2 shows the final representative water chemistry of each input. Castendyk (2005) provides the graphs used to identify the median concentrations for select species and further explanation of this approach.

2.2. Baseline geochemical model: Model 1

Castendyk and Webster-Brown (2006) provide a detailed description of the baseline geochemical model for the Martha Lake. The model used the geochemical computer program PHREEQC, version 2.8 (Parkhurst and Appelo, 1999), implemented through the graphical user interface PHREEQC Interactive, version 2.8.0.0

Table 2
Representative chemical analyses for Martha Lake inputs

	River water[a]	Groundwater[b]	Moderately-acidic runoff (MAR)[c]	Highly-acidic runoff (HAR)[d]	Rainwater[e]
pH	6.9	6.7	5.4	3.1	5.7
Eh	450	200	400	576	600
pe	7.86	3.5	7	10	10.49
Temp (°C)	15	15	15	15	15
n	17	45	13	35	Theoretical
	mg/L	mg/L	mg/L	mg/L	mg/L
Na	9.2	49.7	3.6	2.7	0
K	3.6	9.7	0.7	0.4	0
Ca	12	391	0.49	81.5	0
Mg	3.2	87	0.366	20.9	0
Al	0.069	0.05	0.059	7.23	0
Fe (total)	0.09	1.4	0.04	18.3	0
Mn (total)	0.07	10.2	0.022	1.22	0
Cu (total)	0.0018	0.001	0.0027	0.0465	0
Zn	0.0033	0.4	0.053	0.199	0
NH_4	0.348	0.139	0.026	0.03	0
As (total)	*0.0005*	0.017	*0.0005*	0.003	0
Sb (total)	*0.0005*	*0.001*	*0.0001*	*0.0001*	0
Ba		0.4	*0.005*	0.0418	0
Cd	*0.00005*	0.0025	*0.000025*	0.00032	0
Cr (total)	*0.0001*	0.005	0.0005	0.009	0
Pb	*0.00015*	0.0025	0.0005	0.0016	0
Ni	*0.00025*	0.022	0.0008	0.17	0
Hg (total)	*0.00005*	0.00012	*0.0001*	*0.00005*	0
HCO_3	15	98.8	4.0	0.5	0.122
Cl	14	11.8	5.0	4	0
SO_4	35	1109	4.0	424	0
Se (total)	*0.0005*	*0.001*	*0.0005*	*0.0005*	0
NO_3	4.91	0.04	0.004	0.007	0
NO_2	0.043	0.005	*0.001*	0.006	0
P	0.025	–	0.017	0.109	0
SiO_2	24.3	–	1.7	21.0	0
% Balance	2.17	8.23	9.23	7.02	0

% Balance = % charge balance.

Italicized values are half detection limits.

[a] Data sources: Geochimica (1997a,b); Bioresearches (1997).

[b] Data sources: Waihi Gold Company (1985); Woodward and Clyde (1997b); URS (2003).

[c] Data sources: Waihi Gold Company (1985); Geochimica (1997a); Woodward and Clyde (1997c); EGI (1997).

[d] Data sources: Waihi Gold Company (1985); Geochimica (1997a); EGI (1997); Woodward and Clyde, (1997c); Gurung (1998).

[e] Bicarbonate concentration calculated by PHREEQC based on equilibrium with atmospheric CO_2 and O_2.

(Charlton and Parkhurst, 2002), with the thermodynamic database MINTEQA2 (Allison et al., 1991). The prediction included two stages: lake-filling conditions and steady-state conditions. The lake-filling stage modeled a 5-year period (identified as Year 4 through Year 0) when the empty pit will be flooded with river water, groundwater, direct rainfall, and pit wall runoff, with evaporation being the only source of water loss. The steady-state stage modeled a 50-year period (identified as Year 1 through Year 50) when the lake will receive pit wall runoff, direct rainfall, and groundwater, and will discharge through a surface water overflow that will control lake elevation.

Based on limnologic modeling by Castendyk and Webster-Brown (this issue), we modeled the lake as a 3 layer system with an epilimnion layer (Layer 1) that will be in equilibrium with atmospheric CO_2 and O_2, a hypolimnion layer (Layer 2) that will annually mix with Layer 1, and a permanently isolated monimolimnion layer (Layer 3). Following annual turnover, ferrihydrite, manganite, amorphous gibbsite, and barite were allowed to precipitate from solution if dissolved concentrations exceeded solubility limits, as suggested by Eary (1999).

2.3. Sensitivity analysis on water–rock reactions: Models 2a, 2b, 2c, and 2d

The first sensitivity analysis considered water–rock reactions between lake water and the submerged pit wall rocks in Layers 1 and 2. Castendyk et al. (2005) quantified the concentrations of pyrite, adularia, albite, chlorite, illite, and kaolinite in the wall rock mineral associations of the Martha mine. Calcite was assumed to not be present in the submerged wall rocks. Because pyrite oxidation will lower pH and silicate dissolution will increase pH, this analysis explored the affect of these reactions on the pH of the developing pit lake. Modeling of water rock reactions requires the definition of mineral reaction rates, estimation of reactive mineral surface area, and calculation of the mineral mass reacting with lake solution on an annual basis.

2.3.1. Mineral reaction rates

An overall kinetic reaction rate (R) defines the mass of a mineral (M) reacting with a volume of solution (V) after a given period of time (T):

$$R = \frac{M}{VT}. \tag{1}$$

Appelo et al. (1998) and Parkhurst and Appello (1999) have defined overall reactions in terms of specific reaction rates (r=mol/m^2 s) that have been empirically measured for each mineral (Table 3):

$$R = r\frac{A}{V}\left(\frac{m}{m_0}\right)^n \tag{2}$$

where A is the surface area (m^2) of the mineral in contact with the solution, m represents the moles of the mineral at a given point in time, and m_0 represents the initial moles of the mineral. The exponent n depends upon the geometry of the mineral. Assuming the mineral surface area is constant over time, $(m/m_0)^n=1$, and Eq. (2) reduces to the following expression:

$$R = r\frac{A}{V}. \tag{3}$$

Under this condition, Eqs. (1) and (3) can be combined to define the mass of a mineral reacting with a solution as a function of the specific reaction rate, the mineral surface area, and time:

$$M = rAT \tag{4}$$

Eq. (4) is used to describe the dissolution of silicate minerals, which are generally assumed to have constant surface areas over time (Langmuir, 1997). However, for pyrite oxidation, $(m/m_0)^n$ is <1, and a slower rate is predicted using Eq. (2) than Eq. (3). For this reason, the mass of pyrite calculated by Eq. (4) *overestimates* the mass of pyrite reacting with solution and provides a “worst-case” scenario.

2.3.2. Reactive mineral surface areas

To define the surface area of each mineral in contact with lake water, we first calculated the submerged surface area of each mineral association ($A_{\text{association}}$), and then calculated the volume percent of each mineral in each association (vol%$_{\text{mineral}}$). The three-dimensional area of each mineral association in 2002 ($A_{\text{association 2002}}$) and a hypothetical volume for each lake layer in 2002 ($V_{\text{layer 2002}}$) were measured from a 2002 digital elevation map (DEM) file of the pit using GIS software. The submerged surface areas of the mineral associations in 2012 ($A_{\text{association 2012}}$) were calculated using the steady-state layer volumes used in the water balance and the following relationship:

$$\frac{A_{\text{association 2002}}}{V_{\text{layer 2002}}} = \frac{A_{\text{association 2012}}}{V_{\text{layer 2012}}}. \tag{5}$$

This proportion assumes a 1:1 relationship between layer volumes and the pit wall area in contact with lake water in each layer over time.

