

Supplementary Materials

Incorporating Kinetic Modeling in the Development Stages of hard Rock Mine Projects

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Contents

Figures S1-S3

Equations 1-6

Introduction

This document presents additional information about rate laws collected from the available literature. Furthermore, it details the formula of the main parameters of the model. The first figure displays the geological framework of Akasaba West project. The second figure illustrates the weathering cell test setup and the last figure displays the correlation among the calculated and the measured electrical conductivity.

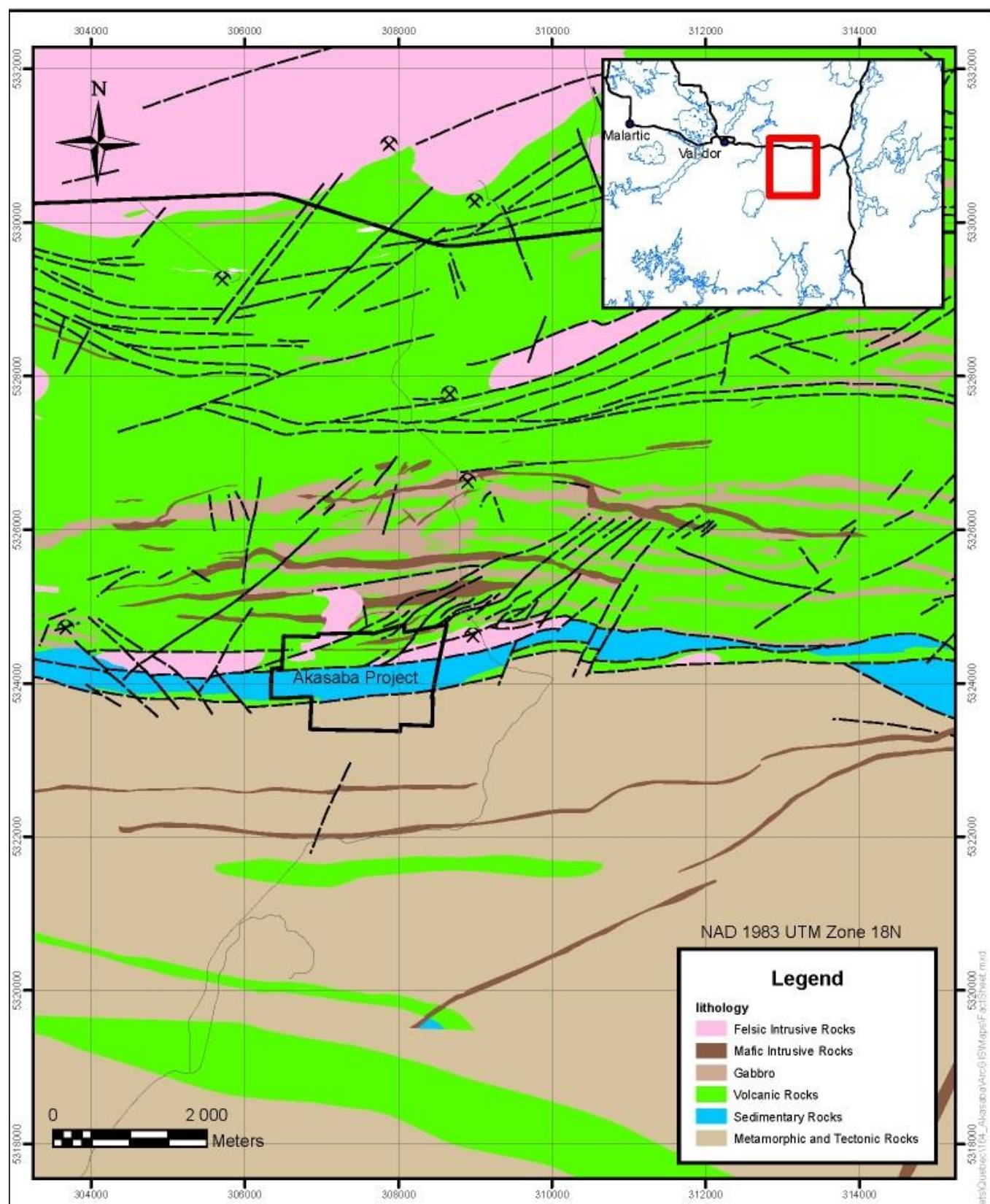


Figure S1. The geological framework of Akasaba West project (<https://www.agnicoeagle.com>).

