



Predicting Metal Attenuation for Mine Closure Planning

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1. Summary

A company operating a copper mine in central British Columbia, Canada is seeking a permit for expansion. Since mine operations pose a potential risk to fish-bearing habitat located adjacent to the Site, provincial regulations require modelling of metal loadings from groundwater as part of a site-wide water quality assessment prior to the mine obtaining the expansion permit. This study was carried out to assess the extent that mineral precipitation and adsorption attenuate metal loadings from groundwater and their potential to inform mine closure planning, including when and where to best direct remediation efforts.

Previous modelling studies used a mass balance approach to predict groundwater metal loadings to surface water; however, this approach over-predicted metal loadings when compared to analytical results from samples collected from monitoring wells. In this study, metal attenuation was modelled using United States Geological Survey (USGS) software PHREEQCI in an alluvial aquifer down-gradient of a pit lake and inactive heap leach pile.

Sensitivity analyses were completed by varying iron-hydroxide and calcium carbonate concentrations, and groundwater velocity. Model results were calibrated to groundwater analytical results from wells located on the flow path. The results predict continued metal attenuation, primarily through metal adsorption and co-precipitation, provided groundwater remains buffered against acidic input. Continued acidic input 30 to 40 years post-closure will result in desorption of weakly adsorbed metals (Cd and Co) and potentially result in adverse impacts to the aquatic environment.

2. Introduction

In operation since the early 1970s, a mine in western Canada has been using a heap leach process to extract copper from the ore body via electrowinning. This extraction process has resulted in metals (primarily copper), sulphate, and acidity impacting the adjacent alluvial aquifer, which discharges to a river. In addition to providing important fish habitat, the river is culturally significant to the local First Nation. In response to the mine proponent's application to expand its mine operations, the regulator now requires predictions of future metal loading to the river.

During previous modelling studies, a mass balance approach was used to estimate metal loading to the river. The source term (pit lake water quality) was used with volumetric flux without attenuation to conservatively estimate mass loading. When compared to analytical results from monitoring wells down-gradient of the heap leach cells, however, the model over-estimates the amount of metal loading by more than an order of magnitude. This suggests that other processes are attenuating metals that have not been incorporated into the existing groundwater model, thus warranting a different approach to predict metal loadings to the river.

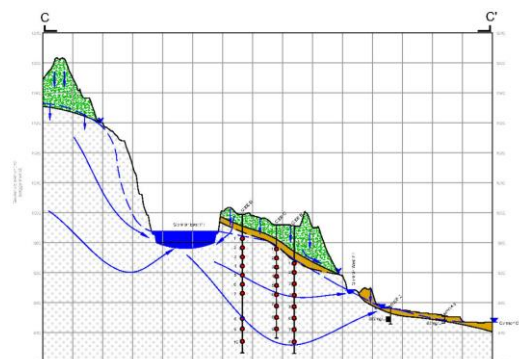
Hemmera's study team addressed this uncertainty by preparing a model using PHREEQCI, which accounted for other important geochemical processes such as solution complexation, mineral dissolution and precipitation, pH buffering, and adsorption using surface complexation and ion competition. The model was calibrated using groundwater monitoring data.

The approach, results, and interpretation of this modelling is the subject of this paper which highlights the importance of accounting for pH buffering and metal adsorption to simulate sub-surface metal attenuation processes at mine sites.

3. Site Setting

The ore body at the mine is a porphyritic copper molybdenum deposit, which is extracted via open pits. Older pits are used to store mine contact water, including spent raffinate from the heap leach piles. Groundwater flow from these pit lakes and surrounding waste rock areas is predominantly through bedrock fractures, which transitions to flow through a porous media aquifer composed of alluvium. Groundwater flows from the pit lakes through the alluvium aquifer and discharges to the river.

Low pH seeps are observed at or near the base of the dumps. The seeps are seen to daylight where there is a change in slope or outcrop of low-permeability till. The seep flows are largely diverted to the mine's water management system; however, deeper flow systems and re-infiltration of seep water may bypass the collection ditches and flows through the alluvial aquifer to the river.