Table 3
Equations, mineral surface areas, specific reaction rates, and reacted masses for water–rock reactions

Mineral	PHREEQC reactions[a]	Mineral surface area $A_{mineral}$ (m^2)	Specific reaction rate r (mol/m^2 s)	Model 2a reacted mass for $A_{mineral} \times 1$ (mol/L year)	Model 2b Reacted mass for $A_{mineral} \times 10$ (mol/L year)	Model 2c Reacted mass for $A_{mineral} \times 100$ (mol/L year)	Model 2d Reacted mass for $A_{mineral} \times 1000$ (mol/L year)
Pyrite[b]	(1) $FeS_2 + 2H^+ + 2e^- = Fe^{+2} + 2HS^-$ (2) $Fe^{+2} = e^- + Fe^{+3}$ (3) $HS^- + 4H_2O = SO_4^{-2} + 9H^+ + 8e^-$ (4) $O_2 + 4H^+ + 4e^- = 2H_2O$	4.22×10^3	6.15×10^{-10}	4.22×10^{-9}	4.22×10^{-8}	4.22×10^{-7}	4.22×10^{-6}
Albite[c]	(1) $NaAlSi_3O_8 + 8H_2O = Na^+ + Al(OH)_4^- + 3H_4SiO_4$ (2) $Al(OH)_4^- + 4H^+ = Al^{+3} + 4H_2O$	1.14×10^4	1.26×10^{-12}	2.33×10^{-11}	2.33×10^{-10}	2.33×10^{-9}	2.33×10^{-8}
Illite[d]	(1) $KAl_3Si_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Al^{+3} + 3H_4SiO_4$	4.84×10^4	4.00×10^{-12}	3.15×10^{-10}	3.15×10^{-9}	3.15×10^{-8}	3.15×10^{-7}
Chlorite[e]	(1) $Mg_5Al_2Si_3O_{10}(OH)_8 + 16H^+ = 5\ Mg^{+2} + 2Al^{+3} + 3H_4SiO_4 + 6H_2O$	2.51×10^4	3.00×10^{-13}	1.22×10^{-11}	1.22×10^{-10}	1.22×10^{-9}	1.22×10^{-8}
Adularia[f]	(1) $KAlSi_3O_8 + 8H_2O = K^+ + Al(OH)_4^- + 3H_4SiO_4$ (2) $Al(OH)_4^- + 4H^+ = Al^{+3} + 4H_2O$	3.77×10^4	3.16×10^{-13}	1.94×10^{-11}	1.94×10^{-10}	1.94×10^{-9}	1.94×10^{-8}
Kaolinite[g]	(1) $Al_2Si_2O_5(OH)_4 + 6H^+ = H_2O + 2H_4SiO_4 + 2Al^{+3}$	1.29×10^4	4.00×10^{-13}	8.39×10^{-12}	8.39×10^{-11}	8.39×10^{-10}	8.39×10^{-9}

[a] From PHREEQC database (Parkhurst and Appelo, 1999).
[b] Pyrite oxidation rate from Williamson and Rimstidt (1994) where dissolved oxygen is the only oxidant and the following conditions are constant: pH = 6.6 and ($O_{2\ liquid}$) = 6.82 mg/L.
[c] Albite dissolution rate from Chou and Wollast (1985) and White et al. (1996) for pH = 5.6.
[d] Illite dissolution rate from Feigenbaum and Shainberg (1975) and Nagy (1995) for pH = 7.5 and 25 °C.
[e] Chlorite dissolution rate from May et al. (1995) and Nagy (1995) for pH = 5.0 and 25 °C.
[f] Adularia dissolution rate based on microcline dissolution rate from Schweda (1989) and Lasaga et al. (1994) for pH = 5.0 and 25 °C.
[g] Kaolinite dissolution rate from Wieland and Stumm (1992) and Nagy (1995) for pH = 5.0 and 25 °C.

The volume percent ($vol\%_{mineral}$) of each mineral in each mineral association was calculated from the weight percent of each mineral reported by Castendyk et al. (2005), the average density of the rocks in each mineral association (M. Simpson, personal communication, 2003), and the density of each mineral reported by Klein and Hurlbut (1993). For each mineral in each mineral association, the mineral surface area ($A_{mineral}$) equaled the product of the submerged association area in 2012 from Eq. (5) and the volume percent of each mineral:

$$A_{mineral} = A_{association\ 2012} \times vol\%_{mineral}. \tag{6}$$

The area used in Eq. (6) equaled the sum of mineral areas from each association. Mineral areas are provided in Table 3 for pyrite, albite, illite, chlorite, adularia, and kaolinite.

This method provides a reasonable approximation of silicate minerals at the Martha mine which are fined grained and homogeneous. However, pyrite is generally coarse grained throughout the deposit, meaning the actual surface area of pyrite is less than the area calculated by this method. By overestimating the surface area of pyrite, again the method overestimated the reactivity of pyrite to create a "worst-case" scenario for pyrite oxidation.

2.3.3. Reactive mineral mass

To calculate the mass of each mineral reacting with Layers 1 and 2 on an annual basis, published specific reaction rates (r) for each mineral (Table 3) were multiplied by the reactive mineral area (Eq. (6)) for a time of 1 year corresponding to annual turnover, according to Eq. (4). The resulting mass was divided by the volume of Layers 1 and 2 in liters (L):

$$(r \times A_{mineral} \times T) \times \frac{1}{V_{layer1} + V_{layer2}} = \frac{mol_{mineral}}{L} \tag{7}$$

Data from Smith et al. (1970) and Willamson and Rimstidt (1994) show that the rate of pyrite oxidation by dissolved oxygen decreases from 1.35×10^{-9} mol/m^{2}s at pH 7.0 to 7.94×10^{-10} mol/m^{2}s at pH 4.0 under oxygen rich conditions. Results from Model 1 showed that the lake attained a maximum pH of 6.6 and had a dissolved oxygen concentration of 6.8 mg/L. These values were used to calculate the pyrite oxidation rate shown on Table 3 using the rate law provided by Williamson and Rimstidt (1994). Since the pyrite oxidation rate was constant and was based upon the highest pH observed in the lake, the rate of pyrite oxidation will be overestimated as the pH drops below this value.

2.3.4. Accounting for uncertainty in mineral surface areas

One of the greatest uncertainties in modeling water rock reactions in pit lakes is the accurate measurement of mineral surface areas. In this study, mineral surface areas (A_{mineral}) were calculated by multiplying the volume % of minerals present in the wall rock (vol%$_{\mathrm{mineral}}$) by the surface area of the inundated wall rocks ($A_{\mathrm{association\ 2012}}$) as shown in Eq. (6). However, predicting the surface area of wall rocks in direct contact with water in a future pit lake is a non-trivial problem because of the heterogeneous surface roughness of the pit walls, the challenge of quantifying the surface area along fractures plains that intersect the pit walls, plus unexpected changes to pit geometry caused by market-driven modifications to mine plans and pit wall collapse events. The authors are not aware of a published method that accurately measures pit wall surface areas and accounts for each of these variables.

To explore the uncertainty in surface area measurements, four models were generated based on the mineral surface area calculated from Eq. (6):

(i) Model 2a used $A_{\mathrm{mineral}} \times 1$;
(ii) Model 2b used $A_{\mathrm{mineral}} \times 10$;
(iii) Model 2c used $A_{\mathrm{mineral}} \times 100$;
(iv) Model 2d used $A_{\mathrm{mineral}} \times 1000$.

The GIS-based surface area measurement described in Section 2.3.2 provided a first-order approximation of the inundated wall rock surface area and was used in Model 2a. Because the area measured by GIS did not account for surface roughness or fracture plains, Model 2a underestimated the true area of the inundated wall rock. To explore the uncertainty in the surface area calculation, the area used in Model 2a was sequentially increased by an order of magnitude in Models 2b, 2c, and 2d, so that the surface area used in Model 2d was 1000× the surface area used in Model 2a. It is likely that the actual surface area will be somewhat less than this value, therefore Model 2d overestimated the true area of the inundated wall rock. Although the range of values used to represent uncertainty was somewhat arbitrary, the models most likely encompass the future surface area of the inundated water rocks.

Table 3 presents the mineral masses reacting with lake water for each model. In PHREEQC, these values were added to the steady-state model on an annual basis after the turnover of Layers 1 and 2 using the "REACT" command which specifies the complete reaction of a specified mineral mass with the solution (Parkhurst and Appelo, 1999). Microcline was used as a proxy for adularia and muscovite was used as a proxy for illite. Thermodynamic data for the phase "Chlorite (14 Å)" were added to the MINTEQ database from the PHREEQC database to model chlorite dissolution.

