Comparison of thermodynamic equilibrium and kinetic approach in the predictive evaluation of waste rock seepage quality in Northern Finland.

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Abstract Accurate predictions of long-term mine water quality are critical for the assessment of potential project impacts. Ideally these should be undertaken during the early stages of planning and development to inform project design and ensure that appropriate engineered controls are established to minimise environmental impacts. The prediction of future contact water quality from waste materials at the Hannukainen Iron-Oxide-Copper-Gold mine was originally assessed using industry-standard thermodynamic equilibrium calculations of scaled HCT release rates. To address the thermodynamic equilibrium challenges, kinetic modelling methods have also been applied allowing for non-equilibrium calculations as the basis for metal release rate.

Key words PHREEQC, Predictive Numerical Calculations, Modelling, Waste Rock Dump, Source Terms

Introduction

The prediction of source term water quality from mine waste disposal facilities forms the initial step for assessing the effects on water quality in waterbodies adjacent to the facilities. This study aims to compare and contrast two numerical predictive calculation methods (thermodynamic equilibrium and kinetic) using the USGS geochemical code PHREEQC v3.3.5.10806 (Parkhurst & Appelo 1999, 2013). The two modelling approaches have been applied to source term predictions for a conceptual waste rock dump (WRD) at the Hannukainen Iron Oxide Copper Gold (IOCG) Project, located in the Kolari area of Northern Finland. The ore at Hannukainen is hosted in diopside skarn and quartz-albite rocks associated with magnetite, chalcopyrite, pyrite and pyrrhotite.

The widely used thermodynamic equilibrium modelling approach utilises geochemical characterisation data from static and kinetic tests. These laboratory data are scaled to field conditions using the planned physical characteristics of the facility (i.e. waste tonnages, surface area, height, grain size, etc.) coupled with climate data, to develop mass balanced predictions of leachate chemistry as a function of time. This scaled and mass balanced leachate chemistry is then equilibrated using PHREEQC and thermodynamically favoured phases are allowed to precipitate, on the basis of the available mineralogical information, kinetic considerations and the professional experience of the user.

The thermodynamic equilibrium approach presents several challenges due to the reliance on scaled humidity cell data which are not representative of a natural system. These challenges can be partially alleviated through the use of a kinetic modelling approach, which allows the dissolution and precipitation of mineral phases likely to be present within the modelled facility on the basis of reactivity equations for each mineral. This study has utilised these two approaches to define the source term for only the potentially acid generating (PAG) portion of waste rock from the Hannukainen project.

Geochemical Characterisation Testwork Methods

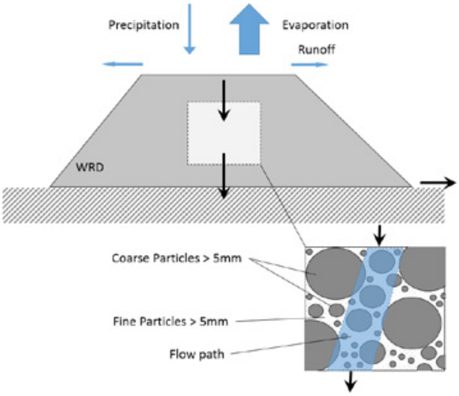
Samples representative of future waste rock were collected from exploration drillcore and characterised in order to assist in the development of source term leachates that could be used as inputs for the geochemical models. A total of 49 samples were collected for static geochemical characterisation testing, which included Acid Base Accounting (ABA) using the modified Sobek method (Sobek et al. 1978), Net Acid Generation (NAG) tests and whole rock analysis by multi-acid digest followed by ICP-OES/ICP-MS analysis. As part of the static testwork program 10 of the samples were submitted for environmental mineralogical assessment; comprising Optical Microscopy (OM); Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The static testwork was carried out in order to characterise the acid generating potential of the samples and to determine the range of reactivity of the waste rock material generated from the Hannukainen open pit operations.

Static test results were used to select samples for kinetic humidity cell testing (HCT), to represent the range in leaching characteristics anticipated for the waste material. HCTs were carried out according to the standard ASTM D5744-96 methodology (ASTM 1996) which is used for the assessment of long-term rates of acid generation and metal mobilisation. Eight samples of moderate to high sulfur waste rock materials (one skarn, one schist, three amphibolite and three diorite) were subjected to 170 weeks of HC testing. Weekly effluents were collected and analysed for a range of laboratory parameters in addition to major and trace element chemistry.

Conceptual Model Methodology

The results of the static and kinetic testwork were coupled with information from the mine plan and water balance to develop numerical predictions of future seepage and runoff water quality associated with the mine facilities. The general modelling approach estimated source term water quality under steady-state conditions after 5 and 10 years into life of mine (LOM). Conceptual geochemical models were developed from a review of background and site-specific data in addition to experience with other similar projects (see fig. 1). According to the geology and mine plan, three broad material type classifications are to be exposed during mine life: Potentially Acid Generating (PAG) waste rock (>0.1% sulfur); Non Acid Generating (NAG) waste rock material (≤0.1% sulfur); and NAG overburden (OB).