[Figure 1 - Granite Creek CSM Cross-Section]

Mineral precipitation is observed where the seeps daylight, indicating that mine contact water is supersaturated with various secondary mineral phases.

Analytical results suggest that some of this mine-impacted water discharges from fracture flow to the alluvial aquifer.

Analytical results from multi-channel (WestBay) wells screened in bedrock show that the groundwater quality is similar to that of the pit lake, suggesting that minimal attenuation occurs within bedrock fractures. This assessment therefore focuses on evaluating and quantifying attenuation mechanisms that take place within the alluvial aquifer prior to discharge to the river.

3.1. Mineralogy Analysis

Sampling locations close to the base of the waste rock dumps were selected to collect continuous soil samples using a Sonic drill and submitted for total element (Sodium Peroxide Fusion, Inductively Coupled Plasma Optical Emission Spectroscopy / Mass Spectrometry (ICP-OES/MS and Eltra) and mineralogical (XRD) analyses. The XRD results indicated up to 14% amorphous material, which warranted analysis using other mineralogical techniques to determine its composition.

Epoxy grain mounts were analyzed using QEMSCAN Particle Map Analysis (PMA) at 3.0 micrometres (μm) pixel resolution to provide modal mineralogy combined with SEM-EDS to investigate the deportment of Cu, Fe, and Mn. QEMSCAN is a definitive quantitative assessment method that uses a combination of energy dispersive spectrometric (EDS) and backscatter energy (BSE) properties of the sample. Groundwater and seep samples were submitted for analysis of major and minor cations and anions, total and dissolved

metals (ICPMS), pH, and electrical conductivity.

The mineralogical results from QEMSCAN improved the resolution of the amorphous materials reported from XRD analysis. The soil mineralogy is predominantly composed of quartz (52%) and feldspar (33%) with minor epidote (4%), Fe,Mg-silicates (3.8%), muscovite (2.9%), chlorite (1.4%). trace hydrous ferric oxides (HFO) (1%), garnet (0.2%), and CuOx/hydrox (0.01%). Approximately 3% was comprised of 'others', low BSE materials (possibly amorphous) that may comprise sulphides, carbonates, oxy-hydroxides, and clays. MnOx/hydrox were generally absent or occurred in very low abundance. Al-hydroxides were not detected but may be present as amorphous phases. Carbonate minerals were not explicitly identified; however, total inorganic carbon analyses using the Elementar method indicated concentrations ranging from 0.1 percent weight (wt%) – 0.68wt%.

3.2. Physical Hydrogeology

Groundwater impacts associated with heap leaching appear to infiltrate into bedrock and flow along fractures before transitioning to porous media flow through the alluvial aquifer, as shown in the cross-section in **Figure 1**.

Hydraulic conductivity testing has estimated that the groundwater velocity in the alluvium ranges from 10 metres per year (m/year) to 100 m/year. This observation warranted the use of a simplified approach in the geochemical model.

4. Modelling Approach

Geochemical modelling was conducted using United States Geological Survey (USGS) PHREEQCI (pH-redox-equilibrium-

calculations-interactive) software (version 3.3.11) using the MINTEQ version 4 database of parameter constants.

Metal attenuation processes considered included: mineral dissolution/precipitation, pH buffering, and adsorption/desorption. The primary mineralogy of the aquifer was determined using XRD, SEM-EDS, QEMSCAN, and Elementar on soil samples collected from an unimpacted area of the aquifer. Secondary mineral phases were also defined in conjunction with input from an external expert at a local university.

The proposed expansion of the mine is anticipated to extend the mine life by 5 years. The regulator requires metal loading predictions to be made for a further 100 years following the end of mine life. As a result, the models were run for 105 years to satisfy permitting requirements.

Details regarding the conceptual site model and the specifics regarding the model inputs are presented in the following subsections.

4.1. Conceptual Site Model

As presented in **Section 3.2**, the groundwater flow path from the older pits used to store process water and spent raffinate includes flow through bedrock fractures, and transitions to flow through an alluvium porous media.

Owing to the inherent uncertainty and complexity in simulating groundwater flow and corresponding attenuation mechanisms within a bedrock fracture flow setting, and drawing from the observation that little attenuation is occurring within bedrock fractures, the reactive transport model considered a flow path within the alluvial aquifer material only.