2.4. Sensitivity analysis for surface adsorption reactions: Models 3a and 3b

The second sensitivity analysis explored the effect of the adsorption of trace metals onto HFO represented by ferrihydrite precipitate. Studies into the surface adsorption properties of ferrihydrite have shown that "fresh" or unweathered ferrihydrite has a significantly larger capacity to adsorb trace metals than "aged" or weathered ferrihydrite (Webster et al., 1998). For this reason, surface adsorption reactions considered in this study focus only on fresh ferrihydrite precipitated within the water column and exclude weathered ferrihydrite and other oxides present in the pit wall rocks.

In both the lake-filling and steady-state models, the mass of ferrihydrite annually precipitating from Layers 1 and 2 was specified as the mass of the HFO adsorption surface in PHREEQC. Because samples of the future precipitate were unavailable for laboratory analysis, the characteristics of the ferrihydrite surface were set equal to the characteristics of the HFO used by Dzombak and Morel (1990), with 0.2 mol of weakly adsorbing sites per mole Fe, and 0.005 mol of strongly adsorbing sites per mol Fe. The gram formula weight of the ferrihydrite was assumed to be 106.8 g/mol. The reactions were incorporated using a generalized diffuse-layer model by Dzombak and Morel (1990). To address uncertainty in the surface area of ferrihydrite, two models were created:

(i) Model 3a used a ferrihydrite surface area of 600 m^2/g;
(ii) Model 3b used a ferrihydrite surface area of 300 m^2/g.

3. Results

3.1. Baseline geochemical model: Model 1

During the 5 years of lake filling, the pH of Layer 2 increased from pH ~ 5.4 to ~ 6, and Layer 1 increased

~5.8 to >6.5, owing to the addition of river water, lake turnover, and the removal of CO_2 from Layer 1 (Fig. 2). River water was the largest source of water and carbon during lake-filling conditions, and exhibited high pH (pH 6.9), moderate alkalinity (HCO_3 15 mg/L), and low acidity (Fe 0.09 mg/L; Mn 0.07 mg/L). Hence, the addition of river water to Layer 1 and annual turnover between Layer 1 and 2 caused the pH and alkalinity of Layer 2 to rise, whereas Fe, Mn, and all trace metal concentrations decreased due to dilution (Figs. 3, 4 and 5). After turnover and mineral precipitation, Layer 2 was equilibrated with atmospheric CO_2 to generate the

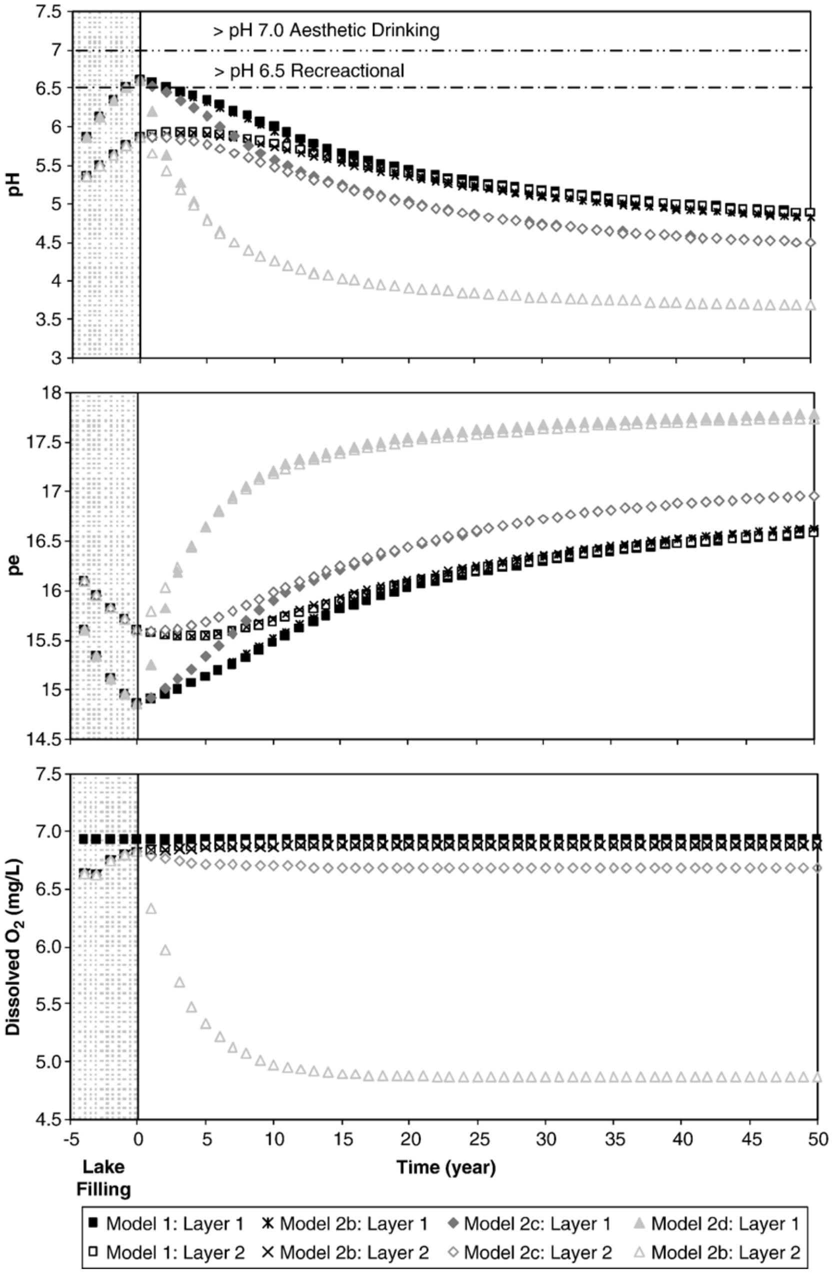

Fig. 2. pH, pe, and dissolved O_2 results from Model 1, and the water–rock reactions models: Model 2b (mineral area × 10), Model 2c (mineral area × 100), and Model 2d (mineral area × 1000). Model 2a overlaps with Model 2b and is not shown. Water quality guidelines are from ANZECC (2000).

