The role of metal-attenuation in groundwater quality prediction

G. Papini, P. Geo[1], J. Gossen, P. Eng[1], B. Pierce[2]

[1]Hemmera, an Ausenco company, Burnaby, British Columbia, gpapaini@hemmera.com
[2]Gibaltar Mines Limited

Abstract

In this study we used PHREEQC to model metal attenuation in groundwater at a mine in central British Columbia. The results of the study were used to estimate metal loadings from groundwater in a site-wide water quality model. The focus was metal mobility in alluvial material downgradient of a pit lake and inactive heap-leach pile. The study included analysis of aquifer mineralogy and the model was calibrated using the mine's environmental monitoring database. The data were used to predict possible future concentrations at model prediction nodes (receptor) when loadings were combined with numerical groundwater model flow predictions.

Keywords: geochemical modelling, heap-leach, raffinate, pit lake, breakthrough curve

Objective

Previous water quality models have used rock dump and tailings seepage quality as the groundwater source term without consideration of metal attenuation. When applied in catchment-based, mass-balance models, these conservative source terms are thought to over estimate the groundwater loadings to surface water. This can lead to unrealistic predictions of potential environment effects and instill a sense of urgency for groundwater recovery and treatment. Our aim has been to incorporate metal attenuation considerations so that less conservative metal loadings from groundwater can be applied in site-wide water quality modelling.

Introduction

The mine has operated since the early 1970s and in 2013 increased mill throughput from 55 ktpd to 85 ktpd. Parts of several dumps were heap leached from 2007 to 2015. The pregnant leach solution was collected in ponds at the base of the leach facilities and pumped to the solvent extraction and electrowinning plant. Although underlain by naturally-occurring low permeability materials, seepage through the base of the heap-leached rock piles and collection ponds is thought to constitute the primary contaminant source to groundwater.

Important metal attenuation processes at mining sites include pH buffering and acid neutralization; adsorption at the mineral-water interface; mineral precipitation and dilution / dispersion (Wilkin 2007). Previous model predictions considered only dilution/dispersion because of uncertainty quantifying the long-term stability of other processes. Field studies and column tests have shown that mineral assemblages present in tailings piles, underlying aquifers, and receiving waters play a pivotal role in controlling pH (Blowes and Ptacek 1994). Mineral phases important in buffering pH are calcite/siderite, iron and aluminium hydroxides and aluminosilicates.

Oxidation of iron sulphides in mine wastes results in the release of iron, sulphate, acidity and metals to solution. High aluminium and silica concentrations can occur from weathering of aluminosilicate minerals at low pH. Oxidation and hydrolysis reactions can subsequently lead to the precipitation of a wide array of hydroxide, sulfate and/or hydroxy-sulphate minerals depending on the geochemical and biogeochemical conditions (Nordstrom and Aplers 1999). These secondary minerals play important roles in attenuating contaminants from mine effluents. Examples of secondary minerals formed from acid mine waters that sorb or co-precipitate metals include hydrous ferric oxides (HFO); gibbsite (aluminium hydroxide); goethite (iron oxyhydroxide) and schwertmannite (hydroxysulphate).

Site Setting

The mine catchments vary in elevation from approximately 1,260 metres above sea level (masl) in the east to a lake and wetland-filled valley in the west at elevation around 830 masl. The flow path considered in this study is from a pit lake elevation at approximately 896 masl over approximately 500 m to a creek. The mean annual precipitation is 524 mm/year with about one quarter occurring as snow. Creek flows are seasonal (2 – 200 L/s) and higher in spring because of snow melt. Temperatures are below freezing from November through March when much of the precipitation falls as snow. Mean monthly temperatures vary from -12°C to 17°C.

The deposit host rocks are late Triassic to Early Jurassic intrusive granites. The deposits are classified according to structural system, and referred to as porphyry ores, and shear zone ores. The southerly dip of the mineral zones is offset by a series of northerly trending, generally steeply west dipping faults. The area has been intensely glaciated and most of the bedrock is covered by lodgement till, accompanied in places by ablation moraine and glaciofluvial deposits.

Older pits are used to store process water, including spent raffinate from the heap leach piles. Groundwater flow from these pit lakes and surrounding waste rock areas is predominantly through bedrock but also through glaciofluvial deposits downgradient of the waste rock dumps and within alluvial deposits west of the mining area. Shallow bedrock in the mining areas appears to have elevated hydraulic conductivity (1E-06 m/s to 5E-07 m/s) in comparison to undisturbed areas. The average hydraulic conductivity measured in glaciofluvial materials is

4E-06 m/s; however, there is a two to three order-of-magnitude difference in hydraulic between silty-clay till and the glaciofluvial sand and gravel.

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; although evidence for this is not conclusive.