PHREEQCI allows for a multi-component, one-dimensional reactive transport simulation. The transport component of the simulation is conducted using equal volume cells (Cell 1 to Cell 'n') along the inferred centreline of the plume. Each cell has a defined solution composition and primary mineralogy. The flow path modelled is shown in **Figure 2**.



[Figure 2 - plan view figure of flow path modelled]

4.1.1. Primary Mineralogy

Primary mineralogy in each cell of the transport simulation was defined based on results presented in **Section 3.1**. Conceptually, the primary mineralogy of the aquifer material is generally non-reactive (i.e., silicates) and is not interpreted to represent attenuating mechanisms for acidity or copper. Important attenuation mechanisms attributed to the primary mineralogy of the aquifer material are pH buffering by the dissolution of calcite and adsorption of copper and other metals onto hydroxy-ferrous oxide (HFO) surfaces.

QEMSCAN results indicated samples in the unimpacted aquifer contained up to 1.0 wt% HFO. To evaluate the sensitivity of model outputs to varying concentrations of

HFO, simulations were run with HFO concentrations equal to 1.0 wt%, 0.1 wt%, and 0.05 wt%.

Elementar analytical results indicated samples in the unimpacted aquifer contained between 0.1 wt% and 0.68 wt% inorganic carbon. To evaluate the sensitivity of the model to the extent that inorganic carbon comprised calcite, simulations were run with calcite concentrations equal to 0.68 wt%, 0.1 wt%, and 0.05 wt%.

Mineral concentrations were converted from wt% to molar concentrations using soil bulk density, effective porosity and the molecular weight of the mineral.

For HFO, the molar concentration was converted to moles of strong adsorption sites and moles of weak adsorption sites. This is done using constants determined by Dzombak and Morel (1990) who determined each mole of HFO has 0.2 moles of weak adsorption sites and 0.005 moles of strong adsorption sites per mole of HFO. The affinity of various metals for these adsorption sites is defined in the MINTEQ database file.

Molar concentrations of calcite and HFO were inputted into PHREEQCI as *Equilibrium Phases* and allowed to dissolve and/or participate in adsorption reactions during reactive transport calculations, respectively. Molar concentrations calculated using mineralogical analytical results defined the amount of each mineral available for chemical reaction in each cell along the modelled flow path.

Owing to low groundwater velocities at the Site, it was assumed that the system reaches equilibrium along the groundwater flow path. This assumption is consistent with the observed reaction rates for calcite dissolution and copper adsorption onto

HFO surfaces at other sites and based on professional judgement.

4.1.2. Solution Zero

In PHREEQCI, the source term in a reactive transport simulation is referred to as "Solution '0'".

As presented in **Section 4.1** and owing to the inherent complexity of reactive transport modelling through a fractured bedrock system, the PHREEQC model considered groundwater through the alluvial aquifer only.

Pit lake water quality was used to define Solution '0'. This interpretation is supported by analytical results from samples collected from Westbay multi-level monitoring wells screened across bedrock fractures (see **Figure 1**), which indicated water quality similar to pit lake water quality. This finding supports the interpretation that minimal attenuation occurs within bedrock fractures. In addition, this finding supports the decision to use pit lake water quality to define Solution '0' for a reactive transport model through the alluvial porous media aquifer.

The oxidation-reduction potential of pit lake water was not measured during historical sampling of pit lake water quality. Thus, to define the initial redox state of the source term and be consistent with pit lake water being exposed to the elements, pit lake water quality results were pre-equilibrated with atmospheric oxygen concentration to define the initial redox state of Solution '0'.

4.1.3. Secondary Mineralogy

Of particular focus for this assessment and critical to the attenuation of metals and acidity is the formation of secondary

minerals. Using PHREEQCI, secondary minerals are defined as *Equilibrium Phases* and are allowed to precipitate in the simulation as their constituent concentrations become super saturated.

Important metal attenuation processes including pH buffering, adsorption on mineral-water interfaces, and the precipitation of secondary minerals are described in Wilkin (2007). Additional secondary minerals included in the model were determined through correspondence with a local university professor.