It is intended that these materials will be segregated during mining and disposed in individual PAG, NAG and overburden cells within the WRD. Quantitative Numerical Predictions (QNP) have been carried out using the thermodynamic equilibrium and kinetic approach in order to predict the source term seepage characteristics for LOM at 5 and 10 years from the PAG cell in the East WRD only.



Material type	Year 5 - East	Year 10 - East
	Tonnes*	
PAF AMPHIBOLITE-Moderate S	197,633	882,599
PAF DIORITE-Moderate S	53,153	237,373
PAF AMPHIBOLITE-HIGH	328,053	1,465,030
PAF DIORITE-High S	394,932	1,763,703
PAF SCHIST	7,698	34,376
PAF SKARN	34,418	153,705
PAF PEG-High S	46,713	208,614
Sum	**1,062,600**	**4,745,400**
NAF AMPHIBOLITE-Low S	121,432	292,865
NAF DIORITE-LOW	281,516	678,950
NAF MONZONITE-Low S	347,925	839,113
NAF PEG-Low S	34,527	83,271
Sum	**785,400**	**1,894,200**

***Figure 1**: Conceptual model of the Hannukainen WRD*

Thermodynamic Equilibrium Model Methodology

The thermodynamic equilibrium approach for the Hannukainen WRD incorporates aspects of both mass balance calculations from scaled laboratory data and thermodynamic equilibration using PHREEQC. The overall approach can be summarised as follows:

- Geochemically characterise the waste rock types and associated tonnages and proportions that will report to the WRD. Characterise the overall leach behaviour as a release rate that is representative of an equivalent kinetic cell of representative WRD composition.
- Evaluate the local climate data (e.g. rainfall and evaporation rates) and WRD design (footprint, cover, tonnage, likely particle size distribution (PSD)) to predict seepage rates.
- Apply a scaling factor to the laboratory-derived solute leach rates to predict the rate of solute release from the overall waste rock facility (Kempton 2012). Divide the solute release rate by the WRD seepage flow rate to calculate the seepage composition as follows:

$$WRD\,Seepage\,water\,quality\,\frac{mg}{L}=\frac{\sum Solute\,release\,rate\left(\frac{mg}{kg}/week\right)\times Reactive\,mass\,of\,material\in WRD(kg)}{Total\,infiltration\,rate\,into\,WRD\left(\frac{L}{week}\right)}$$

- Evaluate mineral saturation indices for the predicted solute composition within a geochemical software package, identifying likely solubility controls on solution composition. Allow feasible and kinetically viable mineral precipitation to occur, thereby determining the final WRD seepage quality. A modified version of the Minteq.v4 thermodynamic database supplied with version v3.3.5.10806 of PHREEQC (released June 3rd, 2013) was used. The Minteq.v4 database was selected for this study because it includes a comprehensive range of elements and solid phases for consideration in water quality predictions as well as key sorption reactions for iron oxyhydroxides. The database was modified to include sorption data for manganese species from the PHREEQC database together with corrections for weak strong site adsorption of anions to hydrous ferric oxide and adsorption data for uranium (VI) to ferrihydrite (Waite et al. 1994).

- Compare the predicted water compositions with those observed from on-site sampling, and determine if site conditions indicate additional controls on water quality and solute concentration.

The predicted rate of solute release from the waste rock mass (R_{field}) is calculated from the laboratory leach rates multiplied by a cumulative scaling factor, derived as the product of several individual scaling factors. The relationship between R_{field} and the laboratory rates can be represented by the following scaling factors (based on work taken from Kempton, 2012):

$$R_{field} = R_{lab} \text{ x } SF_{moist} \text{ x } SF_{size} \text{ x } SF_{contact} \text{ x } SFt_{emp} \text{ x } SF_{O2}$$

R_{field} calculated field leaching rate; R_{lab} laboratory determined leach rates; SF_{moist} reduced oxidation due to low moisture; SF_{size} reactivity reduction due to HCT vs field PSD; $SF_{contact}$ reduction due to unflushed mass (retained solutes); SF_{temp} rate relationship for temperature using Arrhenius equation; and SF_{O2} reactive mass reduction due to O_2 diffusion limits.

SF_{moist} was neglected in the calculations due to the continuous presence of water in the WRD. $SF_{contact}$ describes the proportion of material within the WRD that will be wetted, thus mobilising solutes. This wetting effect is dependent on channelling and development of flow paths within unsaturated waste rock (Birkholzer and Tsang, 1997), which in turn depends on PSD and infiltration rates. Temperature within the PAG material is assumed to be the same as in the laboratory testwork and therefore SF_{temp} is 1. Oxygen ingress has been calculated using the Bennett et al. (2000) equation and shows that oxygen is fully available throughout the WRD therefore SF_{O2} is neglected.

