



# Development of a prediction method for contaminated neutral drainage: Case of Lac Tio, Québec

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## Abstract

Water quality prediction tools are an essential part of responsible mining. Large efforts have been made to develop tools relevant to acid mine drainage (AMD) contexts because of its well-known causes and consequences. However, contaminated neutral drainage (CND) can be challenging to predict using tests designed to predict AMD. Indeed, as AMD prediction tests aim to predict whether a material will generate acidic waters with only secondary emphasis on the dissolved species concentrations, CND prediction requires predicting if the concentrations of dissolved species will exceed regulatory limits while the pH remains near neutral. Previous research using sorption tests and modified kinetic testing demonstrated that the delay before the onset of CND was caused by the gradual saturation of sorption sites on the mine waste surfaces. The goal of this study is to propose a prediction testing protocol to assess the risk of CND, where sorption capacity is considered as a component of metal leaching potential.

Waste rocks from the Lac Tio mine are known to generate nickel (Ni) concentrations in drainage waters above the governmental regulation guidelines after approximately 10 to 25 years of exposure. In previous research, small-scale humidity cells (called weathering cells), containing less than 100 g of sample, used a chelating agent solution instead of deionized water to periodically leach the materials. Chelating agents are known to impede ion interactions with surfaces (sorption) and secondary precipitation. In this study, the approach was scaled up to column experiments containing approximately 18–20 kg of representative sample. The concentration of the chelating agent was optimized to prevent excessive leaching of refractory phases, and the leaching potential was compared to the results of sorption experiments.

The main findings are: 1) Column experiments are suitable for modified kinetic leaching and the results can be used for CND prediction; 2) Optimization of the chelating agent concentration is key to prevent overleaching; and 3) Coupling kinetic prediction tests with sorption experiments provides a better assessment of the risk of CND generation than current practices.

The objective of this novel prediction method is to improve the risk assessment associated with CND. The approach will enable us to predict mine water quality and the water treatment needs more accurately. Overall, this will contribute to improving environmental practices in the mining industry.

**Keywords:** Contaminated neutral drainage, prediction, risk assessment, kinetic leaching, sorption experiments

## Introduction

Mining has substantially increased over the last decades due to resource necessity (increased demand for electronic materials and rapid urban development which require metals). This demand is deemed to expand even further with the electrification challenges that arise as efforts are made to mitigate the carbon footprint in the upcoming years (Wei et al. 2019). Governments are putting in place strategies to ensure access to those resources which are important in terms of technological development.

However, with an increase in mining activity also comes an increase in mining waste production. The solid waste can be divided into two large categories: waste rocks and tailings. Waste rocks and tailings might both contain sulfide minerals, and those minerals are unstable when they are exposed to oxygen and water. Through their oxidation, most sulfides produce acidity which can be neutralized by buffering minerals such as carbonates and silicates (e.g. Blowes et al. 2005; Nordstrom et al. 2015). If the acidity potential is higher than the neutralizing potential of the material, acid mine drainage (AMD;  $\text{pH} < 6$ , elevated dissolved aqueous species, including metals and sulfate) will ultimately be produced.

Different methods have been developed to predict the onset of AMD. One of the most widely used concepts to predict AMD is acid and base accounting (ABA), such as the Sobek method (Sobek et al. 1978) and its derivatives (Lawrence et al. 1989; Ptacek and Blowes 1994; Lawrence and Wang 1997; Kwong and Ferguson 1997; Lawrence and Scheske 1997). Those methods have been able to provide a better understanding of the geochemical fate of the different mine wastes in terms of acid generation (MEND 2009).