As will be presented in **Section 5**, the results support the interpretation that, although secondary minerals do form along the flow path, the predominant attenuation mechanisms are pH buffering/calcite dissolution, and adsorption onto HFO.

4.1.4. Reactive Transport Simulation

PHREEQCI considers one-dimensional flow along the centreline of plume migration. The flow path is defined as a number of cells (Cell 1 to Cell 'n') of equal length. Each cell has a specified initial solution composition (defined using analytical results from down-gradient wells) and a specified primary mineralogy as described in **Section 4.1.1**. As shown in **Figure 2**, the flow path considered is 440 m long. Thus, the transport simulation considered 44 10-m cells.

Transport calculations are formulated using "shifts". During the first shift, Solution 0 enters Cell 1, Solution 1 enters Cell 2, and so on. PHREEQCI calculates chemical reactions between Solution 'n' and Cell 'n+1' and a new solution composition and mineralogy are calculated. This process is repeated for a set number of shifts.

Groundwater velocity is specified by cell length and shift duration. For example, a groundwater velocity of 100 m/year and a cell length of 10 m equate to one-tenth of a year for each shift; thus, a 10-year simulation duration would require 100 shifts.

For this study, groundwater velocity ranged between 10 m/year and 100 m/year. To evaluate the sensitivity of groundwater velocity to model results, groundwater velocities of 10, 50, and 100 m/year were considered.

4.1.5 Modelling Approach

Multiple scenarios were run prior to calibration to simulate contaminant transport and metal attenuation over the range of parameter values measured at the Site.

As presented in **Section 4.1.1**, three HFO concentrations were considered in the simulations: 1.0 wt%, 0.1 wt%, and 0.05 wt%. Also presented in **Section 4.1.1**, three calcite concentrations were considered in the simulations: 0.68 wt%, 0.1 wt%, and 0.05 wt%. In addition, three groundwater velocities were considered in the simulations (**Section 4.1.4**): 10 m/year, 50 m/year, and 100 m/year. Thus, for the range of parameter constants presented above, 27 unique simulations were run.

Model results were calibrated by comparing simulation results to analytical results from down-gradient monitoring wells at known locations along the flow path. Results of the modelling are presented in the following subsections.

5. PHREEQCI Results

Results from PHREEQCI simulations were used to prepare spatial profiles and breakthrough curves. Spatial profiles

present select mineral concentrations and pH along the centreline of the plume at a specified time, typically 105 years. The concentration of select metals adsorbed onto HFO surfaces is also presented. Spatial profiles allow for the identification of zones with specific geochemical characteristics along the groundwater flow path. In other words, the spatial profiles show where minerals are dissolving/precipitating, in what order, and the corresponding effect on pH.

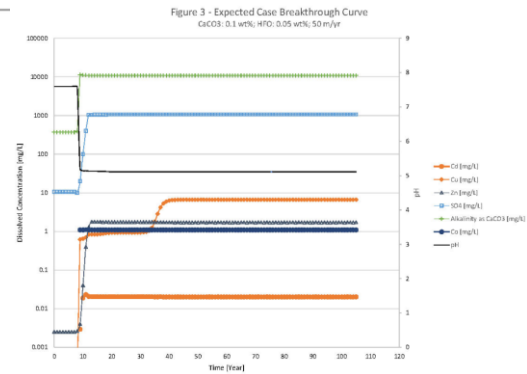
Breakthrough curves present the pH and concentration of select dissolved species over time reaching the river (i.e., the predicted groundwater concentration at cell 44 over time). Breakthrough curves allow for prediction of if/when metals and acidity will reach the river, which allows for implementation of appropriate mitigation measures as needed. Both the spatial profiles and the breakthrough curves are presented in the following sections.

5.1. Model Calibration

The flow path considered in the simulations is shown in **Figure 2**. Model results were compared to analytical results from down-gradient monitoring wells. The simulation with the mix of copper, sulphate, and pH that most closely fit with the analytical data was determined to be the expected case.