Mineralogical Investigation

Sampling locations were selected as close to the toes of waste rock dumps that could be accessed by a drilling rig. Continuous soil samples were collected using a Sonic drill and submitted for total element (Sodium Peroxide Fusion, ICP-OES/MS & Eltra) and mineralogical analyses (XRD). Epoxy grain mounts were analysed using QEMSCAN Particle Map Analysis (PMA) at 3.0 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 method based on 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 conductivity.

The mineralogical results from QEMSCAN improved the resolution of the 'amorphous materials' reported from XRD analysis. The soil mineralogy is comprised predominantly of quartz (52%) and feldspar (33%) with minor epidote (4%), Fe,Mg-silicates (3.8%), muscovite (2.9%) and chlorite (1.4%); and trace HFO (1%), garnet (0.2%), and CuOx/hydrox (0.01%). Approximately 3% was comprised of 'others', which are 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 from 0.1% – 0.7 wt%. Carbonates (up to 6% calcite and 12% ankerite-dolomite) are present in waste rock samples collected as part of ML/ARD monitoring (SRK 2016).

Geochemical Modelling

Contaminant transport modeling was conducted using PHREEQC to simulate advective and dispersive groundwater flow; aqueous complexation; mineral dissolution and precipitation along a groundwater flow path; and adsorption and desorption on/off mineral surfaces. PHREEQC calculates onedimensional transport using a series of equal volume cells with specified groundwater composition and primary mineralogy. Secondary mineral phases are specified that can precipitate if they reach saturation. Each cell also has a defined surface which specifies the concentration of adsorbent minerals such as HFO. Contaminant transport through bedrock was not modeled because it has a lesser role in metal attenuation and is difficult to model.

Water quality from the pit lake was used as the source term (solution zero) and invariant over the model run of 105 years to predict potential post-closure groundwater quality. The initial mineral and groundwater composition along the flow path was based on unimpacted conditions. Important minerals considered to control Cu concentrations included calcite; copper carbonate; copper molybdenate; goethite and hydrous ferric oxide (HFO). PHREEQC separates HFO into strong binding sites (Hfo_s) and weak binding sites (Hfo_w). Dzombak and Morel (1990) determined that HFO has 0.2 mol Hfo_w sites/mol-HFO and 0.005 mol Hfos sites/mol-HFO.

Multiple simulations were completed by varying the input parameters to assess range in the results and sensitive parameters. Model calibration was carried out by comparing model results to analytical results from down-gradient monitoring wells to identify the best fit for multiple parameters. A good fit in both the monitoring results matching the predicted results as well as the input parameters matching field measured parameters (e.g. carbonates and HFO) provided confidence that the best fitting simulation could be used to predict concentrations at the prediction nodes. The breakthrough curve (Figure 1) shows pH, sulphate and metal concentrations (mg/L) over a 105-year period at a prediction node considered to be the receiving environment.

Results

The model indicates that pH will drop in several incremental steps from around pH 7.6 to pH 6.68 at the receptor over the modelled period. Sulphate increases to approximately 1,500 mg/L early in the modelled period. Copper and Zn increase but stabilize at 0.12 mg/L and 0.0018 mg/L respectively after 12 years Cobalt increases to 0.34 mg/L after about 25 years and Cd to 0.017 mg/L after about 75 years. (Figure 1).

Table 1 shows that Solution zero pH is buffered in the aquifer to pH 7.49 at the end of mining (2021) and at pH 6.68, 100 years post-closure (2121). All the metals are attenuated several orders of magnitude (up to four orders of magnitude for Cu) at the end of mining; however, Co and Cd breakthrough in the post-closure because of loss of attenuation in the aquifer.

A spatial profile for dissolved metals, pH and sulphate (Figure 2) shows dissolved concentrations along the flow path in 2121. After 105 years, the pH near the source is approximately 3.9 creating conditions conducive to alunite and $CuMoO_4$ precipitation. At this pH, HFO reacts to form goethite and mineral precipitation appears to attenuate molybdenum concentrations.

Where calcite is present, pH remains buffered at approximately 6.7. Adsorption of cadmium, cobalt, copper and zinc onto HFO is an important attenuation mechanism at this pH. Early precipitation of goethite along the flow path is expected to provide adsorptive sites for dissolved metals.