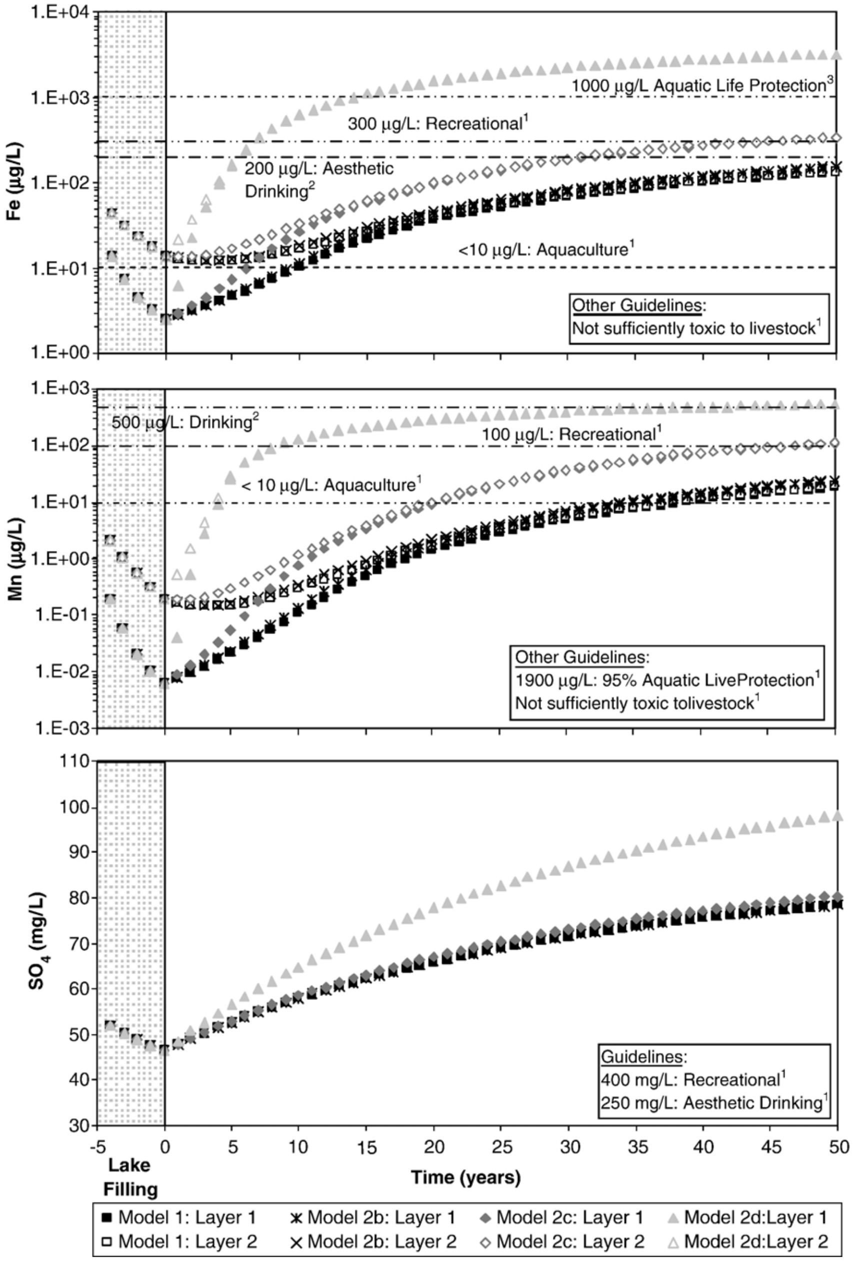

Fig. 3. Fe, Mn, and SO_4 results for the Model 1 and the water–rock reaction models: Model 2b (mineral area × 10), Model 2c (mineral area × 100), and Model 2d (mineral area × 1000). Model 2a overlaps with Model 2b and is not shown. Water quality guidelines are from: [1]ANZECC (2000); [2]WHO (1998); [3]USEPA (2002).

chemistry of Layer 1. Equilibration removed CO_2 from solution which raised pH, according to the following reactions:

$$H^+ + HCO_3^- \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O. \quad (8)$$

This reaction increased the pH of Layer 1 with respect to 2 during lake-filling conditions (Fig. 2), whereas the dissolution of O_2 into Layer 1 elevated the pe of Layer 1. These factors affected the solubility of Fe and Mn in each layer (Fig. 3). Annual turnover increased dissolved oxygen concentrations in Layer 2 to levels in Layer 1 (Fig. 2), in addition to homogenizing SO_4, As, Cd, Cu, Pb, Ni, and Zn concentrations between each layer (Figs. 3, 4 and 5). Because field trials described by Kirby et al. (2006) have been unsuccessful at degassing CO_2

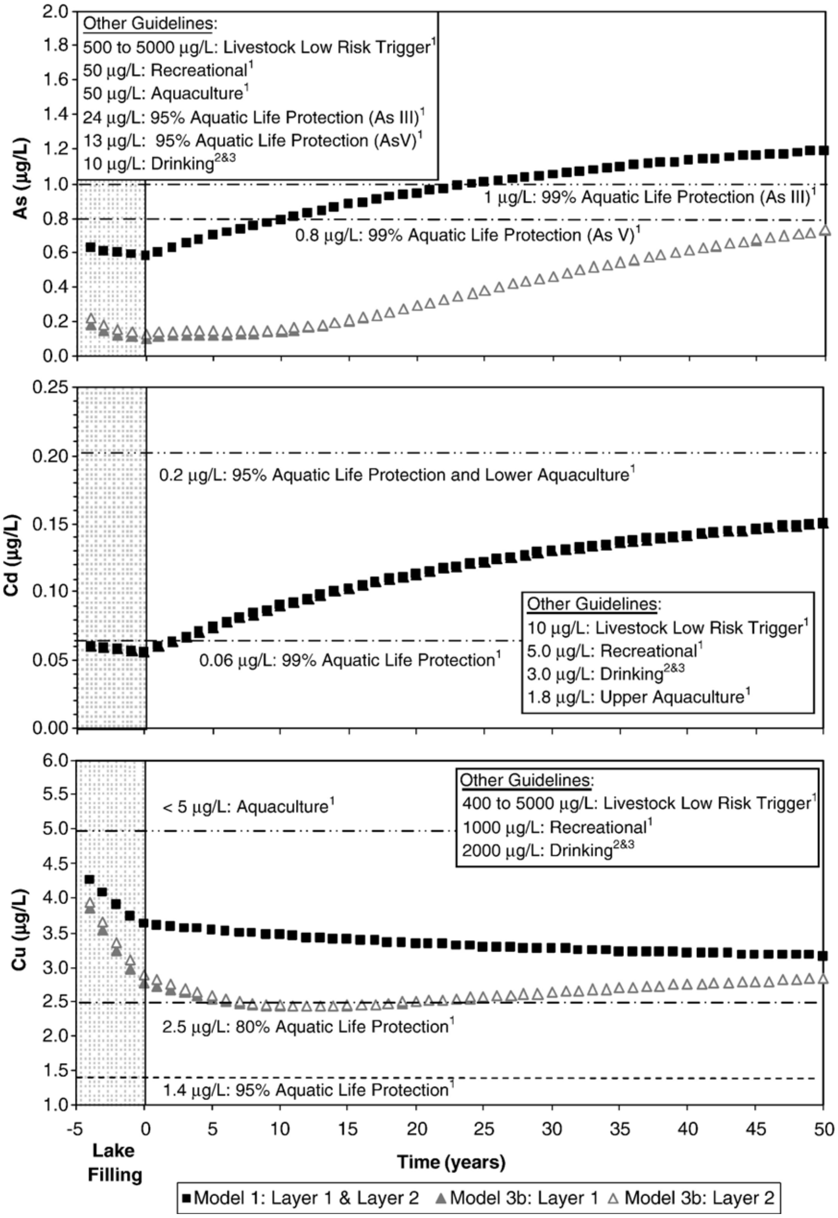

Fig. 4. As, Cd, and Cu results from Model 1 and surface adsorption Model 3b (HFO surface area = 600 g/m^2). Model 3a (HFO surface area = 300 g/m^2) overlaps Model 3b, and is not shown. Water quality guidelines are from: [1]ANZECC (2000); [2]WHO (1998).

from acid mine drainage, our model may overestimate the pH of Layer 1 due to the specification of CO_2 equilibrium in this layer.

Insomuch as lake-filling conditions were geochemically controlled by river water input, steady-state conditions were controlled by low alkalinity, high acidity runoff inputs, which caused the pH of both layers to drop to 4.8 by Year 50. The termination of river water input removed the primary source of carbon and high pH water, whereas HAR and MAR provided low pH waters of 3.1 and 5.4 respectively, that lowered pH over time. The HAR input also contained elevated concentrations of Fe (18.3 mg/L), Mn (1.22 mg/L), and Al (7.23 mg/L), and the precipitation of ferrihydrite, manganite, and amorphous gibbsite produced H^+ which contributed to the drop in pH. As the alkalinity in Layer 2 was consumed, less CO_2 was released from solution upon atmospheric equilibration, and the pH difference between Layer 1 and