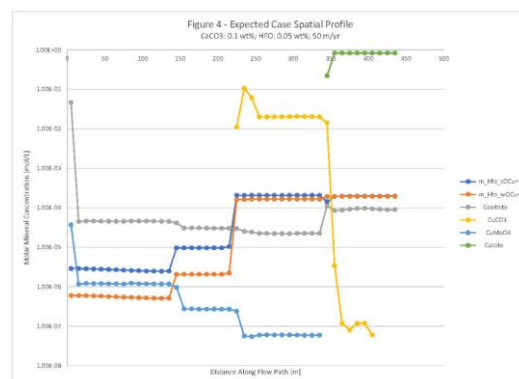
5.1.2 Expected Case

The breakthrough curve for the expected case is shown in **Figure 3**. The spatial profile is shown in **Figure 4**. The interpretation from both is presented in this subsection.



[Figure 3 – Expected Case BTC]

In the expected case, the solution pH remains around pH 5; Cu does not exceed 6.6 mg/L; and Zn does not exceed 1.7 mg/L at the receptor (**Figure 3**).



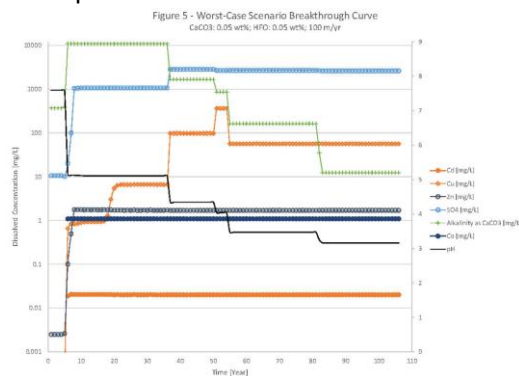
[Figure 4 – Expected Case Spatial Profile]

In the first 10 years, calcite is depleted to 30 m, CuMoO_4 and CuCO_3 precipitate where calcite has depleted, HFO dissolves, and goethite precipitates. Cu is attenuated by adsorption onto HFO for 33 years and maintains Cu at 1 mg/L at the receptor over this period. Once the HFO sites are saturated along the flow path, Cu increases to and maintains around 6.6 mg/L at the receptor from Y33 to Y105.

5.1.1. Worst-case Scenario

The simulation that considered the lowest HFO and calcite concentrations and the maximum groundwater velocity was determined to represent the worst-case scenario. The breakthrough curve for the worst-case scenario is presented below and shown in **Figure 5**. The spatial profile is

shown in **Figure 6**. The interpretation from both is presented in this subsection.



[Figure 5 – Worst Case Scenario BTC]

The rapid groundwater velocity in the worst-case model results in rapid response (i.e. around five years) at the receiver. The model indicates that pH will drop in several incremental steps from around pH 8 to pH 3. Alkalinity decreases to 10 mg/L over the modelled period and Cu, Zn, and SO₄ concentrations increase by factors of 5.5, 2, and 2.5, respectively (**Figure 5**). Cu is initially attenuated via precipitation as CuCO₃ and attenuation onto HFO. After six years, calcite is depleted along approximately 120 m of the flow path and copper concentrations increase to approximately 1mg/L at the receptor. Dissolution of HFO following calcite depletion adds Cu to groundwater. CuMoO₄ is predicted to precipitate where calcite has fully depleted.

Copper and zinc concentrations increase to around 6.6 mg/L and 1.7 mg/L at around Y18 (the 18th year from the beginning of model run) because HFO adsorption sites are fully occupied and cannot further attenuate metals. From Y37 to Y55, calcite is fully depleted and pH and alkalinity decline along entire flow path; maximum Cu breakthrough around 360 mg/L occurs around Y50. The lowering of breakthrough Cu concentration to 56 mg/L after Y53 is ascribed to CuMoO₄ precipitation and adsorption onto HFO but at a lower concentration.

6. Discussion

Solution-zero water quality has changed since regular monitoring started in 1994 because of raffinate inflows since the mid-2000s: pH has declined from pH 8.4 to pH 3.4 over the 22 years to 2016; SO₄ has increased threefold to around 1,500 mg/L and Cu from 2 mg/L to 53 mg/L (Table 1). Although a bedrock well is situated approximately 100 m down-gradient of the source, SO₄ in MW06-2 doubled from 200 mg/L to 400 mg/L between 2010 and 2017, but pH has remained steady around pH 7.1 and Cu has barely varied around 0.013 mg/L. This finding suggests that metal attenuation mechanisms are present within the bedrock aquifer.