Nonetheless, acid generation might not be the only challenge associated with mine wastes. In fact, even though some mine wastes might not generate acidic waters, they might still generate waters contaminated with concentrations of metals and metalloids exceeding the regulated concentrations with near-neutral pH values (pH 6 to 9). The scenarios in which contaminated neutral drainage (CND) (or metal leaching (ML)/

neutral mine drainage (NMD)) occurs can vary. CND can occur before the onset of AMD (during the neutralization phase), but it can also arise when the material contains potential contaminants that are released by the sulfides (even in low concentrations) or by the neutralizing minerals. However, the onset of CND can often be substantially delayed by two co-occurring processes: sorption and (co)-precipitation (Plante et al. 2010).

As a result of those retention mechanisms, CND prediction is substantially difficult. Indeed, a prediction method specific to assess the risk of CND generation is yet to be proposed. We therefore developed such a method that is presented here. The method consists of three main constituents: (1) chemical and mineralogical characterization of the material with respect to its potential contaminant contents and their respective source terms; (2) modified kinetic column testing using a chelating agent as a means of verifying leachability of the potential contaminants identified, and (3) sorption experiment to determine the maximum sorption capacity of these potential contaminants. This method builds on previous work by our group (Plante et al. 2015; Lévesque Michaud et al. 2017), that showed that even though using chelating agents in kinetic tests successfully prevented sorption and secondary precipitation of potential contaminants, their concentrations need to be optimized to prevent over leaching.

In this paper, a material that is known to generate Ni-CND in the long term is submitted to the proposed method as a positive control.

## Material and methods

### *Material*

The material assessed in the study was waste rock provided by Rio Tinto Iron and Titanium from their Lac Tio mine, located 43 km north of Havre-Saint-Pierre, Québec, Canada. The Lac Tio mine opened in 1950 and still operates to this day. Waste rocks are stacked at the site and some of them generated Ni-CND after approximately 25 years (Benzaazoua et al. 2013), making them ideal for the validation of the method.

*Chemical, mineralogical, and physical properties*

The waste rock was sieved to <2 cm so that the material would have the recommended dimensions for the 14 cm inside diameter column kinetic testing. They were homogenized and split in various batches for the different tests and analyses.

Chemical analyses were performed on a pulverized aliquot of the material. The chemical composition of the sample was determined by an inductively coupled plasma (ICP) after a four-acid digestion. The mineralogical composition was determined using an automated analysis under a scanning electron microscope equipped with an EDS detector.

*Kinetic column testing*

Two columns were assembled (14 cm inside diameter, 90 cm height) and filled with < 2 cm sieved material to a total initial height of 70 cm, with a porosity of 0.5 and a total mass of 19 kg. The control column was leached with 1.7 L of deionized water every two weeks. The other column was leached with an ethylene diamine tetraacetic acid (EDTA) solution that was prepared specifically for the expected concentrations of cations leached by oxidation and neutralization. The strategy was to aim for twice the expected concentration of cations in solution, and to adapt it throughout the test; this strategy enables to have a slight excess of EDTA in solution to minimize over leaching. The initial concentration was 0.018 M of EDTA, and it was adjusted after the first 4 flushes to follow the concentration of cations obtained in the leachates. The kinetic tests were carried out for a total of 12 flushes over 183 days.

Leachates were sampled at every flush and analysed for electrochemical parameters (pH, redox potential, electrical conductivity), acidity and alkalinity by titration, anions by

ionic chromatography, as well as dissolved species concentrations by ICP-Optical Emission Spectroscopy (OES) on a 0.45 µm filtered aliquot.

*Batch sorption experiments*

The batch sorption experiments were performed over the fine fraction of the material (<2.5 mm), which is approximately 35wt% of the <2 cm waste rock sample. The same solid to liquid ratio of 4 mL/g was maintained for all sorption experiment by using 7.5 g of material for 30 mL of Ni-containing solution rotated in covered erlenmeyers at 200 revolutions per minute on a stirring plate. The time necessary for stabilization during sorption tests was determined with a preliminary kinetic sorption test conducted on 5 identical tests containing a 100 mg/L Ni solution buffered to pH 6.15 with 0.1 M of 2-(N-morpholino) ethanesulfonic acid hemisodium salt (MES). Sacrificial samples were collected after 1 h, 3 h, 6 h, 24 h and 48 h for Ni analysis; an equilibrium time of 6 h was chosen.