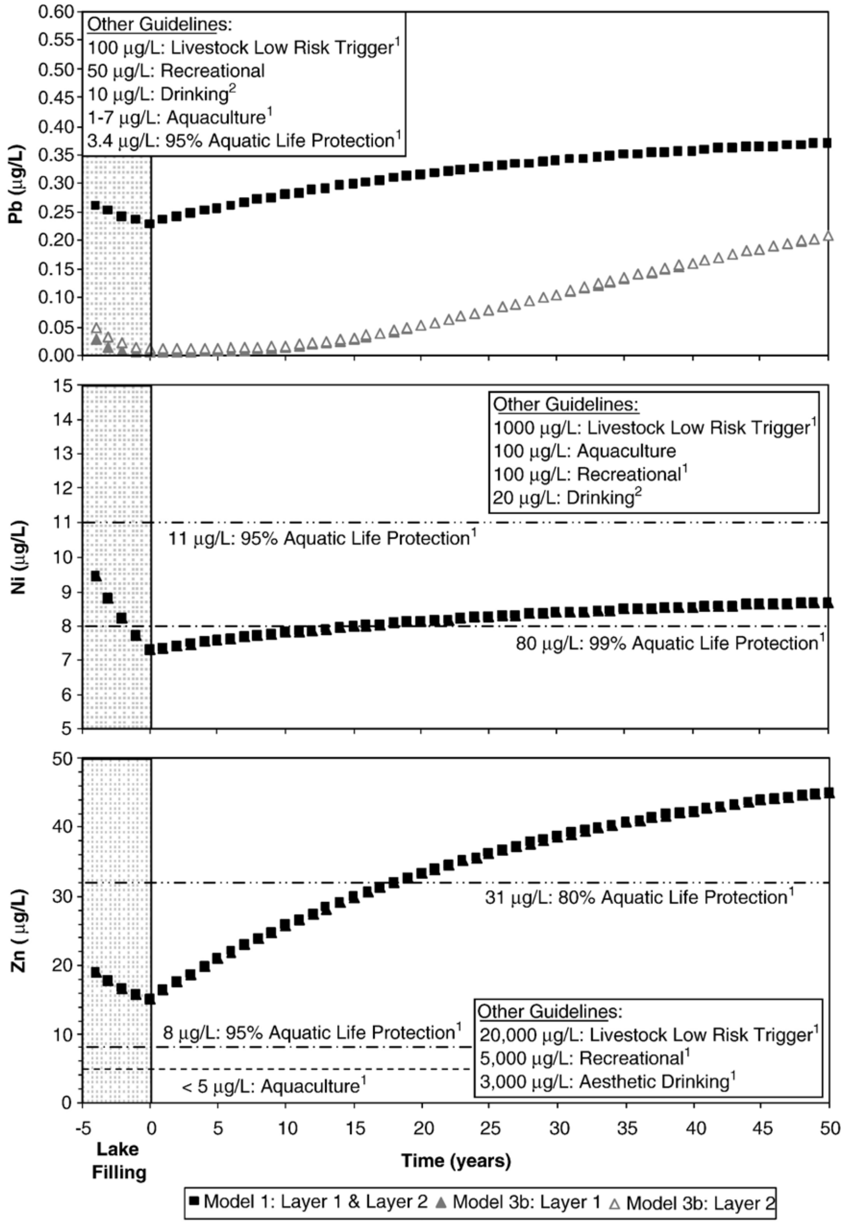

Fig. 5. Pb, Ni, and Zn results from Model 1 and surface adsorption Model 3b (HFO surface area = 600 g/m^2). Model 3a (HFO surface area = 300 g/m^2) overlaps Model 3b, and is not shown. Water quality guidelines are from: [1]ANZECC (2000); [2]WHO (1998).

Layer 2 decreased with time, such that by Year 20 there was no pH difference between the layers. Plots of pe, Fe, and Mn reflect this convergence (Figs. 2 and 3). Owing to the addition of HAR input and decline in pH (Fe and Mn exhibit greater solubility under low pH conditions), dissolved concentrations of Fe and Mn increase over time in spite of the precipitation of ferrihydrite and manganite (Fig. 3).

Atmospheric gas diffusion into Layer 1 followed by annual turnover events between layers 1 and 2 resulted in a homogeneous dissolved oxygen concentration of 6.8 mg/L throughout the lake (Fig. 2). This indicates that there will be sufficient dissolved oxygen available for subaqueous pyrite oxidation to occur.

The influence of groundwater input is observed in the SO_4 and trace metal trends (Figs. 3, 4 and 5). From

Table 2, the concentrations of SO_4, As, Cd, Pb, and Zn show the following general trend:

$$\text{Groundwater} > \text{HAR} > \text{MAR} > \text{River water}. \quad (9)$$

As a result, the small input of groundwater under steady-state conditions, supplemented by HAR inputs, was sufficient to increase the concentrations of these species over time. The concentration of Ni showed only a slight increase over time because HAR contains a greater concentration of Ni than groundwater, exchanging the first two terms in Eq. (9). The one exception to this trend was Cu, which shows the following relationship between input concentrations:

$$\text{HAR} > \text{MAR} > \text{River water} > \text{Groundwater}. \quad (10)$$

The low concentration of Cu in groundwater creates Cu dilution under steady-state conditions and Cu in lake water decreases over time (Fig. 4).

3.2. Water–rock reactions: Models 2a, 2b, 2c, and 2d

For low estimates of wall rock surface area, water–rock reactions had very little effect on the lake water chemistry (Figs. 2 and 3). Surface area estimates of 1× (Model 2a) and 10× (Model 2b) produced identical pH, pe, dissolved oxygen, Fe, Mn, and SO_4 as Model 1. A 100× increase in the measured surface area (Model 2c) decreased the modeled pH at Year 50 from ~5.0 to ~4.5, which increased the solubility of Fe and Mn and slightly increased the concentrations of these species by Year 50. Because the rate of pyrite oxidation is faster than the rate of silicate dissolution (Table 3), water–rock reactions produced more acidity than alkalinity, and pH dropped over time.

A 1000× increase in surface area (Model 2d) produced a significant effect on lake chemistry. Subaqueous pyrite oxidation lowered the pH at Year 50 from ~5.0 to ~3.5, lowered dissolved oxygen in Layer 2 from ~6.8 mg/L to ~4.8 mg/L, and increased the SO_4 concentration from ~75 mg/L to ~95 mg/L (Figs. 2 and 3). The precipitation of barite prevented the concentration of SO_4 from increasing farther. Year 50 concentrations of Fe and Mn increased over an order-of-magnitude relative to Models 1, 2a, and 2b as a product of lower pH and higher solubility of both metals (Fig. 2). Although Fe(II) was added to solution through pyrite oxidation, the Fe (total) concentration did not increase with respect to Mn concentrations because of ferrihydrite precipitation. Concentrations of trace metals were unaffected by water–rock reactions because the pure mineral phases used in Model 2 did not contain As, Cd, Cu, Pb, Ni, or Zn (Figs. 4 and 5), however, it is likely that pyrite in the Martha mine contains low concentrations of these trace metals.

3.3. Surface adsorption: Models 3a and 3b

The results of Model 3a (surface area of 300 g/m^2) directly overlapped the results of Model 3b (surface area of 600 g/m^2) suggesting the surface area of ferrihydrite did not significantly influence the model results for the range of surface areas investigated. For clarity, only the results of Model 3b are presented.

Dissolved concentrations of As, Cu, and Pb were reduced as a result of surface adsorption onto ferrihydrite, whereas dissolved concentrations of Cd, Ni, and Zn remained unaffected (Figs. 4 and 5). These trends are consistent with observed sorption edge plots of cations and oxyanions adsorbed by ferrihydrite, which show the adsorption affinity of cations onto ferrihydrite follow the sequence $\text{Cr} \geq \text{Pb} \geq \text{Cu} \geq \text{Cd} \geq \text{Zn} \geq \text{Ni} \geq \text{Ca}$, while oxyanions release from ferrihydrite according to the following sequence $SeO_4 \geq SO_4 \geq CrO_4 \geq VO_4 \geq AsO_4$, as pH increases from 2 to 12 (Stumm, 1992; Langmuir, 1997). This adsorption affinity sequence is generally consistent with the adsorption affinity of other metal-oxide surfaces, except that the order of Cd, Zn, and Ni adsorption varies somewhat (Schultz et al., 1987; Smith and Macalady, 1991; Smith, 1999).

Under the oxidizing conditions in Model 3b, dissolved As is present in solution as As(V) which is strongly adsorbed onto ferrihydrite as $H_2AsO_4^-$ across the range of modeled pH conditions (pH 4.9 to 6.5), resulting in lower concentrations of As in solution compared to Model 1 (Fig. 4). Dissolved Pb and Cu are strongly adsorbed at pH 6.5, but are released from ferrihydrite as the pH decreases to 4.9 by Year 50. As a result, Cu and Pb concentration show a more rapid increase over time in Model 3b than in Model 1, beginning at Year 20 (Figs. 4 and 5). The rate of Cu increase is more dramatic than the rate of Pb increase because Pb shows stronger adsorption to ferrihydrite than Cu at low pH (Stumm, 1992). Dissolved concentrations of Cd, Ni, and Zn are less affected by surface adsorption under the pH range modeled, and show similar concentrations in Model 3b and Model 1 (Figs. 4 and 5).