Table 1 Average solution zero and down-gradient monitoring well data (mg/L) in 2016

Parameter	Solution zero	MW06- PW6 ²	MW14-5
Distance (m)	0	100	400 500
pH	3.4	7.1	7.6 7.7
Cu	53	0.013	0.08 0.01
Zn	2.3	<0.005	<0.005 <0.005
SO ₄	1,585	400	77 54

¹ Bedrock well; ² Average data 2007 – 2009

Monitoring well PW6 is approximately 400 m from the pit lake but monitoring was discontinued in 2009. The elevated Cu, SO₄, and low pH compared to MW14-5 suggest metal attenuation occurs around Y10, although pH remains well buffered at pH 7.6 compared to predicted pH 5.1 in **Figure 3**. A current sample from PW6 would be valuable as it may indicate that breakthrough has occurred. MW14-5 is approximately 100 m down-gradient of PW6 and does not show significant mining impact. Given the travel time between these wells, several years would be required

to reach the breakthrough curves in **Figure 3**.

Assuming an average annual groundwater velocity of 50 m, solution zero (pit lake water in 2007) is currently near the receptor (MW14-5), which is some 500 m distant (**Figure 3**). The breakthrough curves in the expected case (**Figure 2**) suggest that Cu, Zn, and SO₄ concentrations could soon increase by several orders of magnitude over a three- to four-year period. Zn and SO₄ would equilibrate at 1.7 mg/L and 1,000 mg/L in Y13, but Cu would increase in Y40 to 6.3 mg/L from desorption off HFO. The predicted concentrations would exceed water quality guidelines and may require diversion and pumping back to the mine's water management system. A factor ameliorating this prediction is that 2016 pit lake quality was used, whereas the groundwater reaching the receiver is from around 2006.

These findings have informed performance metrics to monitor contaminant transport and attenuation mechanisms at the Site. For example, if a pH decrease is observed at sentinel wells, active steps can be taken to neutralize the pH and prevent breakthrough of metals to the aquatic environment.

7. Conclusion

Geochemical modelling was carried out to simulate pH buffering, metal adsorption, and secondary mineral precipitation along the groundwater flow path with the objective of predicting groundwater metal loadings to surface water. The results indicate that although metal adsorption is significant, it is unsustainable where acidic inputs are ongoing and calcite is depleted in the aquifer. Conservative calcite values (0.1%) were used in the model because of uncertainty regarding the type of carbonate present in the aquifer. For example, siderite

(FeCO₃) does not provide neutralizing potential. The groundwater velocity may over-estimate the timing of the breakthrough curves; monitoring results suggest a slower rate of change than predicted in the breakthrough curves.

The role of Cu-mineral precipitation and adsorption on HFO is important in attenuating metals along the flow path; however, the depletion of calcite and the ensuing decrease in pH causes metal desorption from HFO sites.

This study is preliminary and there is limited site-specific data to confirm the geochemical processes along the groundwater flow path. Ongoing characterization and calibration of the model, coupled with frequent water quality monitoring, will improve confidence in the metal loading predictions. A more detailed understanding of carbonate and HFO distribution in the overburden aquifer would better constrain the model and has been proposed to understand the buffering capacity of the aquifer. Additional investigation of aquifer mineralogy will improve the metal-attenuation predictions.

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Illustrations



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Professional profile

Jake Gossen is an engineering hydrogeologist with 11 years of experience in the environmental consulting field. Jake's work primarily focuses on evaluating the fate and transport of organic and inorganic contaminants in aquifer systems. Of particular interest to Jake is the role of aquifer mineralogy on contaminant migration rates.

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With 30 years of professional experience, predominantly in the mining sector, Gerry Papini has conducted site assessments for mining, landfill, petroleum, government, and private industrial clients. Currently, his work focuses on geochemical characterization and waste rock management plans, groundwater explorations, supply well installs and licensing, groundwater assessments for fish