Batch sorption experiments were conducted using the same MES buffer concentration. Initial Ni concentrations were 1, 10, 25, 50, and 250 mg/L. Samples were filtered and analyzed by ICP-OES to determine the sorption capacity of the material. The linearized Langmuir isotherms (Table 1) were used to model the sorption capacity and determine the maximum Ni sorption capacity at pH 6.15.

**Results**

Table 2 presents a summary of waste rock chemical analyses. Aliquots have been measured in the different columns and had concentrations of Ni varying between 270 and 590 mg/kg. The materials were mostly in the uncertainty zone of the Sobek test, with a net neutralizing potential (NNP) between 0.1 and 2.3 kg CaCO<sub>3</sub>/t.

*Table 1 Linearized Langmuir isotherms from Guo and Wang (2019)*

Model 1	Model 2	Model 2	Model 4
$\frac{C_e}{Q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}}$	$\frac{1}{Q_e} = \frac{1}{q_{max}} + \frac{1}{C_e K_L q_{max}}$	$Q_e = q_{max} + \frac{Q_e}{C_e} \frac{1}{K_L}$	$\frac{Q_e}{C_e} = q_{max} K_L + K_L Q_e$

**Table 2** Chemical characteristics of waste rock samples

Al %	Ca %	Fe %	Ni mg/kg	S %	Si %	Carbon %	NNP Sobek kg CaCO <sub>3</sub> /t
5.2–6.0	2.7–3.0	18–23	270–590	0.17–0.23	14.1–15.4	<0.05	0.1–2.3

Mineralogical tests were conducted on several samples. The material is composed of hemo-ilmenite, plagioclase, enstatite, magnetite, anorthite, apatite, and pyrite. The different pyrite grains that could be analyzed contained most of the Ni. This suggests that Ni is likely to be leached through sulfide oxidation, consistent with prior knowledge on the Lac Tio waste rocks (Plante et al. 2010, 2011).

Ni concentrations in leachates from the EDTA column were greater (mean 16 mg/L) in comparison to the control test (mean 0.12 mg/L Ni). This provides an estimate of the amount of Ni retained by sorption as demonstrated in previous work (Plante et al. 2010). It also justifies the range of concentrations used in the batch sorption tests. The release rate of Ni from the EDTA column was estimated to be 0.105 mg kg<sup>-1</sup> d<sup>-1</sup> whereas the rate was substantially lower in the control column (0.0007 mg kg<sup>-1</sup> d<sup>-1</sup>).

A maximum sorption capacity, in the conditions of the sorption tests (6 h equilibrium time, pH of 6.15 liquid to solid ratio of 4 mL/g), could be estimated with the Langmuir isotherms (Fig. 1) to approximately 273 to 479 mg of Ni per kg of waste rock (<2 mm). This is probably a conservative estimate, as longer equilibrium times during sorption tests likely would have rendered greater sorption capacities.

Microscopy observations were made at the end of the experiment on samples from both columns to appreciate the effect of EDTA on the mineral surfaces, as it was previously observed to attack the surfaces of ilmenite when used in higher concentrations (up to 10 times more EDTA than expected cations in Plante et al., 2015). In this case, no alteration pattern on phases that are refractory to deionized water leachings (that were observed in other studies using more concentrated EDTA solutions) could be observed in the post-EDTA column sample. This demonstrates that the adaptative EDTA concentration, aiming for twice

the expected concentration of dissolved cations, is key to prevent over leaching and excessive weathering of minerals. In addition, the accumulation of secondary iron oxyhydroxide rims around sulfide minerals, typical of sulfide weathering at near-neutral pH, was not observed in the post-EDTA materials, contrary to the control column, which demonstrates the efficiency of EDTA in preventing secondary precipitations.