4. Discussion and conclusions

This study explored the significance of subaqueous water–rock reactions and trace metal adsorption onto HFO surfaces in a pit lake geochemical model. With the exception of Tempel (2000), most pit lake predictions assume that water–rock reactions cease after wall rocks are inundated with lake water owing to the slow diffusion rate of oxygen through water and the slow reaction rate of other minerals (Kempton et al., 1997). Surface adsorption reactions are often acknowledged as being important in limiting trace metal concentration, but few studies demonstrate the affect of these reactions on individual metal species over time. Both processes create uncertainty in geochemical models which can be evaluated through sensitivity analyses.

Contrary to our hypothesis, the models presented in this study support the assumption that water–rock reactions may be insignificant in pit lake chemistry. The models used several assumptions intentionally designed to make wall rocks over-reactive and to create a "worst-case" scenario for subaquous pyrite oxidation. First, all minerals were assumed to be fine grained, which maximized the surface area for reactions. Second, all mineral surfaces were assumed to be fresh, or free of oxidized mineral deposits which inhibit geochemical reactions. Third, the surface area of pyrite was held constant over time, instead of decreasing and producing a less reactive surface. Fourth, the rate for pyrite oxidation was constant based on a pH of 6.6, the highest pH that the lake achieved. In reality, reaction rate will decrease as pH decreases. Regardless of these assumptions, Models 2a and 2b showed that water rock reactions were insignificant, whereas a 100 fold increase in surface area in Model 2c had only a minor effect on pH.

This study shows that pyrite oxidation is limited by the surface area of pyrite available for reaction and not by the supply of dissolved oxygen. Model 2d showed that annual turnover between Layers 1 and 2 transported oxygen to the rock–water interface at sufficient rates to provide dissolved oxygen for subaqueous pyrite oxidation to proceed at a significant rate. Low to moderate estimates of pyrite surface area used in Models 2a (1× measured area), 2b (10× measured area) and 2c (100× measured area) showed that subaqueous pyrite oxidation did not significantly influence lake pH chemistry, whereas a high estimate of surface area in Model 2d (1000× measured area) provided sufficient pyrite to significantly lower lake pH. We conclude that accurate estimation of wall rock surface area and mineral surface area is a prerequisite for to accurate assessment of the effects of water–rock reactions. Unfortunately, estimating the surface area of minerals exposed in an open pit mine is complicated by the stepped topography of the pit batters, the roughness of pit walls, the abundance of fractures in the wall rocks, and amount of fine grained material accumulated at the base of each wall. Assuming that the GIS methods used in this study accurately account for these variables, subaqueous pyrite oxidation will not influence the pH of the Martha lake.

Because dissolution rates of silicate minerals are slower than the rate of pyrite oxidation (Table 3), the amount of acidity generated by pyrite oxidation was much greater than the amount of alkalinity produced by silicate dissolution despite silicate minerals having a combined surface area that exceeded the pyrite surface area by one order-of-magnitude. On a scale of several decades, we may conclude that silicate dissolution will have a negligible effect on the pH of pit lakes that contain both pyrite and silicate minerals. However, on a time scale of several centuries, alkalinity generation from silicate dissolution may be important in pit lakes with long residence times because silicate dissolution will continue to occur after all available pyrite has reacted. For pit lake prediction models that span several centuries, like the prediction Post-Betze Lake by Schafer et al. (2006), the inclusion of silicate dissolution may be appropriate. Future work in this area should consider the reduction of pyrite surface area over time while maintaining a constant silicate surface area.

Surface adsorption reactions played a significant role in the trace metal chemistry of the pit lake as expected, however these reactions did not resolve all trace metal issues. Adsorption reactions had a strong influence on dissolved concentrations of As, Cu, and Pb, whereas Cd, Ni, and Zn were unaffected. These results are consistent with published sorption selectivity of ferrihydrite as a function of pH (Stumm, 1992). For the initial lake pH (6.5), As, Cu, and Pb were strongly adsorbed onto ferrihydrite and concentrations of these species were reduced in solution (Figs. 4 and 5). As the pH of the lake decreased over time toward pH 4.9, Cu was released from ferrihydrite, and the dissolved concentration of Cu increased. Concentrations of Pb also increased in solution over time but to a lesser degree than Cu, because Pb is more readily adsorbed onto ferrihydrite at low pH. For the range of pH modeled (4.9 to 6.5), As remained strongly adsorbed to ferrihydrite, whereas Zn, Cd, and Ni concentrations were unaffected because these species require higher pH conditions to adsorb to ferrihydrite. We conclude that the effectiveness of mineral or organic surfaces to naturally remediate pit lake water depends upon the pH of the lake solution and the adsorption affinity of available surfaces towards the trace metals in solution.

One potential limitation of the model is the exclusion of dissolution reactions involving secondary minerals. As Bowell and Parshley (2005) observed in the Summer Camp pit lake, Nevada, USA, the dissolution of secondary minerals can significantly influence pit lake water chemistry in arid climates. The reason these minerals were not included in the geochemical model of water–rock reactions is that a quantitative study of the wall rock mineralogy of the Martha Mine by Castendyk et al. (2005) did not identify significant amounts of secondary minerals in the wall rocks. There are at least three explanations for not finding secondary minerals in the Martha Mine:

(1) The procedure used by Castendyk et al. (2005) removed most of the oxidized layer from rock samples prior to analysis which may have removed most of the secondary minerals present.
(2) Secondary minerals may have been present in too small a quantity to generate characteristic °2θ peaks that were discernable from background scatter using the bulk X-ray diffraction method employed by Castendyk et al. (2005). Alternatively, some of these secondary minerals may have amorphous structures that do not refract X-rays.
(3) The humid climate at Waihi generates frequent rain events that flush secondary minerals from wall rocks and prevent these minerals from accumulating in sufficient quantities prior to lake filling.

If explanation (3) is true, than the flushing of secondary minerals by frequent rain events may be one of the most significant affects that climate can have on pit lake chemistry.

To improve the geochemical prediction presented herein and to confirm the presence or absence of secondary minerals in humid climate mines, wall rock samples should be reexamined for secondary minerals and the results of this study added to the geochemical model. Analyses should focus on the oxidized layer covering wall rocks, and the depth of this layer should be measured at various locations in the pit. Bulk X-ray diffraction analysis may not be the best procedure to identify secondary minerals and an additional sample preparation procedure may be required to separate secondary minerals from primary minerals prior to X-ray analysis. This preparation should be a “dry” method that avoids dissolving the secondary minerals. A “quantitative X-ray diffraction” procedure described by Raudsepp and Pani (2003) has been used to quantify secondary minerals in tailings piles in arid regions of Australia (Harris and Lottermoser, 2003), and could be used to identify secondary minerals in pit wall rocks. However, it should be noted that the petrology community has yet to fully embrace this approach. Problems with this method include the misinterpretation of overlapping °2θ peaks, exclusion of amorphous phases, and the differentiation between a true mineral peak and background scatter. The results of quantitative X-ray diffraction methods should be verified using optical petrology and/or electron microprobe analysis prior to inclusion in pit lake prediction models.