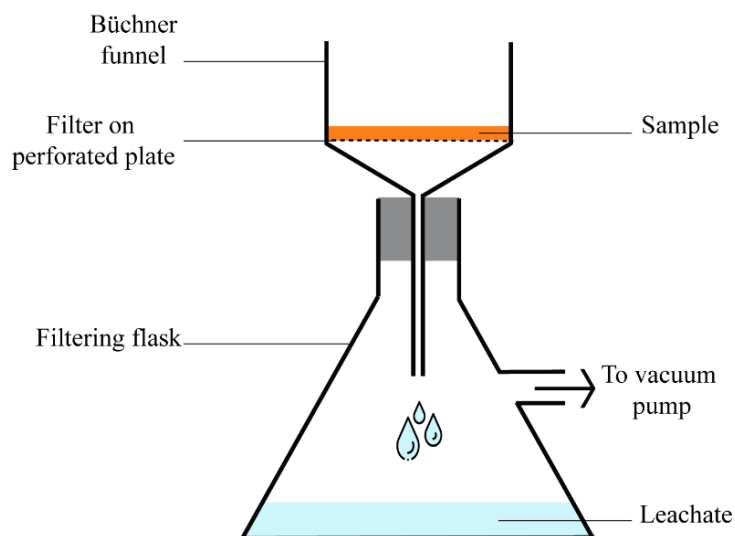


Figure S2. The experimental setup of weathering cell test.