Once calcite has depleted, the pH drops to approximately 4.9. Under these conditions, goethite stops precipitating and mala-

Table 1. *Average solution zero (mg/L) and predicted concentration at prediction node*

Parameter	Solution zero	2021	2121
pH	4.42	7.49	6.68
Cu	355	0.0002	0.002
Co	0.31	0.00	0.33
Cd	0.011	0.000	0.017
Zn	2.4Cd	0.006	0.120
SO4	1,520	100-1,000[1]	1,480

[1] Sulphate curve range based on breakthrough in Figure 1

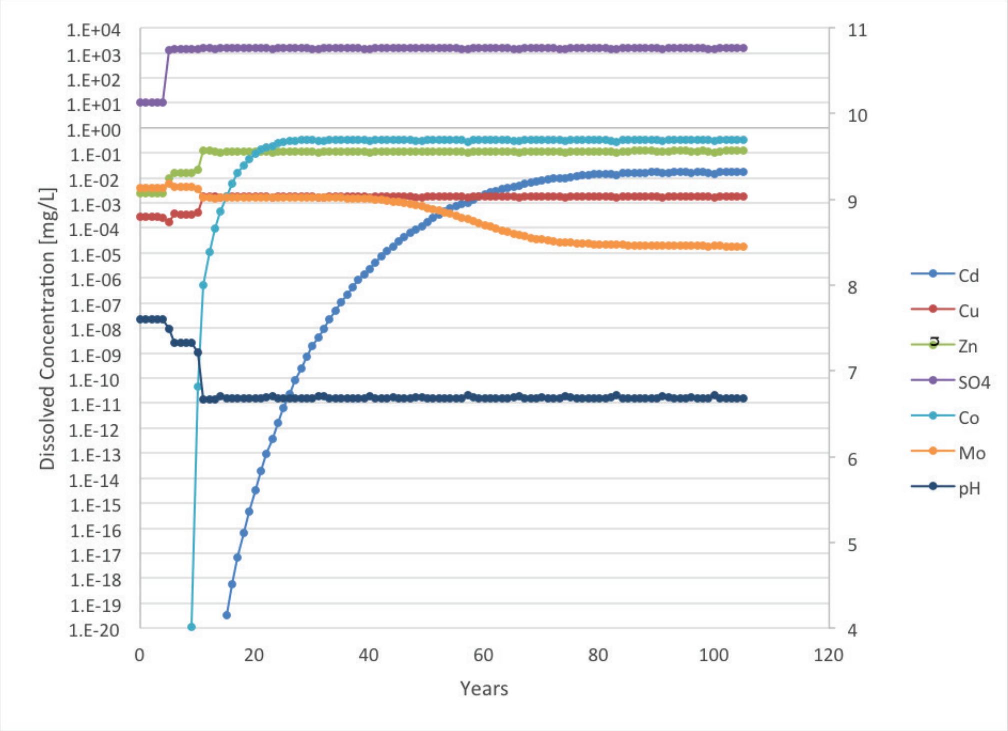

Figure 1 Breakthrough curve at prediction node approximately 500 m from source ($CaCO_3$ 0.4%; HFO 0.02%; v - 100 m/y).

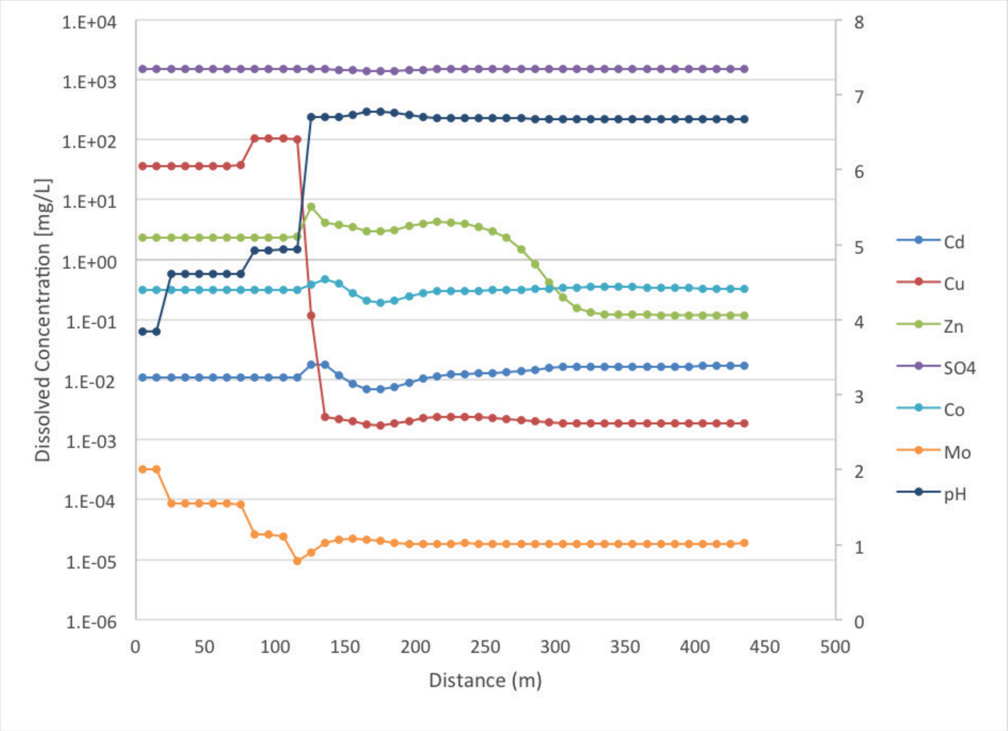

Figure 2 Post Closure (2121) concentrations (mg/L) along flow path (CaCO3 0.4%; HFO 0.02%; v - 100 m/y).