In conclusion, the sensitivity analyses provide a useful tool to explore the significance of various reactions in future pit lakes. Given that water–rock reactions were shown to be insignificant and surface adsorption reactions where shown to be significant, our prediction for the future Martha lake combines the pH, pe, dissolved oxygen, Fe, Mn, and SO_4 results from Model 1 with the trace metal data predicted from surface adsorption modeling results in Model 3b. The basic geochemical model, Model 1, could be further improved by using a kinetic leaching test on wall rock to predict the geochemical evolution of runoff over time, by inclusion of secondary mineral phases in the wall rock, and by incorporating these results into the prediction. As aerially-exposed pyrite becomes consumed over time, these tests will most likely show a reduction in the amount of acidity (H, Fe, Mn, Al) annually released to the lake, resulting in a higher pH after 50 years. In spite of this reduction, the lake will still lack a continuous source of alkalinity. The prediction could also be improved by linking the geochemical model to an updated climate/surface water hydrology prediction that provides an estimate of daily runoff volumes in a changing climate, rather than rely upon the 50-year daily rainfall and evaporation averages used in this study. To calibrate the prediction prior to lake filling, a laboratory model of the future lake could be developed as described by Schafer et al. (2006). Ultimately, the accuracy of this prediction should be evaluated by comparing modeled lake water chemistry to observed lake water chemistry in the post-mining pit lake. Only by means of a post-mining pit lake audits can pit lake geochemical predictions be validated and methods for predictions become substantiated and improved.

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References

Allison, J.D., Brown, D.S., Novo-Gradac, K.J., 1991. MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0 user's manual. EPA Report 600/3-91/021, Environmental Research Laboratory. U.S. Environmental Protection Agency, Athens, Georgia. (93 pp.).

ANZECC, 2000. Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council, Ministry for the Environment, Wellington, New Zealand.

Appelo, C.A.J., Verweij, E., Schäfer, H., 1998. A hydrogeochemical transport model for an oxidation experiment with pyrite/calcite/exchangers/organic matter containing sand. Applied Geochemistry 13, 257–268.

Bioresearches, 1997. A report on the effects of the existing mining operation on the water quality and aquatic biology of the Ohinemuri River and tributaries, and an assessment of the potential effects of the proposed extended project; Martha Mine Extended Project. Technical report. Waihi Gold Company, Waihi, New Zealand.

Bowell, R.J., 2002. The hydrogeochemical dynamics of mine pit lakes. In: Younger, P.L., Robins, N.S. (Eds.), Mine Water Hydrogeology and Geochemistry. Special Publications, vol 198. Geological Society, London, pp. 159–185.

Bowell, R.J., Parshley, J.V., 2005. Control of pit-lake water chemistry by secondary minerals, Summer Camp pit, Getchell mine, Nevada. Chemical Geology 215, 373–385.

Brathwaite, R.L., Faure, K., 2002. The Waihi epithermal gold–silver-base metal sulfide-quartz vein system, New Zealand: temperature and salinity controls on electrum and sulfide deposition. Economic Geology 97, 269–290.

Castendyk, D.N., 2005. An Interdisciplinary Approach to the Prediction of Pit Lake Water Quality, Martha Mine Pit Lake, New Zealand. PhD thesis, The University of Auckland, Auckland, New Zealand, 191 pp.

Castendyk, D.N., Webster-Brown, J.G., 2006. Geochemical prediction and remediation options for the proposed Martha Mine Pit Lake, New Zealand. In: Barnhisel, R.I. (Ed.), Proceedings from the 7th International Conference on Acid Rock Drainage. American Society for Mining and Reclamation, Lexington, KY, pp. 306–324.

Castendyk, D.N., Mauk, J.L., Webster, J.G., 2005. A mineral quantification method for wall rocks at open pit mines, and application to the Martha Au–Ag mine, Waihi, New Zealand. Applied Geochemistry 20, 135–156.

Castro, J.M., Moore, J.N., 2000. Pit lakes: their characteristics and the potential for their remediation. Environmental Geology 39 (11), 1254–1260.

Charlton, S.R., Parkhurst, D.L., 2002. PHREEQCI — A graphical user interface to the geochemical model PHREEQC. USGS Fact Sheet FS-031-02. U.S. Geological Survey, Denver, Colorado. (2 pp.).

Chou, L., Wollast, R., 1985. Steady-state kinetics and dissolution mechanisms of albite. American Journal of Science 285, 963–993.

Davis, A., Ashenberg, D., 1989. The aqueous geochemistry of the Berkeley Pit, Butte, Montana, U.S.A. Applied Geochemistry 4, 23–36.

Davis, A., Eary, L.E., 1997. Pit Lake water quality in the western United States: an analysis of chemogenetic trends. Mining Engineering 49, 98–102.

Davis, A., Fennemore, G.G., 1998. A method to predict evolving post-closure pit lake chemistry. Proceedings of the 25th Anniversary and 15th Annual Meeting of the American Society for Surface Mining and Reclamation. American Society for Surface Mining and Reclamation, Lexington, Kentucky, pp. 315–321.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling-Hydrous Ferric Oxide. John Wiley, New York. (393 pp.).

Eary, L.E., 1998. Predicting the effects of evapoconcentration on water quality in mine pit lakes. Journal of Geochemical Exploration 64, 223–236.

Eary, L.E., 1999. Geochemical and equilibrium trends in mine pit lakes. Applied Geochemistry 14, 963–987.

EGI, 1997. Waste geochemical issues and acid drainage control, Storage 1A and mine closure, Martha Mine Extended Project. Technical report. Waihi Gold Company, Waihi, New Zealand.

Feigenbaum, S., Shainberg, I., 1975. Dissolution of illite — a possible mechanism of potassium release. Proceedings of the 39th Annual Meeting of the Soil Science Society of America. Madison, Wisconsin, pp. 985–990.

Geochimica, 1997a. Hydrogeochemistry of the pit lake, extended project, Martha Hill Mine, Waihi, New Zealand. Technical report. Waihi Gold Company, Waihi, New Zealand.

Geochimica, 1997b. Hydrogeochemistry of the tailings pond at closure, extended project, Martha Hill Mine, Waihi, New Zealand. Technical Report. Waihi Gold Company, Waihi, New Zealand.

Gurung, S., 1998. Characterization and Amelioration of low pH Conditions in Pyritic Mine Pitwall Materials, Martha Mine, Waihi, New Zealand. PhD thesis, Massey University, Palmerston North, New Zealand.

Ingle, D.A., 2002. Newmont Waihi operations — an overview. Proceedings from the Australasian Institute of Mining and Metallurgy Conference 2002. Australasian Institute of Mining and Metallurgy, Carlton, Australia, pp. 105–109.

Harris, D.L., Lottermoser, B.G., 2003. Control of acid mine drainage from partly oxidized, polymineralic mine wastes using phosphate coatings. In: Farrell, T., Taylor, G. (Eds.), Proceedings of the 6th International Conference on Acid Rock Drainage. Australasian Institute of Mining and Metallurgy, Carlton, Australia, pp. 1039–1042.

Havis, R.N., Worthington, S.J., 1997. A simple model for the management of mine pit-lake filling and dewatering. Tailings and Mine Waste '97. Balkema, Rotterdam, Holland, pp. 478–549.

Kempton, J.H., Locke, W., Atkins, D., Nicholson, A.D., Bennett, M., Bliss, L., Maley, P., 1997. Probabilistic prediction of water quality in the Twin Creeks mine pit lake, Golconda, Nevada, USA. Proceedings from the 4th International Conference on Acid Rock Drainage, Mine Environment Neutral Drainage Program, Ottawa, Ontario, pp. 1729–1744.

Kirby, C.S., Dennis, A.M., Kahler, A.K., 2006. Aeration of net alkaline mine drainage to degas CO_2, increase pH and iron oxidation rates. Abstracts with Programs, 2006 Annual Meeting of the Geological Society of America, vol. 38, no. 7, p. 331.

Klein, C., Hurlbut, C.S., 1993. Manual of Mineralogy, 21st ed. John Wiley & Sons, New York. (681 pp.).

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice Hall, Upper Saddle River, New Jersey. (600 pp.).

Lasaga, A.C., Soler, J.M., Ganor, J., Burch, T.E., Nagy, K.L., 1994. Chemical weathering rate laws and global geochemical cycles. Geochimica et Cosmochimica Acta 58 (10), 2361–2386.

Lewis, R.L., 1999. Predicting the steady-state water quality of pit lakes. Mining Engineering 51, 54–58.