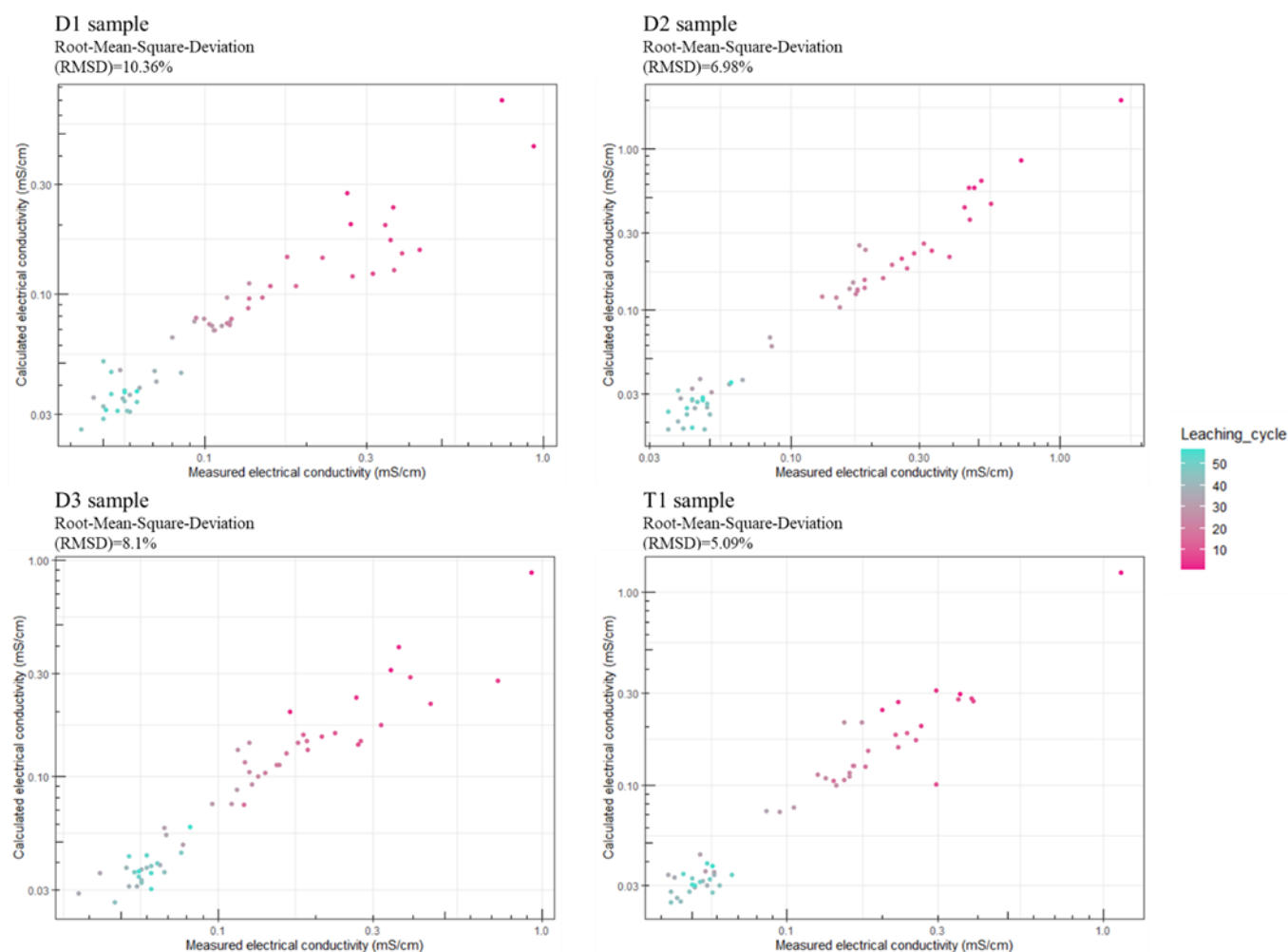


Figure S3. Comparison of calculated and measured electrical conductivity.

1. Model parameters

In order to perform 1D reactive transport in PHREEQC, the weathering cell height was discretized into 30 transport cells evenly distributed along a total height of 1 cm. A time step of 163296s with 100 shifts was chosen to achieve a total simulation time of 189 days that corresponds to the kinetic test duration. Amounts of reacting minerals in PHREEQC should be specified in moles [1]. Eary and Williamson [2] set forth a normalization basis for water-rock systems to compute initial molar amounts available for reaction with a specified mass of water (m_{mineral}):

$$m_{\text{mineral}} \left(\frac{\text{mole}}{\text{kg H}_2\text{O}} \right) = F_{\text{mineral}} \times \left(\frac{1-n}{n} \right) \times \left(\frac{\rho_{\text{solids}}}{\rho_{\text{H}_2\text{O}}} \right) \times \left(\frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} \right) \times \left(\frac{1}{M_{\text{mineral}}} \right) \quad (1)$$

where F_{mineral} is the fractional content of the mineral in bulk sample, n is the fluid-filled porosity of the bulk sample, ρ_{solids} is the bulk solid density, $\rho_{\text{H}_2\text{O}}$ is water density, and M_{mineral} is the molar mass of the mineral. The above-mentioned formula considers a water-rock system that contains 1 kg of water, as it is the default water mass used in PHREEQC. In the present study, the default water mass was changed to 50 g to match 50 ml of deionized water used as flushing solution throughout the kinetic test ($\rho_{\text{H}_2\text{O}} = 1 \text{ g/cm}^3$). Accordingly, the available molar amounts for reaction with 50 g H_2O were calculated and used within the KINETIC keyword block of PHREEQC.

Water-rock interaction involves the surface area of solids available per volume of water (SA/V) as a key parameter. It is computed as a function of the initial molar amounts (m_{mineral}) and the estimated geometric specific surface area (S_{Geo}) or BET measurement of specific surface area (S_s) [3]:

$$\text{Surface area} \left(\frac{\text{m}^2}{\text{dm}^3} \right) = S_{\text{Geo}} \times M_{\text{mineral}} \times m_{\text{mineral}} \times X_{\text{mineral}} \quad (2)$$

$$\text{Surface area} \left(\frac{\text{m}^2}{\text{dm}^3} \right) = S_s \times M_{\text{mineral}} \times m_{\text{mineral}} \times X_{\text{mineral}} \quad (3)$$

where X_{mineral} is the volumetric fraction of the mineral. S_{Geo} was estimated using the procedure described by Chapuis and Aubertin [4]. Samples were loosely placed in a Buchner funnel at an estimated porosity of 0.6. The average volumetric flow rate in the four weathering cells was set at $2 \times 10^{-6} \text{ L/s}$, resulting in a residence time of 7h. The residence time was slightly increased in the simulation from $4 \text{ h} \pm 0.5$ to 7h, as a portion of the recovered filtrates was retained even after applying suction. The effect of residence time on the kinetic reactions will be covered later.