Kinetic Model Methodology

Site-specific geochemical and mineralogical characterisation data were coupled with literature reaction rates to define kinetic predictive calculations (fig. 2) and determine a realistic reactivity for the mineral phases within the Hannukainen WRD. Mineral precipitation rates were generated directly from the corresponding dissolution rate equations. The majority of these rates were obtained from work carried out by the CarbFix Project no.28348. Within PHREEQC, the rate equations for the different minerals were defined within the RATE data block and integrated over time using the implicit CVODE method (Cohen and Hindmarsh 1996) which can resolve the integration of widely varying rate equations.

All parameters in the rate equations (example of pyrite in tab. 1) are calculated/defined by PHREEQC except the surface area (S_A) in m^2/kg and the mass of the different mineral phases (from SRK 2013). Mineral mass and surface area were defined for each reactive mineral phase and were calculated on the basis of the surface area of a volume of material contacted by the infiltrating water. This surface area is proportionated to each the primary minerals. Any eventual secondary kinetic phases are defined here with an initial mass and surface area of zero. Fast-reacting secondary minerals such as amorphous silica, gibbsite and gypsum are defined at equilibrium. The system was allowed to react for 10 years.

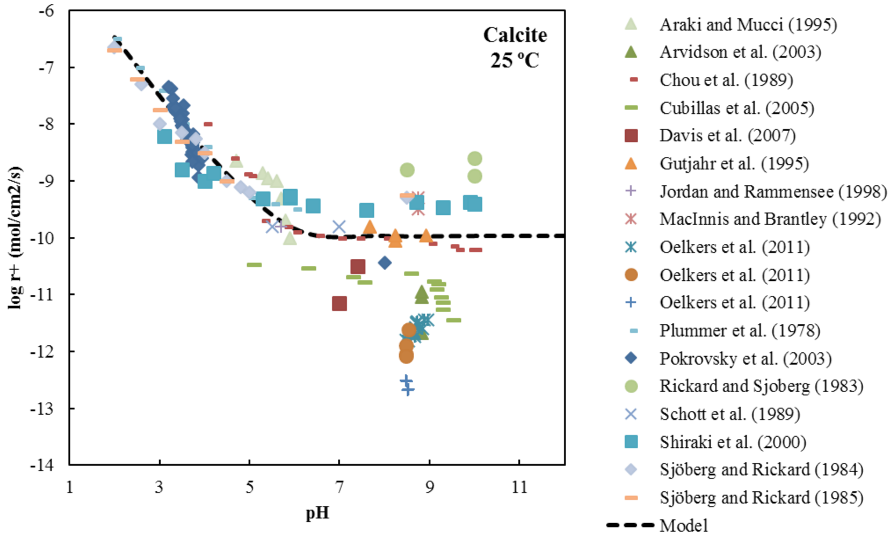


***Figure 2**: Measured and predicted calcite dissolution rate at 25 oC*

***Table 1**: Rate equations for pyrite based on Palandri and Kharaka (2004)*

Equation	Equation No.
$-n$ $H^{¿} a^{n}_{Fe^{+3}} \times S_A$ $r_{+,a} = A_a \times e^{\frac{-E_A}{RT}} \times a_{¿}$	(Pyr_1)
$r_{+,b} = A_b \times e^{\frac{-E_B}{RT}} \times a^{n}_{O_2} \times S_A$	(Pyr_2)
$+¿ = r_{+,a} + r_{+,b}$ $r_{¿}$	(Pyr_3)
$+¿ \times \left(1 - \frac{IAP}{K} / \sigma\right)$ $r = r_{¿}$	(Pyr_4)

It can be expected that the total mineral mass is unlikely to be available for weathering reactions due to partial exposure of minerals and grain size effects (i.e., surface area factors) and potential encapsulation of minerals by non-reactive phases (Kelemen et al. 2011). Determining the reactive surface area of specific minerals within a waste rock dump is challenging, but can be inferred from the PSD of the waste rock (Cepuritis et al. 2017). The surface area in the system was calculated from PSD measurements carried out on trial pits and the use of the GRAIN 3.0 software.

The dissolution of the different mineralogical phases releases solutes consistent with their stoichiometric proportions as defined by their mineralogical formula. This implies that most major elements e.g. Ca, Si, S, will be controlled by the mineral dissolution or oxidation. However, trace elements such as Hg and As are present as replacements within the mineralogical structure. In the absence of direct chemistry measurement of the different mineralogical phases it has been assumed that most trace elements are controlled by the oxidation of pyrite.