Madison, J.P., Gammons, C.H., Poulson, S.R., Jonas, J.P., 2003. Oxidation of pyrite by ferric iron in the acidic Berkeley pit lake, Montana, U.S.A. In: Farrell, T., Taylor, G. (Eds.), Proceedings of the 6th International Conference on Acid Rock Drainage. Australasian Institute of Mining and Metallurgy, Carlton, Australia, pp. 1073–1078.

May, H.M., Acker, J.G., Smyth, J.R., Bricker, O.P., Dyar, M.D., 1995. Aqueous dissolution of low-iron chlorite in dilute acid solutions at 25 °C. Clay Minerals Society, Program with Abstracts, vol. 32. (Clay Minerals Society, Aurora, Colorado, 88 pp.).

Meyer, W.A., Williamson, M.A., Warren, G.C., Brown, A., 1997. Suppression of sulfide mineral oxidation in mine pit walls Part II: Geochemical modeling. Tailings and Mine Waste '97. Balkema, Rotterdam, Holland, pp. 433–441.

Miller, G.C., Lyons, W.B., Davis, A., 1996. Understanding the water quality of pit lakes. Environmental Science & Technology 30 (3), 118A–123A.

Moreno, J., Sinton, P., 2002. Modeling mine pit lakes. Southwest Hydrology 1 (3), 20–22.

Morin, K.A., Hutt, N.M., 2001. Prediction of water chemistry in mine lakes: the minewall technique. Ecological Engineering 17, 125–132.

Nagy, K.L., 1995. Dissolution and precipitation kinetics of sheet silicates. In: White, A.F., Brantley, S.L. (Eds.), Chemical Weathering Rates of Silicate MineralsMineralogical Society of America, Reviews in Mineralogy, vol. 31, pp. 173–233.

Neukirchner, R.J., Hinrichs, D.R., 1997. Effects of ore body inundation — a case study. Proceedings of the 4th International Conference on Acid Rock Drainage. Mine Environment Neutral Drainage Program, Ottawa, Ontario, pp. 1471–1483.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2) — a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey. Water Resources Investigations Report 99-4259, Denver, Colorado. (312 pp.).

Parshely, J.V., Bowell, R.J., Ackerman, J., 2006. Reclamation and closure of the Summer Camp Pit Lake, Nevada: a case study. In: Barnhisel, R.I. (Ed.), Proceedings of the 7th International Conference on Acid Rock Drainage. Society for Mining, Metallurgy and Exploration, Littleton, Colorado, pp. 1495–1513.

Pillard, D.A., Doyle, T.A., Runnells, D.D., Young, J., 1995. Post-mining pit lakes: predicting lake chemistry and assessing ecological risks. Proceedings of Tailings and Mine Waste '96. Balkema, Rotterdam, Holland, pp. 469–478.

Raudsepp, M., Pani, E., 2003. Application of Rietveld analysis to environmental mineralogy. In: Jambor, J.L., Blowes, D.W., Ritchie, A.M.I. (Eds.), Environmental Aspects of Mine WastesMineralogi-Mineralogical Association of Canada, Short Course Series, vol. 31, pp. 165–180.

Schafer, W.M., Logsdon, M., Zhan, G., Espell, R., 2006. Post-Betze pit lake water quality prediction, Nevada. In: Barnhisel, Richard I. (Ed.), Proceedings of the 7th International Conference on Acid Rock Drainage. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado, pp. 1863–1886.

Schultz, M.F., Benjamin, M.M., Ferguson, J.F., 1987. Adsorption and desorption of metals on ferrihydrite: reversibility of the reaction and sorption properties of the regenerated solids. Environmental Science & Technology 21, 863–869.

Schweda, P.S., 1989. Kinetics of alkali feldspar dissolution at low temperature. Water–Rock Interaction. Balkema, Rotterdam, Holland, pp. 609–612.

Shevenell, L.A., Connors, K.A., Henry, C.D., 1999. Controls on pit lake water quality at sixteen open-pit mines in Nevada. Applied Geochemistry 14, 669–687.

Smith, E.E., et al., 1970. Sulfide to sulfate reaction mechanism. Federal Water Quality Administration Water Pollution Control Resource Study #14010-FPS-02-70.

Smith, K.S., 1999. Metal sorption on mineral surfaces: an overview with examples relating to mineral deposits. In: Plumlee, G.S., Logsdon, M.J. (Eds.), The Environmental Geochemistry of Mineral Deposits, Society for Economic Geologists, Reviews in Economic Geology, vol. 6A, pp. 161–182 (Society for Economic Geologists, Littleton, Colorado).

Smith, K.S., Macalady, D.L., 1991. Water/sediment partitioning of trace elements in a stream receiving acid-mine drainage. Proceedings from the 2nd International Conference on the Abatement of Acidic Drainage, Montreal, Canada, vol. 3, pp. 435–450.

Stumm, W., 1992. Chemistry of the Solid–Water Interface. John Wiley & Sons, New York. (428 pp.).

Swedlund, P.J., Webster, J.G., 2001. Cu and Zn ternary surface complex formation with SO_4 on ferrihydrite and schwertmannite. Applied Geochemistry 16, 503–511.

Tempel, R.N., Shevenell, L.A., Lechler, P., Price, J., 2000. Geochemical modeling approach to predicting arsenic concentrations in a mine pit lake. Applied Geochemistry 15, 475–492.

URS, 2003. Favona underground mine; assessment of groundwater issues. Technical Report, Welcome Gold Mines Ltd. and Auag Resources Ltd., Waihi, New Zealand.

USEPA, 2002. National recommended water quality criteria: 2002. United States Environmental Protection Agency, Report EPA-822-R-02-047. (33 pp.).

Waihi Gold Company, 1985. Martha Hill Project: Environmental Impact Report. Waihi Gold Company, Waihi, New Zealand.

Waihi Gold Company, 1997. Martha Mine Extended Project: Assessment of Environmental Effects. Waihi Gold Company, Waihi, New Zealand.

Walder, I.F., Blandford, N., Shelly, T., 2006. Pit lake water quality modeling calibration of the Main Pit, Tyrone Mine, New Mexico, U.S.A. In: Barnhisel, R.I. (Ed.), Proceedings of the 7th International Conference on Acid Rock Drainage. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado, pp. 2240–2261.

Webster, J.G., Swedlund, P.J., Webster, K.S., 1998. Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulfate. Environmental Science & Technology 32 (10), 1361–1368.

Werner, F., Müller, M., Graupner, B., 2006. Predicted and observed water quality data from the coal mine pit lake Bärwalde, Laustz, Germany. In: Barnhisel, R.I. (Ed.), Proceedings of the 7th International Conference on Acid Rock Drainage. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado, pp. 2333–2343.

White, A.F., Blum, A.E., Schulz, M.S., Bullen, T.D., Harden, J.W., Peterson, M.L., 1996. Chemical weathering rates of a soil chronosequence on granitic alluvium: I. Quantification of mineralogical and surface area changes and calculation of primary silicate reaction rates. Geochimica et Cosmochimica Acta 60 (14), 2533–2550.

WHO, 1998. Addendum to Volume 2, Guidelines for Drinking-Water Quality. World Health Organization, Geneva, Switzerland, pp. 281–283.

Wieland, E., Stumm, W., 1992. Dissolution kinetics of kaolinite in acidic aqueous solutions at 25 °C. Geochimica et Cosmochimica Acta 56, 3339–3355.

Williamson, M.A., Rimstidt, J.D., 1994. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. Geochimica et Cosmochimica Acta 58 (24), 5443–5454.

Wolery, T.J., Daveler, S.A., 1992. EQ6, A computer program for reaction path modeling of aqueous geochemical systems: theoretical manual, user's guide, and related documentation (version 7.0). Lawrence Livermore National Laboratory, Report no. UCRL-MA-110662.

Woodward, Clyde, 1997a. Pit lake water balance and preliminary lake outlet design, Martha Mine Extension. Technical report. Waihi Gold Company, Waihi, New Zealand.

Woodward, Clyde, 1997b. Mine dewatering study, Martha Mine Extension. Technical report. Waihi Gold Company, Waihi, New Zealand.

Woodward, Clyde, 1997c. Martha mine extension: Site water management. Technical report. Waihi Gold Company, Waihi, New Zealand.