Using these results, a simple risk assessment can be done by comparing the maximal sorption capacity with the initial Ni concentration in the waste rock. In this case, the initial concentration (270–590 mg/kg) is within the same range as the estimated maximum sorption capacity (273–479 mg/kg), suggesting a risk towards Ni leaching in the long term. The comparison of EDTA column test results with the control column enables appreciating the true extent of Ni released by weathering. Assuming that (1) the “true” Ni release rate (without sorption and/or secondary precipitation, as measured with the EDTA column test) remains 0.105 mg kg<sup>-1</sup> d<sup>-1</sup>; and (2) that sorption sites will saturate at the same rate (almost no Ni is leached in the control, meaning almost all Ni is retained by immobilization processes), the time before the onset of CND conditions can be estimated. This time is expected to be approximately between 7 to 12 years in the conditions of the column test (273–479 mg/kg Ni divided by 0.105 mg kg<sup>-1</sup> d<sup>-1</sup>). However, many sources of uncertainty remain on the extent to which this value can be relied upon and will need to be tackled to gain more precision towards this prediction. For instance, competing cations for the Ni sorption sites, as well as the gradual saturation of the sorption capacity, would likely decrease the onset before CND generation.

## Conclusions

A methodology to predict the onset of CND has been briefly described herein. Combining the information from column kinetic tests

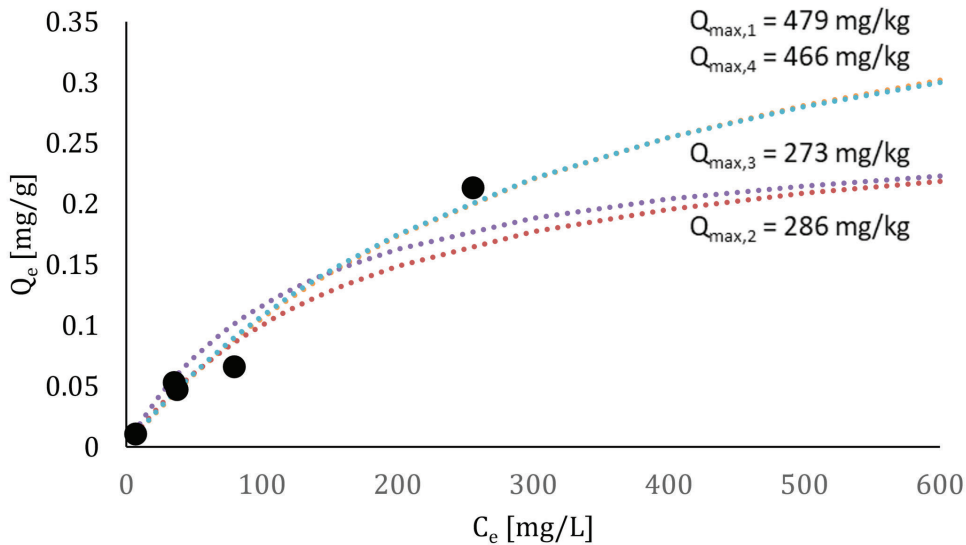


Figure 1 Langmuir linearized isotherms representation of the final sorption capacity with  $Q_e$  the adsorbed Ni,  $C_e$  the concentration of Ni in water at equilibrium, index max maximal sorption capacity

and sorption experiments allowed us to adequately predict the onset of CND on a positive control waste rock sample known to generate Ni-CND after a few decades of weathering. Optimization of EDTA concentrations in modified kinetic testing was shown to be effective to prevent excessive weathering of minerals that should not be altered in the experimental conditions.

Research perspectives are numerous. One of the main questions that remains is the scalability of the method. A comparative study between column tests, weathering cells and field cells would be necessary to adequately judge to which extent the method can be used to scale up to a field prediction. Other materials need to be investigated, particularly materials that may release potentially problematic oxyanions such as arsenate/arsenite in their leachates, as well as other cations that could be problematic at neutral pH such as Zn, Co and Mn. Other positive controls need to be identified and submitted to the procedure to gain confidence in the method and its predictions. Sorption experiments have numerous downsides and limits that should also be tackled (for example, the effects of multi-ion sorption competition, liquid to solid ratio, grain size

distribution, pH). Nevertheless, the approach is promising and provides practitioners with an additional tool for the prediction of CND that can be integrated into the risk assessment relating to mine water quality.