Results and Discussion

Using the thermodynamic equilibrium approach the PAG dump was predicted to generate acidic leachates with a high sulphate load. Metals content is predicted to contain elevated aluminium, cobalt chromium, copper, iron, manganese, mercury, nickel, lead and zinc.

The unscaled kinetic model shows a good agreement with average HCT (pH shown in fig. 3). Consistent with the thermodynamic equilibrium predictions (SRK 2013), calcite disappears within the first year, however the pH remains neutral which supports the hypothesis of silicate buffering, provided by albite, hornblende and kaolinite dissolution. However, this buffering has a limited capacity that is reached by the ongoing generation of acidity by sulfide oxidation. It is predicted that between 3 to 4 years that the pH will turn acid (fig. 3), the onset of this phenomenon can be seen in the HCT data.

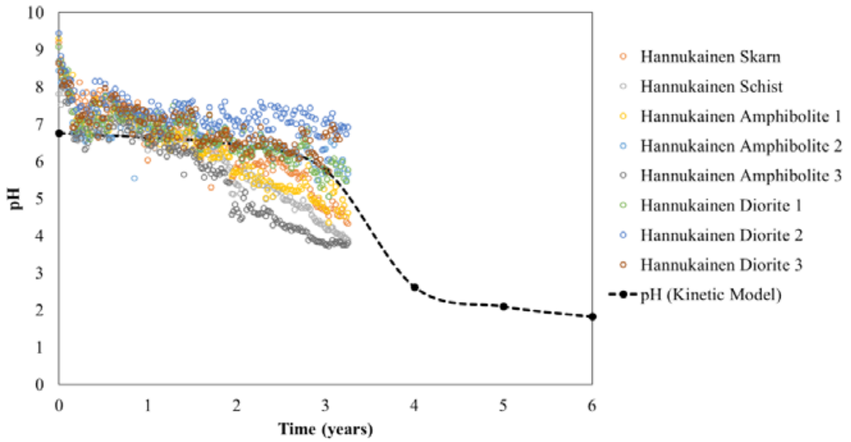


***Figure 3**: Predicted pH variability with time from kinetic modelling approach compared to weekly HCT pH*

The primary advantages of a kinetic modelling approach over the more traditionally-used thermodynamic equilibrium approach are as follows:

- It accounts for minerals with sluggish reaction kinetics, e.g. silicates, allowing their potential neutralisation capacity to be considered within the prediction, as well as addressing the challenge of reactive minerals in sub-arctic conditions;
- It considers both oxidation and dissolution mechanisms and also the precipitation and dissolution of carbonates (depending on the local conditions); and
- It is not limited by equilibrium defined reactions or phases.

The challenges associated with the kinetic predictive numerical calculation approach are generally associated with the fact that chemical kinetic calculations require different input data than chemical equilibrium calculations as follows:

- The surface area of the WRD and the different mineralogical phases must be adequately defined, through the calculation of the surface area from PSD.
- Determination of the reactive surface area (i.e. the proportion of a given mineral phase that will be available for reaction (Jeschke and Dreybrodt 2002)) suffers from the same challenges as the calculation of the reactive mass in the thermodynamic equilibrium method. However, detailed mineralogical assessment can provide insight into the correct proportions of the minerals per lithology as well as potential encapsulation or potential armouring of the phases.
- Trace elements are typically measured by multi element assay, but that analytical technique does not link the elements and their mineralogical host (such as As present in the pyrite structure). This could be overcome by completing a detailed, quantitative mineralogical analysis as part of the geochemical characterisation study. This would allow the mineralogical composition to be determined, and allow the host minerals for various major and trace elements to be identified.
- Dissolution and precipitation rates are defined based the results of laboratory testwork, in which mineral phases dissolve or precipitate in far from equilibrium conditions. As such, the degree to which such rates are representative of field rates are debatable. The rates used in this study are consistent with the dissolution and precipitation rates found in the literature. In addition to the reproduction of HCT results, quantifying the performance of kinetic modelling would require the modelling of kinetic field tests such as field cribs as a validation step.

Conclusions

This study compares thermodynamic equilibrium and kinetic modelling methods for the prediction of source term water quality from a mine waste rock dump at a proposed IOCG deposit in northern Finland. Using an approach based on the definition of kinetic equations for the reactivity of the material allows the decoupling of the calculations from laboratory HCT results as the basis for defining metal release rates. Kinetic equations are based on rate equations from the literature, using mineralogical, temperature, PSD and reactive surface area parameters to calculate seepage chemistry while laboratory and field testwork results are used to validate the approach. This approach accounts for minerals with sluggish reaction kinetics, e.g. silicates, allowing their potential neutralisation capacity to be considered within the prediction, as well as addressing the challenge of reactive minerals in sub-arctic conditions.

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