2. Equilibrium reactions

PHREEQC was designed to cope with a large range of geochemical calculations in saturated medium [1]. The conceptual model was intended to circumvent PHREEQC limitations with respect to unsaturated systems. Setting an unlimited supply of O_2 and CO_2 in mobile and immobile cells is suitable for kinetically controlled unsaturated systems. This alternative was previously employed by Embile Jr, Walder and Mahoney [3] to simulate column tests; also Nicholson, *et al.* [5] utilized an open system approach to assess the environmental footprint of a rock stockpile. Thus, equilibrium reactions with the atmosphere ($\log [p(\text{O}_2)] = -0.7$ and $\log [p(\text{CO}_2)] = -3.5$) were embedded at ambient temperature. The Minteq.v4 database supplied with PHREEQC package was used to carry out mass balance and mass-action calculations.

3. Abiotic kinetic rates

The general rate expression (R_k) for kinetic modeling in PHREEQC is as follows:

$$R_k = r_k \frac{A_0}{V} \left(\frac{m}{m_0} \right)^n \quad (4)$$

where r_k is the specific rate ($\text{mol/m}^2/\text{s}$), A_0 is the initial surface area of the solid (m^2), V is the volume of the solution (kgw), m_0 is the initial moles of solid, m is the moles of

solid after a certain time of kinetic reaction, n is the shape factor equal to 0.67 for uniformly dissolving cubes and spheres, and $\left(\frac{m}{m_0}\right)^n$ considers the surface area shrinkage throughout the mineral dissolution [1]. As the Akasaba West project is still in the development stage, no site-specific rates were available. Therefore, monomineral specific rate expressions from literature were used to simulate the weathering cells. Opting for specific rates from literature aimed to: i) assess their reliability for a mixture of minerals and their relevance for the upstream geochemical assessment, and ii) provide prompt scoping surveys during data-limited situations.

Chalcopyrite was present as thin disseminations and could result in Cu lixiviation. However, throughout previous kinetic testing Cu concentrations remained below or slightly above the detection limit [6]. There are no published chalcopyrite rate laws that describe its oxidation by O_2 alone. However, Kimball, *et al.* [7] defined a nonoxidative dissolution rate law in the presence and absence of O_2 :

$$r_k = 10^{1.88} e^{\frac{-48100}{RT}} [H^+]^{0.8} [Fe^{3+}]^{0.42} \quad (5)$$

where R is the gas constant (J/mol/K) and T is temperature (K). This rate law is applicable for pH values less than 3. As Cu concentrations from kinetic tests were expected to remain below or slightly above the detection limit, the chalcopyrite rate law was not included in the simulation. Despite the shortcomings related to the nonoxidative dissolution rate law of chalcopyrite, it was used only during the parametric analysis to approach Cu lixiviation scenarios.

The generic form of the specific rate is as follows:

$$r_k = \left(k_{H^+} e^{\frac{-E_{H^+}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right)} [H^+]^{n_1} (1 - \Omega^{p_1})^{q_1} + \right. \\ \left. k e^{\frac{-E}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right)} (1 - \Omega^{p_2})^{q_2} + \right. \\ \left. k_{OH^-} e^{\frac{-E_{OH^-}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right)} [H^+]^{n_2} (1 - \Omega^{p_3})^{q_3} + \right) \quad (6)$$

where k_{H^+} , k_{OH^-} , and k are rate constants for acidic, alkaline, and neutral conditions, respectively, E_{H^+} , E , and E_{OH^-} are the activation energies in acidic, alkaline, and neutral conditions, respectively, n_i denotes reaction order (n_2 is negative and could be positive when alkaline mechanism equation is expressed in function of OH^-), Ω is the mineral saturation index, and p_i and q_i are dimensionless empirical parameters to take into account chemical affinity that slows down the dissolution rate at near-equilibrium conditions. Palandri and Kharaka [8] compiled a large set of rate expressions by fitting a wide range of experimental data to the generic equation. Their experimental database covers oxic and anoxic conditions, as O_2 could have a slight indirect effect on dissolution rates when iron is present in gangue minerals.

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