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## References

- Benzaazoua M, Bussière B, Demers I, et al (2013) Comportement géochimique et hydrogéologique des stériles de la mine Lac Tio. Environnement, Ingénierie & Développement N°64-Juin 2013:7837. <https://doi.org/10.4267/dechets-sciences-techniques.2238>
- Blowes DW, Ptacek CJ, Jambor JL, Weisener CG (2005) The Geochemistry of Acid Mine. Environmental geochemistry 9:149
- Guo X, Wang J (2019) Comparison of linearization methods for modeling the Langmuir adsorption isotherm. Journal of Molecular

- Liquids 296:111850. <https://doi.org/10.1016/j.molliq.2019.111850>
- Kwong YTJ, Ferguson K (1997) Mineralogical changes during NP determinations and their implications. In: 4th Int. Conf. on Acid Rock Drainage. Nat. Resour. Canada, Vancouver, BC, Canada, pp 435–447
- Lawrence RW, Poling GP, Marchant PB (1989) Investigation of predictive techniques for acid drainage. Energy and Mines ressources, Canada
- Lawrence RW, Scheske M (1997) A method to calculate the neutralization potential of mining wastes. *Environmental Geology* 32:100–106. <https://doi.org/10.1007/s002540050198>
- Lawrence RW, Wang Y (1997) Determination of neutralization potential in the prediction of acid rock drainage. In: Proc. 4th International Conference on Acid Rock Drainage, Vancouver, BC. pp 449–464
- Le vesque Michaud M, Plante B, Bussiere B, et al (2017) Development of a modified kinetic test using EDTA and citric acid for the prediction of contaminated neutral drainage. *Journal of Geochemical Exploration* 181:58–68. <https://doi.org/10.1016/j.gexplo.2017.07.001>
- MEND (2009) Report 1.20.1: Prediction manual for drainage chemistry from sulphidic geological materials. Natural Resources Canada, Ottawa, Canada
- Nordstrom DK, Blowes DW, Ptacek CJ (2015) Hydrogeochemistry and microbiology of mine drainage: An update. *Applied Geochemistry* 57:3–16. <https://doi.org/10.1016/j.apgeochem.2015.02.008>
- Plante B, Benzaazoua M, Bussiere B, et al (2010) Study of Ni sorption onto Tio mine waste rock surfaces. *Applied Geochemistry* 25:1830–1844. <https://doi.org/10.1016/j.apgeochem.2010.09.010>
- Plante B, Benzaazoua M, Bussiere B (2011) Kinetic testing and sorption studies by modified weathering cells to characterize the potential to generate contaminated neutral drainage. *Mine water and the environment* 30:22–37
- Plante B, Benzaazoua M, Bussiere B, et al (2015) Use of EDTA in modified kinetic testing for contaminated drainage prediction from waste rocks: case of the Lac Tio mine. *Environmental Science and Pollution Research* 22:7882–7896. <https://doi.org/10.1007/s11356-015-4106-6>
- Ptacek C, Blowes DW (1994) Influence of siderite on the pore-water chemistry of inactive mine-tailings impoundments. ACS Publications
- Sobek A, Schuller W, Freeman J, Smith R (1978) Field and Laboratory methods applicable to overburdens and minesoil. U.S. Environmental Protection Agency, Washington, D.C.
- Wei M, McMillan CA, de la Rue du Can S (2019) Electrification of Industry: Potential, Challenges and Outlook. *Current Sustainable/ Renewable Energy Reports* 6:140–148. <https://doi.org/10.1007/s40518-019-00136-1>