chite and cupricferrite precipitate. Low pH favors copper adsorption onto HFO surfaces whereas these conditions are less favorable for cadmium, cobalt and zinc adsorption. Adsorption of cadmium and cobalt appears to be less favorable where pH is buffered to circumneutral values (Figure 2).

Conclusions

Geochemical modelling was carried out to simulate metal attenuation along the groundwater flow path with the objective of constraining groundwater metal loadings to surface water. The results indicate that although metal attenuation is significant, it is unstable where calcite is depleted in the aquifer. The groundwater velocity may overestimate the timing of the breakthrough curves; monitoring results suggest a slower rate of change than predicted in the breakthrough curves.

Metal precipitation and adsorption on HFO is important in attenuating metals along the flow path, however, the depletion of calcite and ensuing reduction in pH can result in metal desorption from HFO sites and metal breakthrough at the receptor. Cobalt and Cd do not appear to attenuate to the extent of Cu and Zn and breakthrough occurs post closure.

This study is a preliminary attempt to understand the geochemical processes along this groundwater flow path. Ongoing characterization and calibration of the model coupled with frequent water quality monitoring will improve confidence in the metal loading predictions. Better understanding of carbonate distribution in the overburden aquifer would better constrain the model.

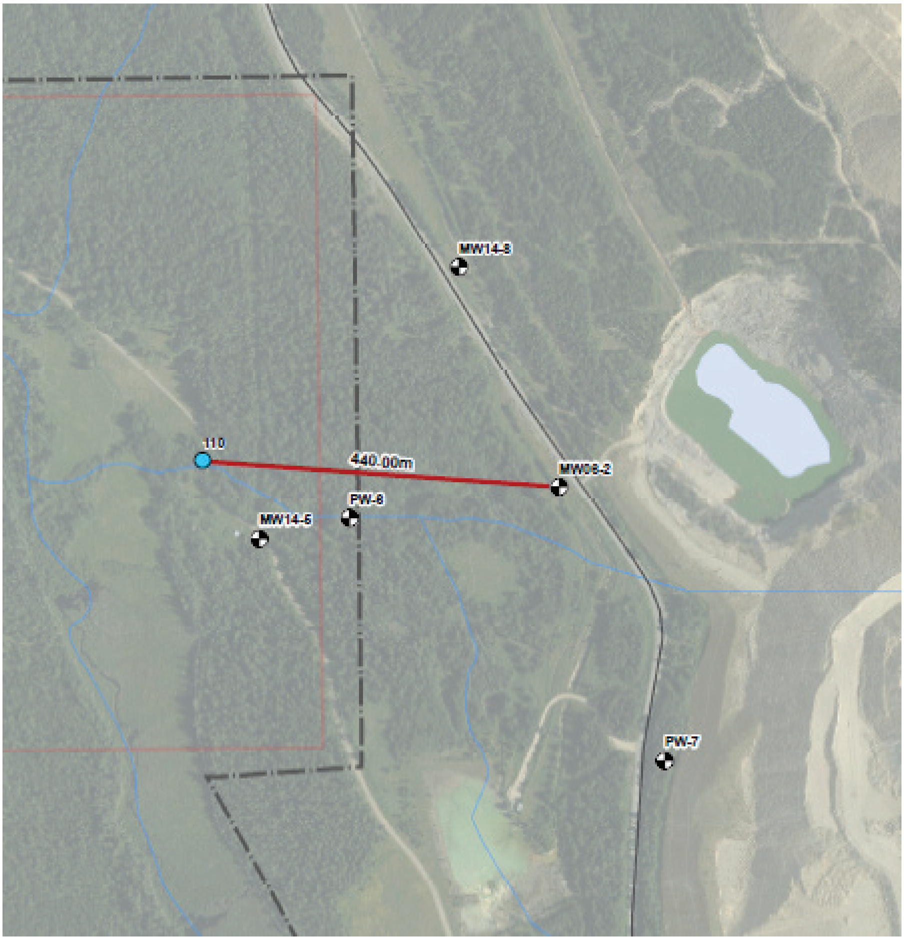

Figure 3 Pit lake, monitoring wells and prediction node

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